SOLUTION AND SOLID-STATE STUDIES OF

SOME BLEACHABLE SEMI-CONDUCTING PHOTOGRAPHIC DYES

by

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ABSTRACT

A number of monomeric and oligomeric hydroxypyridone mono- and poly-methine bridged oxonol and merocyanine dyes have been prepared and their solution and solid-state properties have been investigated.

One particular and commercially important feature of the solution chemistry of the oxonol dyes is the reaction with sulphite ion leading to bleaching of the dye. The mechanism of this process has not previously been investigated. A detailed kinetic and spectroscopic study supports the previously proposed mechanism in which the nucleophile adds to the methine bridge in a Michael-type fashion. The reaction intermediates have been detected spectroscopically for several nucleophiles but in general are too unstable to be isolated.

Oxonol and merocyanine dyes readily undergo molecular aggregation in both solution and the solid-state. One previous X-ray diffraction analysis of an oxonol dye has been carried out which revealed that the anions formed planar molecular stacks. Such an arrangement is well suited to intermolecular charge transfer and hence electronic conduction. The main objective of the current work has been to investigate how this stacking might be influenced by variation of substituents and counter-ions with a view to modifying the conduction properties. X-ray structure studies reveal that variation of the cation leads to three different types of solid-state structure: herringbone; uniform; and dimeric. The electrical properties have been investigated in detail by d.c. conductivity and a.c. dielectric spectroscopy measurements. They suggest that in general, the simple hydroxypyridone trimethine oxonols are

semi-insulating ($10^{-8} < \sigma < 10^{-12}$ Ω^{-1} cm^{-1}) though some exceptions

have been found. Any observable d.c. conduction is essentially ionic in

nature. The merocyanines and pentamethine oxonols are semi-conducting

($10^{-4} < \sigma < 10^{-8}$ Ω^{-1} cm^{-1}) as a consequence of added electronic

contributions to the conduction mechanism. The most highly conducting

oxonol salt, containing the tetrathiafulvalene (TTF) radical cation has a

d.c. conductivity, $\sigma \simeq 10^{-3}$ Ω^{-1} cm^{-1} (compacted powder, room

temperature). In this case electronic conduction dominates.

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CHAPTER 1

Bleachable Dye Photography

1.1 Bleachable Dyes[1,2].

A bleachable dye, in the photographic sense, may be broadly
defined as a dyestuff component of a photographic assembly (film, paper,
etc.) which is not present in the final version of that assembly, having
been removed during one of the processing stages. It does not,
therefore, refer to dyes formed during chromogenic development to give
colour prints, etc., and also by convention it does not refer to
dyestuffs added to sensitise silver halide crystals to light. A
simplified picture of a typical photographic assembly, is a colour
negative film, shown in figure 1.1. This shows seven basic layers (A-G)
and a film base (H). The backing layer (I) is not present in a colour

A	Non-stress and u.v. absorber
B	Blue-sensitive emulsion
C	Yellow filter layer
D	Green-sensitive emulsion
E	Magenta filter layer
F	Red-sensitive emulsion
G	Underlayer
H	Base
I	Backing layer

Figure 1.1

negative film but has been included for the sake of completeness; the use

of such a layer will be described shortly. Layer (A) is a mechanically

protective coating and may also contain an ultraviolet light absorber.

Since all silver halide crystals are activated by ultraviolet light a

u.v. absorber is incorporated to prevent incorrect colour rendition (for

example, it is essential that the red-sensitive layer should be excited

only by red light). Layer (B) is an emulsion sensitive to blue light (λ

= 400 - 500 nm). As it is desirable that no blue light reaches the other

emulsion layers, layer (C) is inserted. This layer is a yellow filter

layer and this absorbs blue light, blue and yellow being complementary

colours. Below this are a green-sensitive emulsion (D) (λ = 500 - 600

nm) and associated green-absorbing layer (E), followed by a red-sensitive

emulsion (F) (λ = 600 - 700 nm) and an underlayer (G). This latter

absorbs all the light that negotiates regions (A) to (F) without

absorption. Layer (I) is only present in certain films (microfilms and

X-ray films) and performs the same function as layer (G). It may also

serve to balance the load of gelatin on either side of the base, thus

keeping the film flat (a particular problem in X-ray films).

Bleachable dyes find their uses in the filter layers (C),(E), (G)

and (I), all of which require coloured components that must be absent in

the final picture. However, unlike the dyes of layers (B) to (F), the

dyes of layers (G) and (I) have to cover a much wider range of the

visible spectrum, indeed they must cover the whole range to which the

film is sensitive.

Probably the main use of dyes in underlayers and backing layers is

as antihalation agents. Halation is a phenomenon resulting from

reflection of unabsorbed light from the gelatin/base or base/air

interfaces. This results in activation of a number of silver halide

crystals, figure 1.2. The result is a foggy edge around what might have
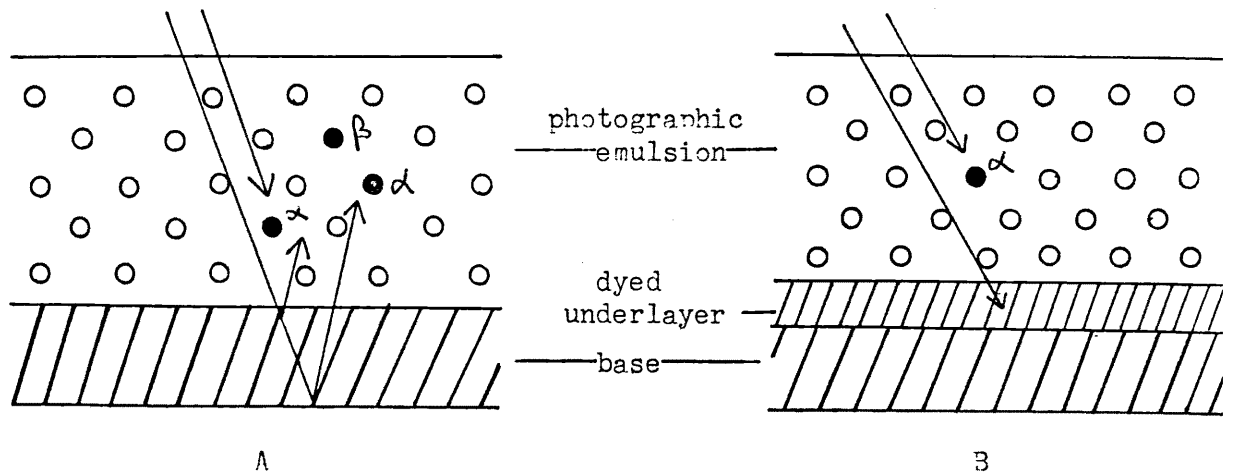
Figure 1.2

been a sharply defined image, a halo. In (A) light is absorbed directly

by silver halide crystal α to give a latent image. Light from the same

image source that fails to hit a silver halide crystal reaches the base

and may be reflected from either surface, thus activating crystals β and

γ. In (B) a dyed underlayer prevents all reflections and a sharper image

α is obtained. It can be seen that a backing layer would perform the

same function as an underlayer, but less efficiently as now only light

that reaches the far side of the base will be absorbed.

It is also possible to eliminate halation by uniformly

distributing a dye (known as an acutance dye) throughout the emulsion

layer. A disadvantage of this is that light which would normally have

reached a silver halide crystal may be absorbed before it finds its

target, with the result that a longer exposure is required. Acutance

dyes, to their credit, increase the definition of an image by eliminating the light scattered by the individual silver halide crystals.

One cannot, at random, select a dye from the Colour Index and insert it into a photographic assembly and assume perfect performance. Bleachable dyes must be compatible with all the other components and processes occurring in a photographic assembly. Thus a bleachable dye should not sensitise or desensitise an emulsion. This rules out many cationic dyes. Strictly speaking, an acutance dye has a desensitising effect on the film as a whole, but not specifically on the halide crystals. The dyes should be removable at some point between the end of exposure and the end of processing i.e. the dyes should be "bleachable". As a first approximation, most water-soluble dyes can be used as photographic antihalation dyes, as they, in theory, wash out during aqueous processing. In practice they do not wash out completely, leaving delicately tinted stains, and they turn the processing solutions highly coloured. In practice, therefore, dye destruction is used to complement, or even supplant, dye desorption.

In the majority of cases it is the sulphite of the developer which destroys the bleachable dye, although mechanistic details have, up until now, been lacking. Since the majority of bleachable dyes contain an α,β-unsaturated carbonyl centre, Scheme 1.1, this is available for Michael-type attack, and consequently the chromophore is broken and the leuco-dye is made more water soluble.

SO_3^{2-} X   Z   O

$\longrightarrow$

SO_3^{-} X   Z   O^{-}
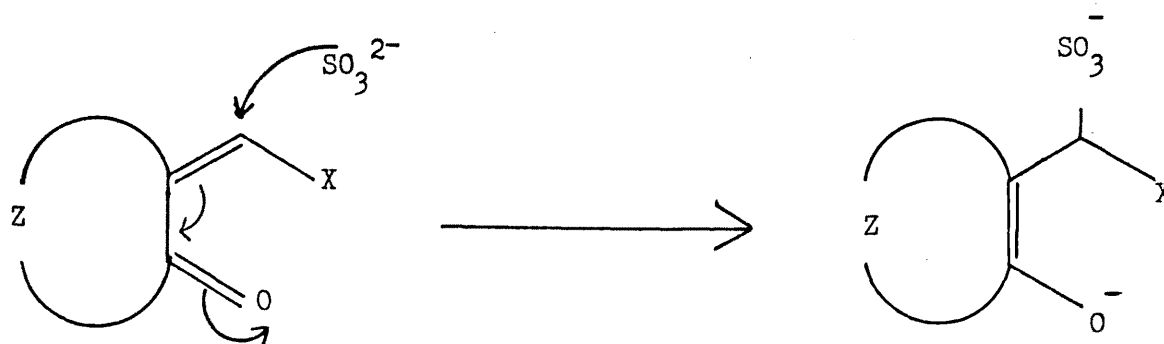
Scheme 1.1

What is not known is the part played by other nucleophiles in the processing brews. The developer often contains thiol-containing moieties which, were they to be present in large enough concentrations, might also add in Michael-type fashion. Hydroxylamine, ethylenediamine and hydrazine are other nucleophiles sometimes present. The fixer consists largely of thiosulphate ion, itself a good, soft nucleophile.

A bleachable dye must also be 'substantive', that is, the dye should stay where it is put. For an acutance dye this means everywhere in the film, and this means that a freely gelatin-soluble (effectively, water soluble) dye can be used, assisting also the bleaching phase. For a filter or antihalation dye, the requirement of layer-specificity (substantivity) is more severe. A first approach to layer-specificity treats the gelatin as a 3-D array of inert strands and designs a dye which is bulky enough to be caught in this "fishing net". This works very well but a dye too bulky to bleed from the gelatin layer in which it is put is often also too bulky to wash out during processing and can regenerate later. It is most difficult to obtain dyes of exactly the right bulk to be layer specific, yet to bleach completely, and other methods of achieving substantivity have been devised. Dyes bristling

Bleachable dyes used today in photography fall largely into four classes.

(a)   Oxonols (1). The dye may be present as a salt, usually

$$(n = 0 - 2)$$
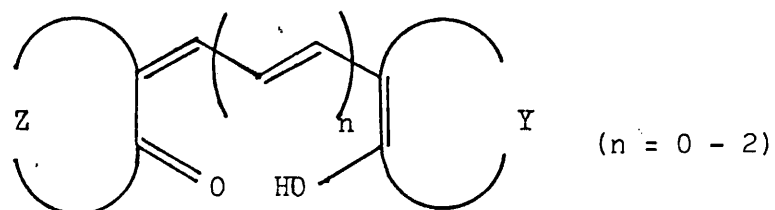
(1)

both z and y represent heterocyclic rings, frequently z = y. In the main, the oxonols form the subject of this research project, the hydroxypyridone methine bridged oxonols (2) being of particular interest, where M = metallic

$$\frac{1}{m} M^{m+}$$
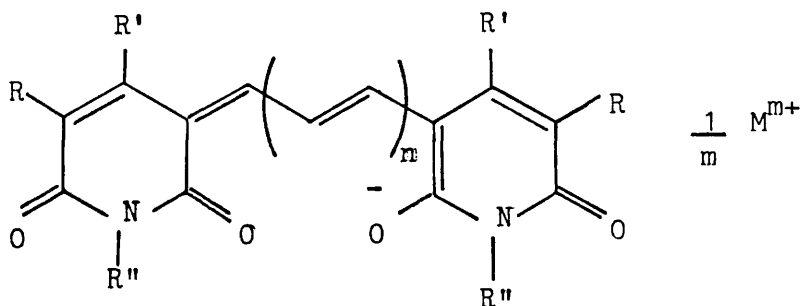
(2)

or organometallic cation, R = CN, $CONH_2$,H; R' = H, Me, NH_2, OH,

CO_2H; R" = H, alkyl, aryl.

(b)   Benzylidene and Cinnamylidenes (3). Z = heterocyclic,

(3)

(n = 0, 1)
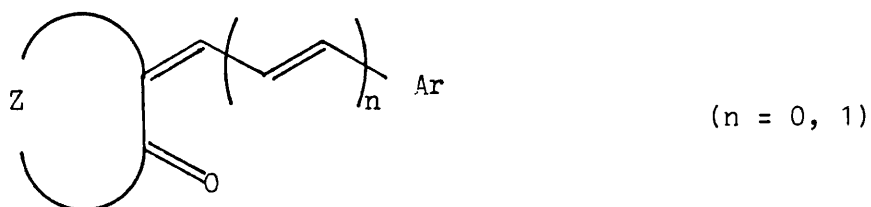
Ar = ⟨O⟩ NR$_2$ or a nitrogen containing heterocycle, e.g. 3-indolyl.

(c)   Merocyanines (4). X, z = heterocyclic rings, the first

(4)

(n = 0, 1)
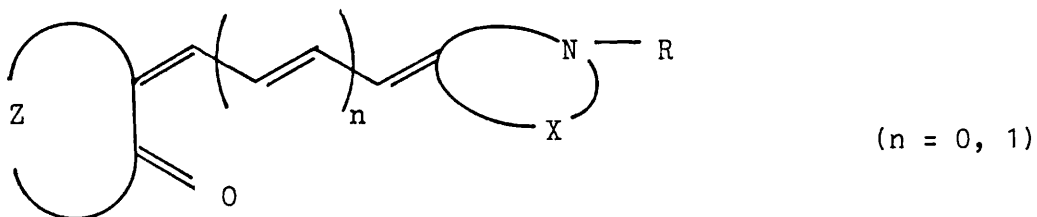
dye in Scheme 1.2 is an example.

(d)   Azamethines (5).
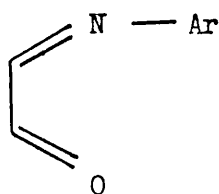
azamethine
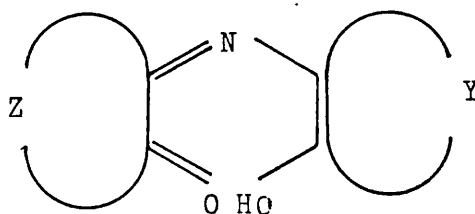
azamethine oxonol

(5)

1.2 Dye Aggregation

Most dyes, when present in a concentrated form (solution, coating in gelatin, solid state[4]) form aggregates. Interactions take place between the electron-rich portions of the dye (the chromophoric system) and these lead to electronic transitions which result in new absorption maxima in the visible region. Aggregation may lead to dimers, trimers or oligomers in solution and is, of course, most prevalent in the solid state, in this case, the aggregation is of a different sort[5]. The subject has been well treated for dyes in general[4,6] including the cy anine dyes used in photography[7,8]. Polarography[6,9] has thrown much light on the mode of aggregation, as has X-ray crystallography[4,8]. Little, however, is known about the aggregation of bleachable dyes. Bleachable dyes readily form aggregates in solution and in gelatin coatings. This can accelerate to the point of precipitation in the coatings and their visible spectra show D and H-bands corresponding to aggregation. Electronic transitions corresponding to aggregate formation may also be induced by dyes stacked correctly onto polymeric mordant backbones[6], a phenomenon known as metachromasy.

The advantages of aggregation are twofold in bleachable dyes, provided that it can be controlled. Firstly, the fact that new absorption maxima are obtained means that one dye now covers a rather greater portion of the visible spectrum and secondly, the aggregates formed are inevitably so bulky that they are caught in the gelatin "fishing net" yet revert to leuco-monomers during bleaching.

Amidinium pyrazolones (6) aggregate strongly in concentrated solution or gelatin coating.
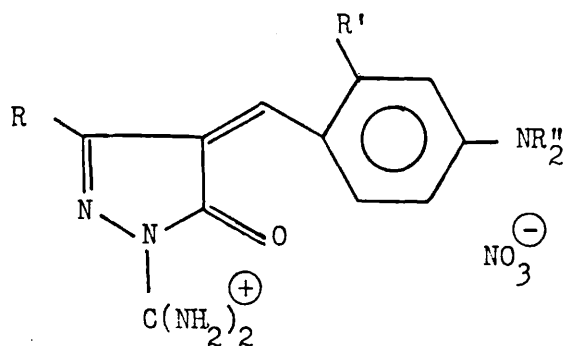
(6)

For example, the dye (R = Me, R' = OCH_2CO_2Et, R" = Et) in aqueous solution gives three new species, figure 1.3[1]. The monomer (dotted line)
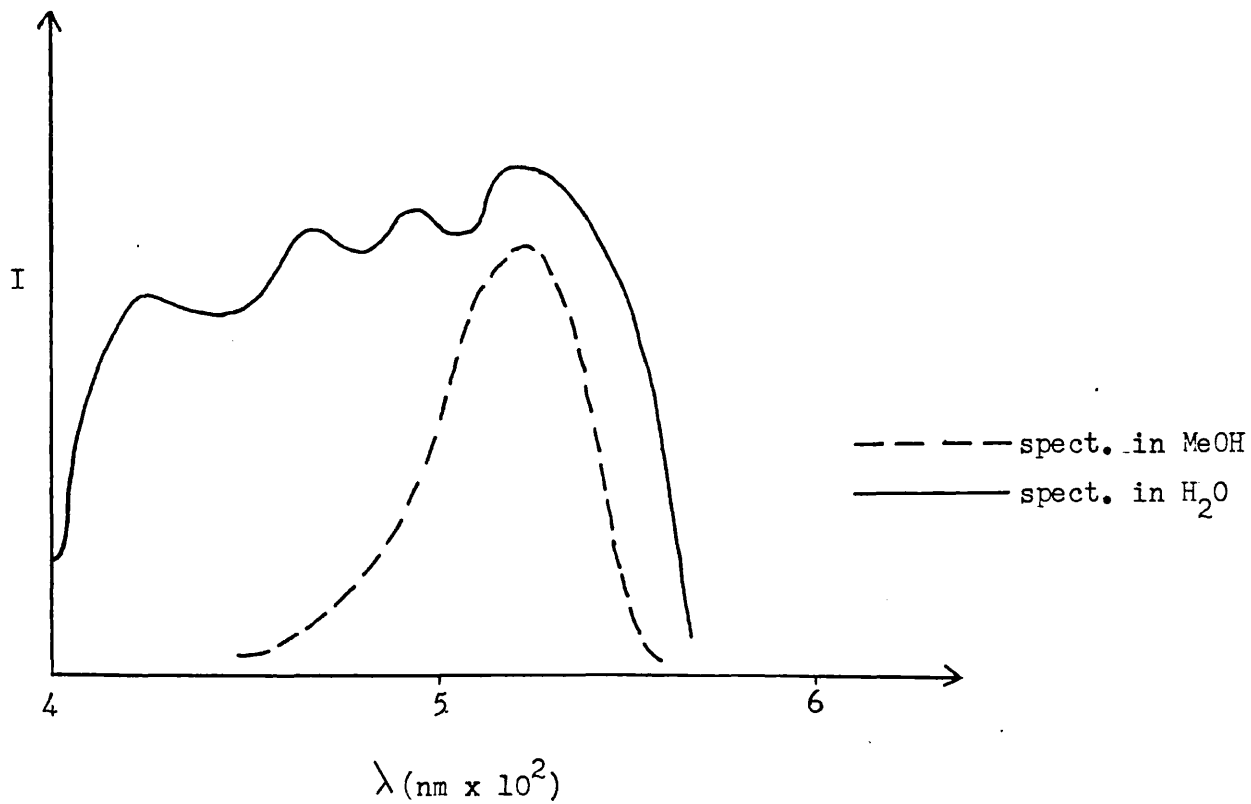
Figure 1.3

has λ_{max} = 510 nm and the oligomers (solid lines) at ca. 490 nm, 470

nm and 430 nm. The aggregation of these dyes is influenced by R, R' and

R". When R' = H and R" = Me, aggregate peaks occur thus: ca. 475 nm

(R = Me), ca. 430 nm and 480 nm (R = P_r^n), ca. 455 nm (R = Ph), but

for R = Bu^t only the monomer is seen. Hydrophobic interactions are thus

seen to be of great significance. The imidinium residue is important,

too, for replacing it either by H-, Ph-, -$CONH_2$ or -$C(NHMe)_2^+$ leads

to non-aggregating dyes. Furthermore, the anion also affects the

aggregate species. Replacement of NO_3^- by Cl^-, for example, gives

stronger aggregates and, in the dye of figure 1.3, each aggregate peak

may, in turn, be removed by increasing concentrations of anionic wetting

agent, and is different for sulphate and sulphonate-type wetting agents.

The water content of gelatin coatings is yet a further factor to be

considered.

Pigments are the ultimate form of dye aggregates, and a pigment of

a water-insoluble dye will, of course, be layer-specific. It has been

found that certain bleachable dye types, when used as pigments and

possessing base-soluble or "hydrophilicising" groups (e.g. hydroxyl)

bleach rapidly enough to be of value. Hydroxypyridone trimethine oxonols

are of great interest as pigments and aggregated species.

1.3 Aims and Objectives (Photographically)

(a) To investigate the development of new anti-halation underlayer

dye systems. This would take a variety of forms and is the subject of

chapter 3.

(b) To make a comprehensive study of the bleaching reaction, being not only concerned with sulphite bleaching but also studying the effects of a whole range of other nucleophiles. This would involve investigation by ^{13}C, ^{1}H n.m.r. and visible spectroscopy. Attempts would also be made to isolate the bleached adducts. This investigation forms the subject of chapter 4.

(c) To study aggregate formation by concentration - dependent solution spectroscopy. For a wide range of dyes examples can be drawn and a study of H-band appearance with increasing concentration made, again using ^{13}C, ^{1}H n.m.r. and visible spectroscopy.

CHAPTER 2

Syntheses

2.1.　Preparation of Hydroxypyridones

2.1.1.　Preparation of cyanoacetamides

In general cyanoacetamides are readily prepared by treatment of an

ester of cyanoacetic acid with an amine (Scheme 2.1). In a similar manner
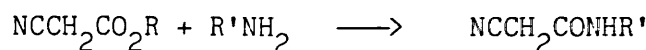
$$NCCH_2CO_2R + R'NH_2 \longrightarrow NCCH_2CONHR'$$
(Scheme 2.1)

bis-amides can be prepared (Scheme 2.2) and these are useful intermediates

to oligomeric dyes (see Chapter 3). The basic procedure of Carson,Scott
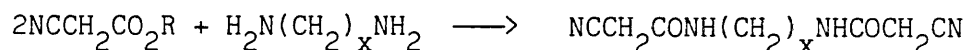
$$2NCCH_2CO_2R + H_2N(CH_2)_xNH_2 \longrightarrow NCCH_2CONH(CH_2)_xNHCOCH_2CN$$
(Scheme 2.2)

and Vose[10] used (where R' = H,Me,Et) was modified for the preparation of

more complex amides (where R' = aryl, styryl; and bis-cyanoacetamides).

2.1.2.　Conversion of cyanoacetamides to hydroxypyridones

The procedure followed for the preparation of simple hydroxy-

pyridones (where R' = H, Me, Et) was that of Bobbitt and Scola [11] who

had investigated the preparation and reactions of 4-methyl-3-substituted

pyridines. This involved condensation of the cyanoacetamides with ethyl

acetoacetate (Scheme 2.3). The synthesis of more complex

$$NCCH_2CONHR' + CH_3COCH_2CO_2Et \xrightarrow{Base}$$
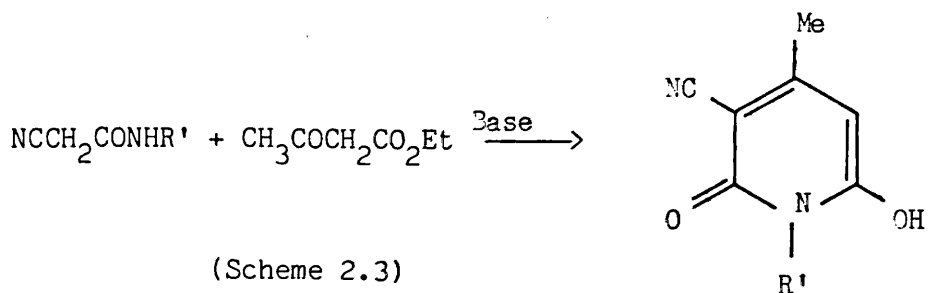
(Scheme 2.3)

hydroxypyridones (where R' = aryl, styryl) and bis-hydroxypyridones

(Scheme 2.4) required modification of the basic procedure,

$$NCCH_2CONH(CH_2)_xNHCOCH_2CN + 2CH_3COCH_2CO_2Et \longrightarrow$$

(Scheme 2.4)
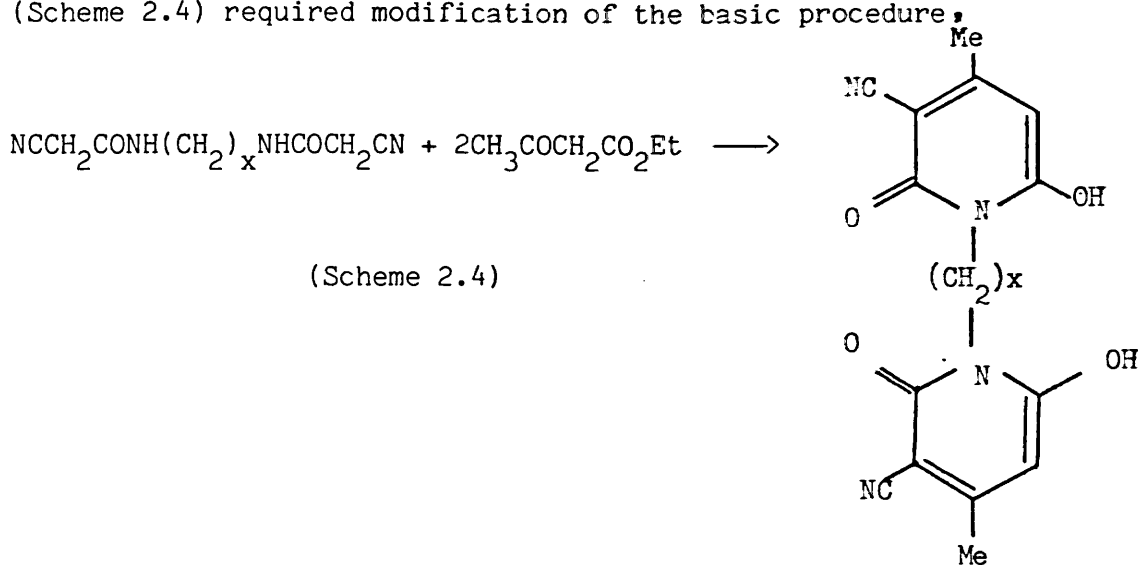
usually involving change of solvent, base (e.g. OH^-, MeO^-, NH_3),

mole ratios or reaction time. Hydroxypyridones can also be prepared

without isolation of the cyanoacetamide but, in general, we have preferred

to purify the synthetic intermediates.

2.1.3. Preparation of potentially polymerisable hydroxypyridones

One important objective of the synthetic work was the preparation

of oxonol dyes attached to a polymer chain. Several approaches to this

problem were investigated (see Chapter 3). One of these required the

synthesis of a hydroxypyridone having an N-styryl substituent. The

synthetic approach chosen required the preparation of m-aminostyrene

(Scheme 2.5) which could then be converted to its cyanoacetamide and
thence to the hydroxypyridone. α-Methyl-(m-nitrobenzyl) alcohol was

(Scheme 2.5)
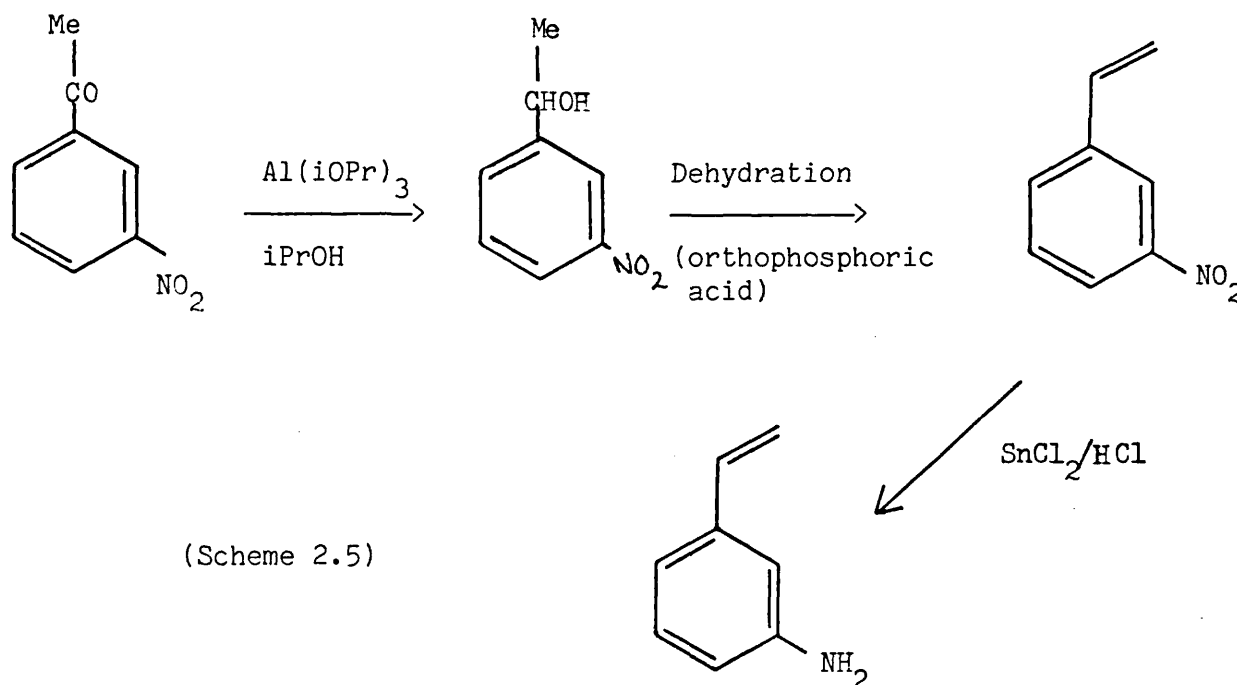
prepared by the method of Lund[12] using the Meerwein-Ponndorf-Verley
reduction of m-nitroacetophenone. This alcohol was then dehydrated with
o-phosphoric acid, which is now the method of choice for such
dehydrations[13]. The m-nitrostyrene so obtained was cleanly reduced to
m-aminostyrene using stannous chloride and concentrated hydrochloric
acid[14].

The conversion of the amine to amide proved to be a difficult
process. Meanwhile other more convenient routes to oligomeric oxonol dyes
were discovered and time did not permit the further investigation of the
syntheses of N-styryl oxonol dye salts.

2.2 Intermediates for the synthesis of unsymmetrical (merocyanine) dyes

The standard routes to the symmetrical hydroxypyridone methine bridged oxonols (2.4.1) do not permit efficient preparation of unsymmetrical structures and a step-wise reaction sequence has been devised to circumvent this problem. β-Anilinoacrolein anil hydrochloride which is readily prepared by reaction of two molar equivalents of aniline with 1,1',3,3'-tetramethoxypropane in the presence of concentrated hydrochloric acid[15] (Scheme 2.6) reacts with a hydroxypyridone in the

$$2 \quad + \quad (MeO)_2CHCH_2CH(OMe)_2 \xrightarrow{HCl} PhNHCHCHCHNHPh \; Cl^-$$
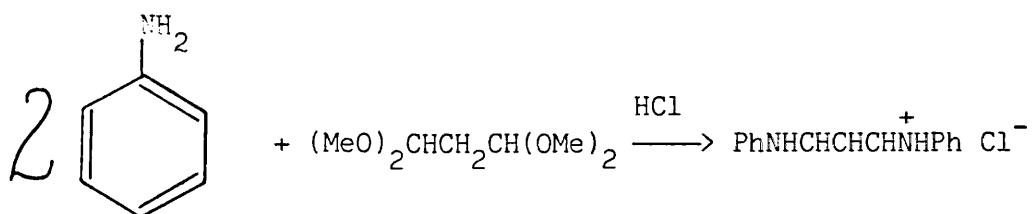
(Scheme 2.6)

presence of acetic anhydride to form an 3-(3'-acetanilidoallylidiene) hydroxpyridone intermediate[16] (Scheme 2.7) which can be isolated.

$$+ \quad PhNHCHCHCHNHPh \; Cl^-$$
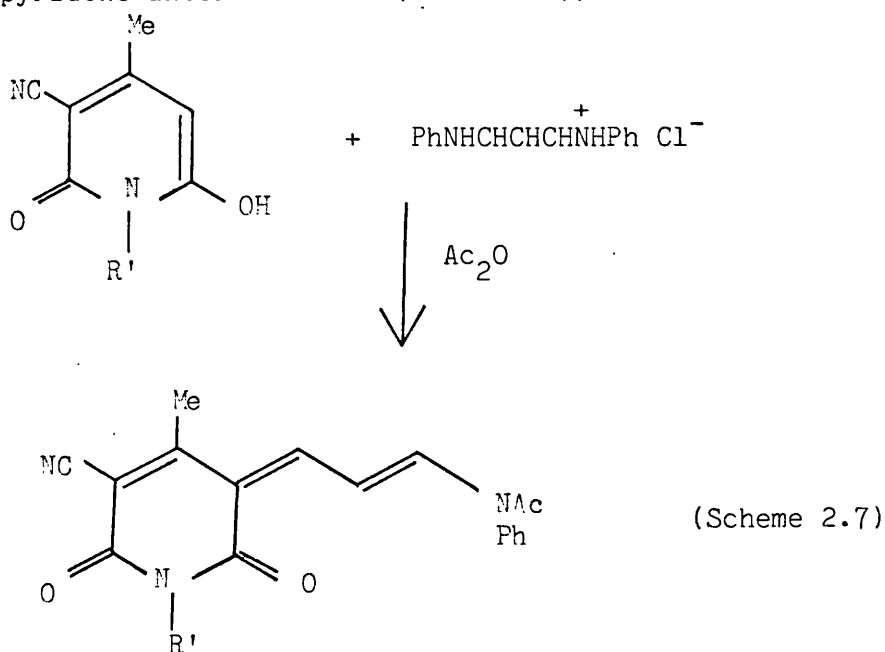
(Scheme 2.7)

When this is treated with an active methylene compound, for example, a

different hydroxypyridone molecule or a 2-methyl benzothiazolium salt, an

unsymmetrical dye is obtained (Scheme 2.11).

Dyes containing an extra bridging double bond may be prepared in a

similar manner using glutaconic dialdehyde dianil hydrochloride. This

intermediate is derived by reaction of N-(2,4-dinitrophenyl) pyridinium

chloride with three molar equivalents of aniline[17] (Scheme 2.8) and its
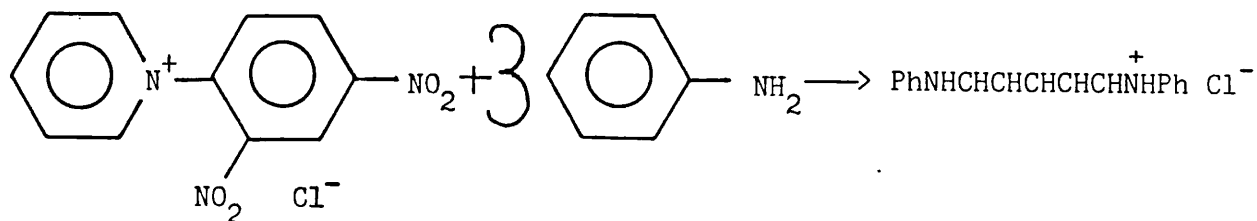
(Scheme 2.8)

subsequent reaction with a hydroxypyridone yields the penta-methine

bridged intermediate[16]. Glucaconic dialdehyde dianil hydrochloride is

also used for the preparation of symmetrical penta-methine bridged oxonol

dyes (2.4.1).

2.3.   An intermediate in the preparation of a radical-cation oxonol dye

The aprotic diazotisation of anthranilic acid by isopentyl nitrite

in the presence of carbon disulphide and isopentyl alcohol in boiling

1,2-dichloroethane yielded 2-isopentoxy-1,3-benzodithiole. Thermal

decomposition of the benzodithiole at 200° produced dibenzotetrathia-

fulvalene[18] (Scheme 2.9).

(Scheme 2.9)

$(R = C_5H_{11} - iso)$
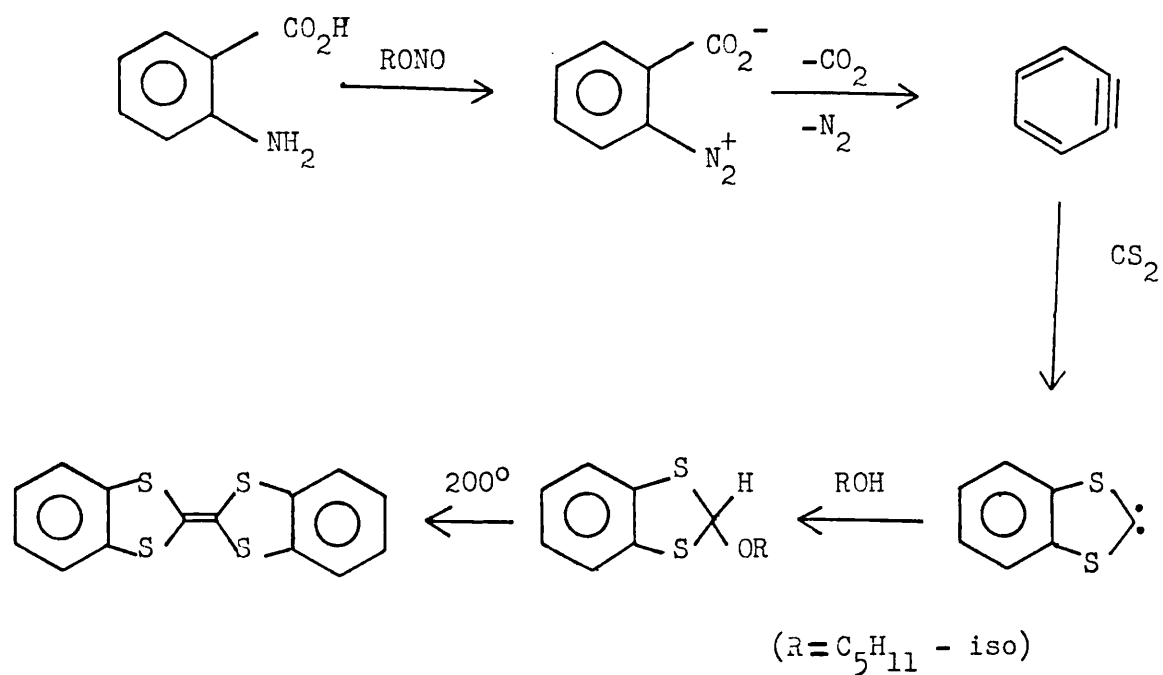
2.4. Preparation of dyes

Five general classes of dye have been prepared:

(a) symmetrical hydroxypyridone mono-, tri-, and penta- methine bridged oxonols;

(b) unsymmetrical hydroxypyridone methine bridged oxonols and merocyanines;

(c) cationic hydroxypyridone methine bridged oxonols;

(d) polymeric and polymerisable hydroxypyridone methine bridged oxonols;

(e) radical-cation hydroxypyridone methine bridged oxonol salts.

Dyes of type (d) and (e) form the subjects of Chapters 3 and 7, respectively, and hence are not covered here.

2.4.1. Preparation of symmetrical hydroxypyridone methine bridged oxonols[19]

The general synthetic route to these materials involves condensation of two moles of hydroxypyridone with one mole of coupling agent in the presence of a base or salt (usually an acetate or halide). For monomethine bridged oxonol salts triethylorthoformate is the coupling agent. For the trimethine analogues 1,1'3,3'-tetramethoxypropane is used and for the pentamethine dyes glutaconic dialdehyde dianil hydrochloride is present. (Scheme 2.10).
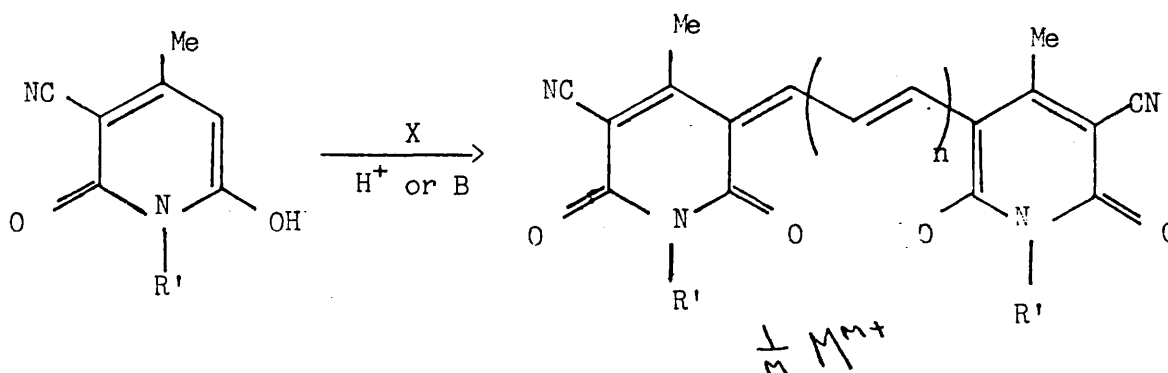
(m = 1-4)

$n = 0$ X $=$ $(EtO)_3CH$

$n = 1$ X $=$ $(MeO)_2CHCH_2CH(OMe)_2$

$n = 2$ X $=$ $PhNHCHCHCHCHCHNHPh \ Cl^-$

(Scheme 2.10)

Table 2.1 lists the hydroxypyridone methine bridged oxonols
prepared by this method.

Table 2.1.
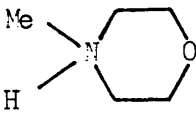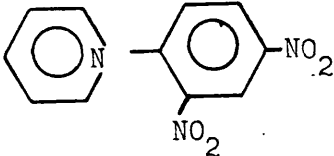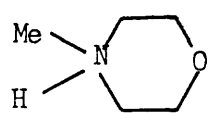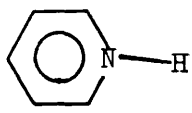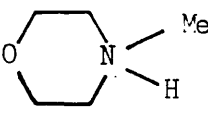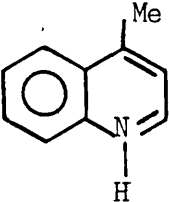
X	R'	M	m
$(EtO)_3CH$	Et	Et_3NH	1
$(MeO)_2CHCH_2CH(OMe)_2$	H	Ca	2
"	Me	Bu_4N	1
"	"	Et_4N	1
"	"	Ph_3MeP	1
"	Et	Ca	2
"	"	Co	2
"	"	Ni	2
"	"	Al	3
"	"	Ag	1
"	"	Et_3NH	1
"	"	Ph_4P	1
"	"	$Ph_3PCH_2CH_2PPh_3$	2
"	"	$H_2C=CHCH_2PPh_3$	1
"	"	Bu_4N	1
"	"		1
"	"		1

Table 2.1 (continued)

X	R'	M	m
"	"	$H_2C = \overset{\underset{\|}{Me}}{C} - \overset{\underset{\|\|}{O}}{C} - OCH_2CH_2\overset{\underset{\|}{H}}{N}Me_2$	
"	Bu^n	H	1
"	"	Na	1
"	"	Li	1
"	"		1
"	"	Bu_4N	1
"	Hex^n	Bu_4N	1
"	Phenyl	H	1
"	Tolyl	Ca	2
"	Anisyl	Ca	2
$\overset{+}{PhNHCHCHCHCHCHNHPh}$ Cl⁻	Et	Et_3NH	1
	"		1
			1
			1

The dye parent acid is obtained from reaction of hydroxypyridone and, for example, 1,1'3,3'-tetramethoxypropane in the presence of acetic acid.

2.4.2. Preparation of unsymmetrical hydroxypyridone methine bridged oxonols and merocyanines.[20]

These materials are prepared by the treatment of 3-(3'-acetanilido-allyldiene)hydroxypyridone with active methylene compounds in the presence of pyridine/triethylamine (Scheme 2.11). Where a second mole of a different hydroxpyridone is used unsymmetrical trimethine bridged oxonols result. Tetramethine formally neutral merocyanines result when active heterocycles such as 2-methyl benzothiazolium bromide are present.
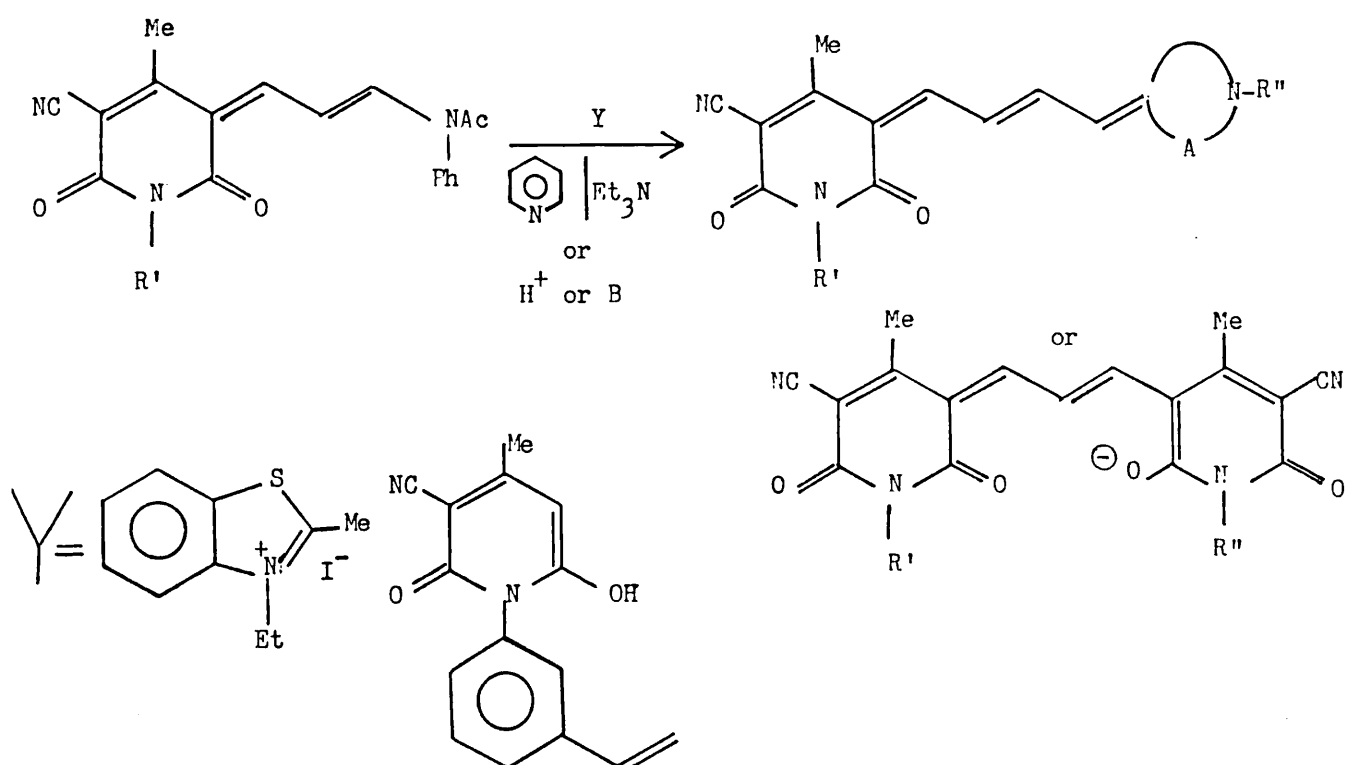
(Scheme 2.11)

2.4.3. Preparation of cationic hydroxypyridone methine bridged

oxonols [21]

The only cationic oxonol synthesised was that obtained by reaction

of N-dimethylaminopropyl hydroxypyridone with coupling agent 1,1',3,3'-

tetramethoxypropane in the presence of hydroiodic acid/iodine (Scheme

2.12).
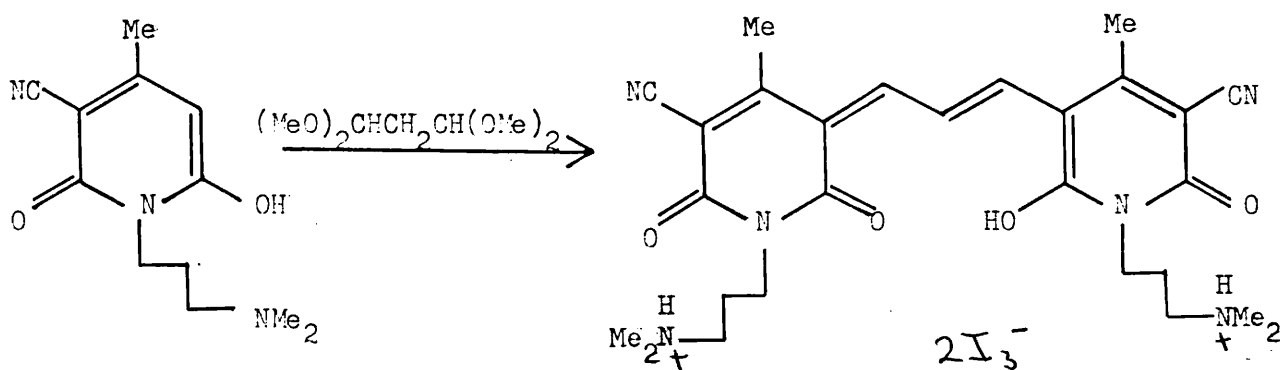
(Scheme 2.12)

This enabled a cationic oxonol with non-stoichiometric iodine content to

be obtained.

CHAPTER 3

Polymeric Dye Systems as Bleachable

Antihalation Underlayers

3.1. It is the function of the antihalation underlayer to prevent any

unabsorbed rays of light which have passed through the sensitive film

layers from being reflected, thereby preventing "halation". One might

assume that making the light which reaches the underlayer of a narrow

enough wavelength range could reduce the underlayer composition to a

single dye component. For example, in a colour film, a combination of

yellow and magenta filter layers, coloured colour forming agents called

"masks" and a light-tight camera could reduce the requirement for the

underlayer to merely a red light absorbing (cyan) component. In practice,

however, the inefficiency of the filter layers to absorb all of the light

passing through them and the additional expectancy of the underlayer, in

many cases, to also behave as a backing layer (that is to prevent light

entering through the back of the assembly) means that it more usually has

to deal with a much wider range of the visible spectrum. This is

presently achieved by using a combination of up to three separate dyes and

relying on dye aggregrate formation to provide good overlap of the

individual dye absorptions,[22] figure 3.1.
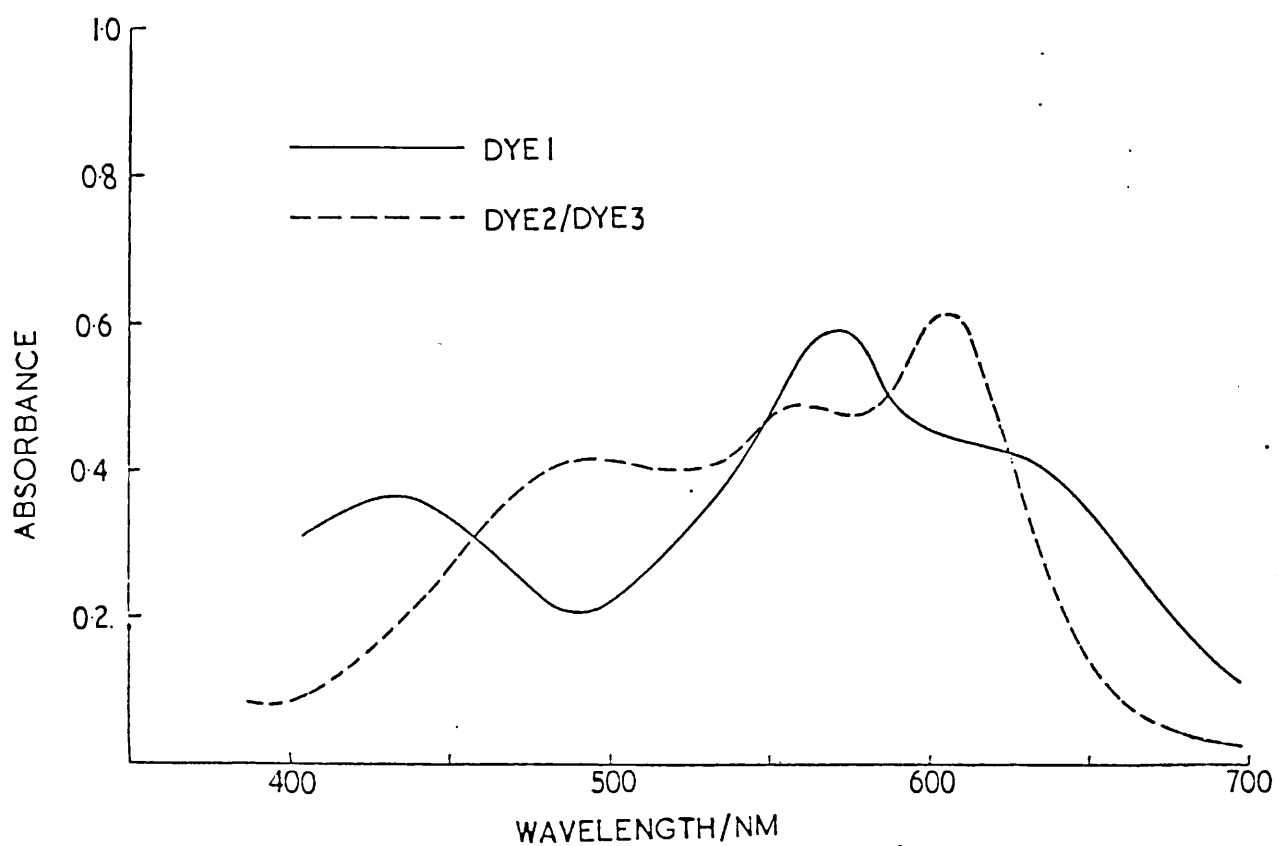
Figure 3.1.

Commercially, underlayer formulation involves separate preparations of the component dyes and polymer, followed by their subsequent co-precipitation. It was our intention to investigate both the simplification of this procedure and other approaches to improving dye substantivity.

3.2. Chain-Growth Polymerisation

3.2.1. Hydroxypyridone oxonol salts of polymerisable cation

We synthesised a monomeric dye-mordant species (I) (Scheme 3.1) which we hoped to polymerise in either solution or the solid state.
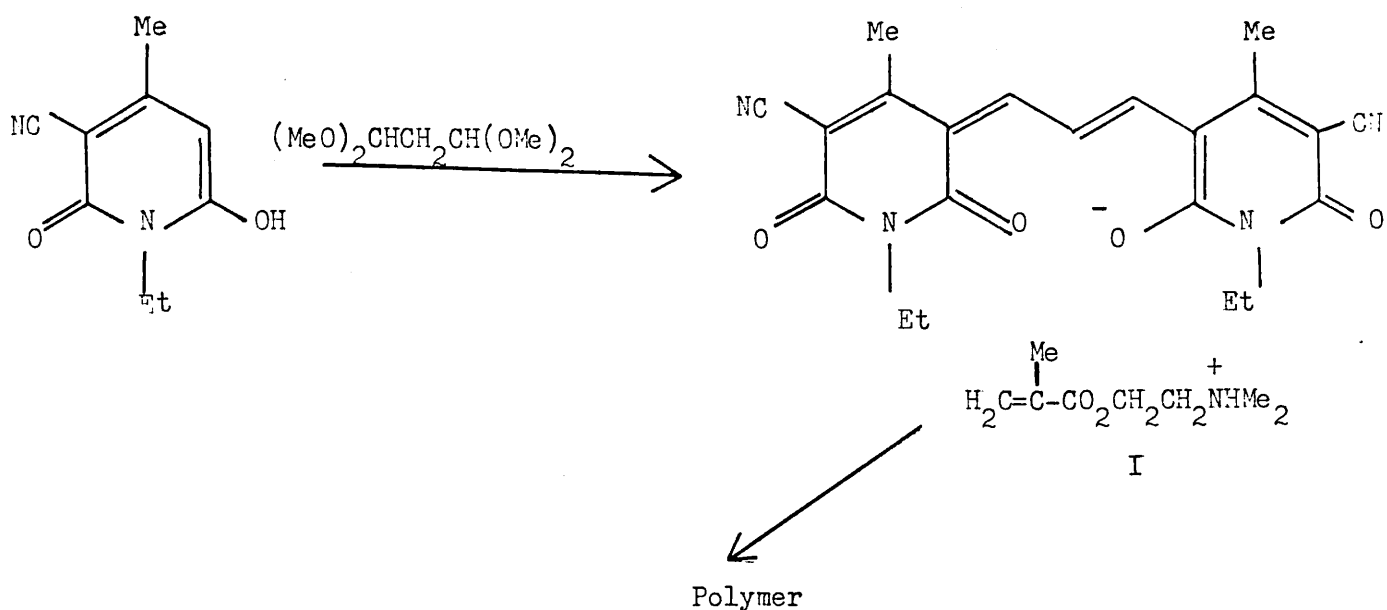
Scheme 3.1

Several methods were tried. These included reacting

(a)   a 10% w/w solution of (I) in water, in the presence of

1 mol % of the initiator 4,4'-azobis(4-cyanopentanoic acid

(ABCPA) at 60°C overnight,

(b)   a 20% w/w solution of (I) in absolute ethanol, in the presence of

0.5 mol % azobisisobutyronitrile (AZBN) at 60°C overnight,

(c)   a 10% w/w solution of (I) in dimethylformamide, in the presence of

0.5 mol % AZBN, at 60°C overnight,

and

(d)   a 20% w/w solution of (I) in dimethylformamide, in the presence of

0.5 mol % AZBN, at 60°C overnight.

In the solid state, solid (I) was:

(e)   heated at 160°C overnight,

and

(f)   exposed to ultraviolet radiation (λ = 207 nm) over a

weekend.

In every case ^{1}H n.m.r. spectra indicated that the vinyl group

protons remained intact. It was thought that the hydroxypyridone oxonol

anion in (I) might be inhibiting the chain-growth polymermisation.

Certainly the chromophore was involved in a reaction of sorts during the

attempted polymerisation since bleaching was seen to occur. This process

was investigated by dilatometric measurements. The progress of a

polymerisation can be determined by means of continuous monitoring of the

volume contraction. Starkweather and Taylor[23] demonstrated that a

linear relationship exists between volume contraction in per cent and the

degree of polymerisation. We have compared the polymerisation of methyl

methacrylate, using azobisisobutyronitrile, AZBN, as initiator in methyl

ethyl ketone at 60°C with and without added (I). In theory, there were

three possibilities:

(a)   (I) could be inhibiting the polymerisation,

(b)   (I) could be retarding the polymerisation,

(c)   (I) could be both retarding and inhibiting the
       polymerisation.

Retarders slow down the rate and inhibitors will completely stop

polymerisation. Both types tend to act in the same way and differ only in

their efficiency in rendering the growing chains inactive. The effect of

the addition of a retarder or an inhibitor to a free-radical

polymerisation system is shown in figure 3.2[24]. Nitrobenzene for example,

acts as a retarder for styrene through a chain-transfer reaction. The

$$H_0 - H_t$$

induction period
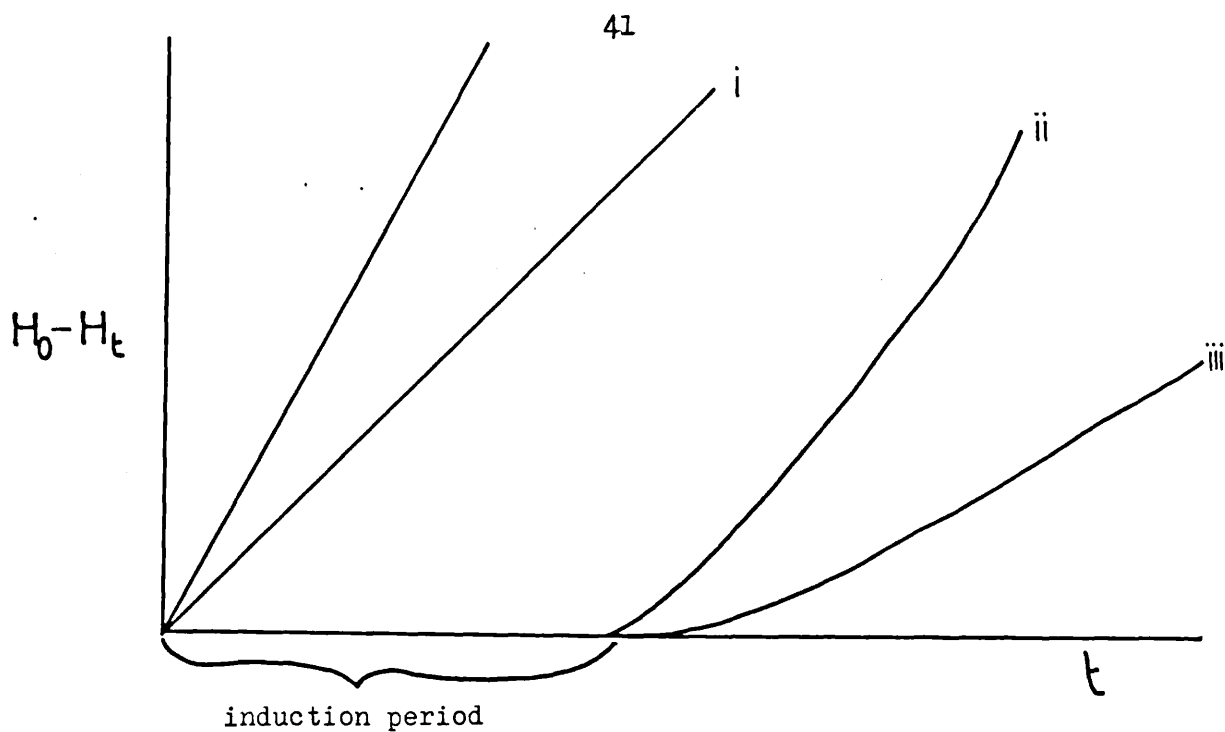
(i) Retardation

(ii) Inhibition (note the induction time during which the inhibitor is
consumed)

(iii) Inhibition and Retardation (the product from the inhibition reaction
is a retarder for the polymerisation)

Figure 3.2

radicals yielded by this reaction are rather inactive and react only

slowly with styrene monomer molecules. In this case both the rate and

degree of polyermisation are reduced. On the other hand benzoquinone

inhibits the polymerisation of styrene by scavenging every polymer radical

formed and converting them into unreactive substances. The inhibitor

itself is rendered inactive by the reaction and this leads to a phenomenon

known as an "induction period" whereby inhibition only takes place for a

limited period of time. After all the inhibitor molecules are used up

polymerisation proceeds in the normal way[24]. Figure 3.3 shows the

observed effects with (ii) and without (i) added (I) on the

polymerisation, clearly demonstrating its inhibiting nature.
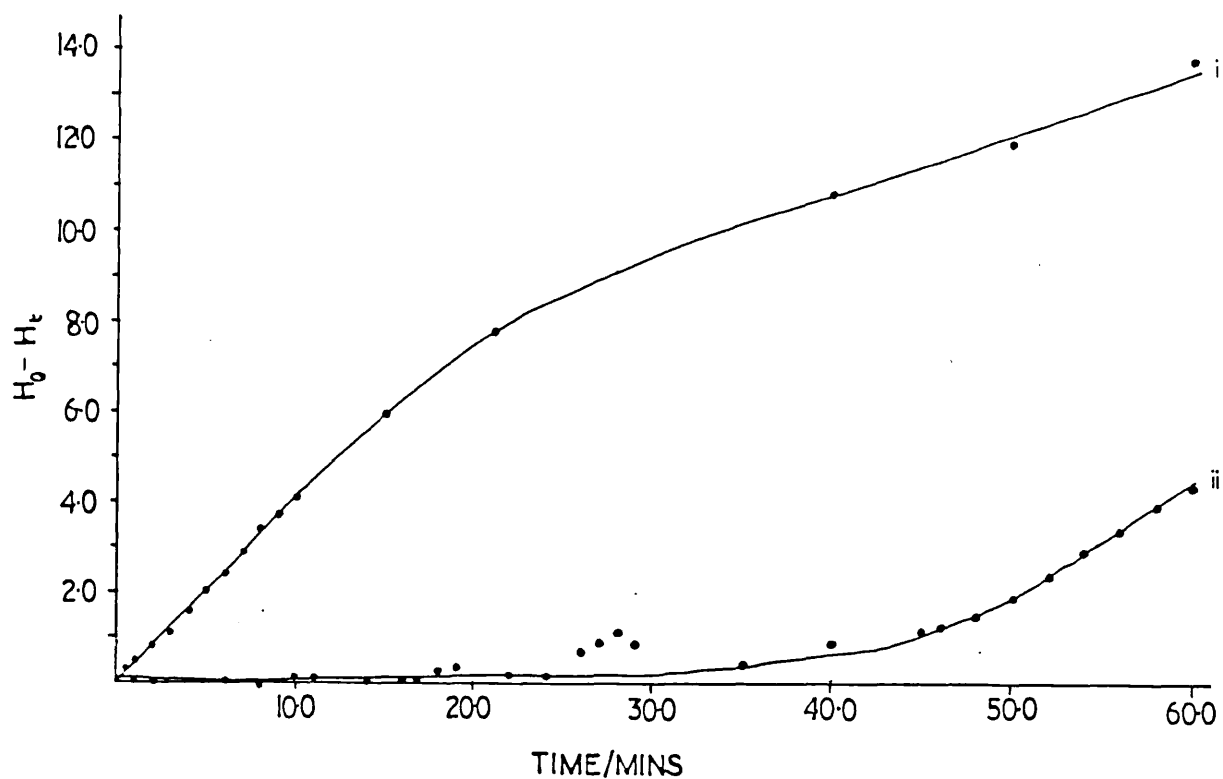
Figure 3.3.

A later X-ray structural study of (I) revealed the closest

proximity between the vinyl groups of adjacent cations in the lattice to

be 13 Å (see Chapter 6). It was therefore not surprising that the solid

state polymerisation was not successful.

3.2.2. Polymerisable hydroxypyridone methine bridged oxonol

anions

Our initial intention was to introduce a polymerisable N-styryl

substituent on to one of the pyridone rings of the oxonol dye anion.

However, as a result of the findings of the dilatometric measurements in

the previous section we decided that the polymerisation would have to be

carried out at the hydroxypyridone stage, Scheme 3.2, as the evidence
tended to suggest that it was the methine bridge of the oxonol dye anion
which was responsible for its inhibiting properties.   The cyanoacetamide
(I) (Scheme 3.2) however, proved difficult to synthesise, and this,
coupled with the discovery of a more convenient route to polymeric/
oligomeric systems (3.3), meant that no further work was done in this
area.
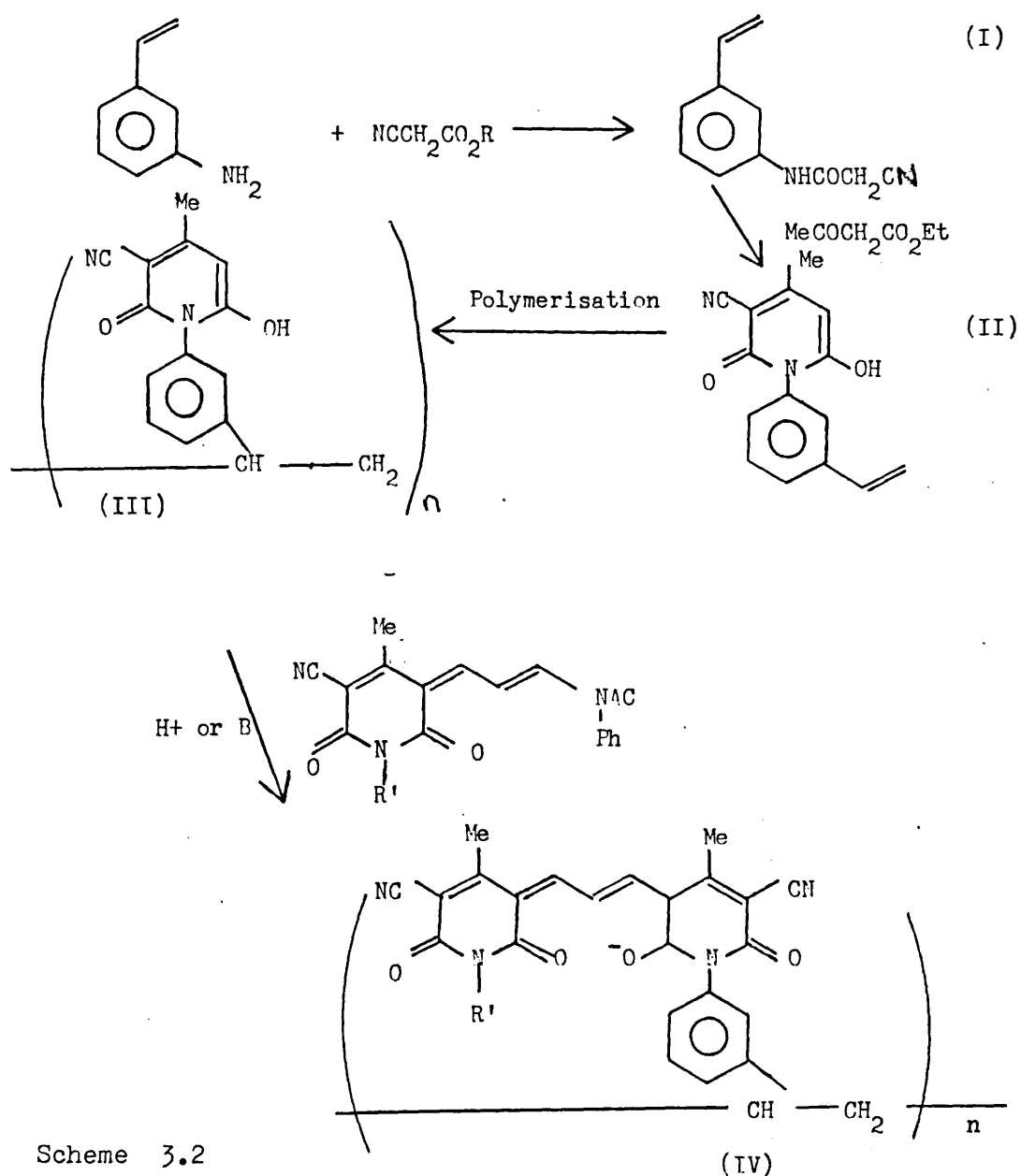
Scheme 3.2

3.3   Step-Growth Polymerisation

This involved the synthesis of symmetrical bis-hydroxypyridones,

hence providing two identical sites at which condensation could take place

(Scheme 3.3).   The subsequent "step-growth" condensation polymerisation

reaction with 1,1',3,3'-tetramethoxypropane, yielded oligomeric species

III, Scheme 3.3.

$$2NCCH_2CO_2R + H_2N(CH_2)xNH_2 \longrightarrow NCCH_2CONH(CH_2)xNHCOCH_2CN$$

(I)

$$2MeCOCH_2CO_2Et$$

(II)

(III)

$(M= Et_3NH ; x =3,4,6 ; n=1-4 ; m=1)$
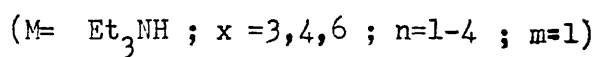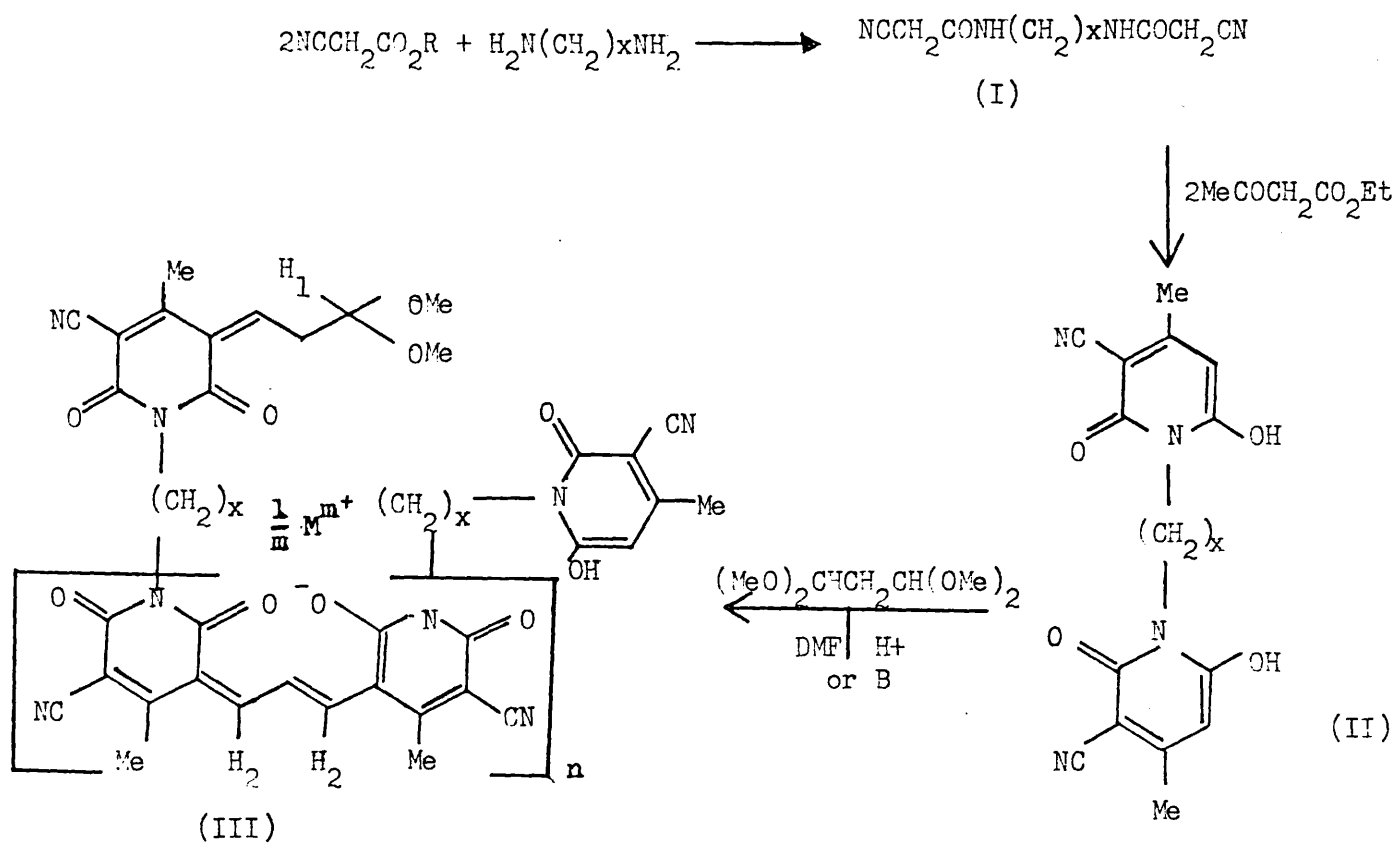
Scheme 3.3

The course of the polymerisation where (III, x = 6, M = Et_3NH and m = 1) was followed with time by removing small aliquots from the reaction mixture (a 40% w/w solution of the bis-hydroxypyridone in dimethyl- formamide with a molar equivalent of 1,1',3,3'-tetramethoxy-propane and excess triethylamine) every four hours. These were then reprecipitated from ethyl acetate and characterised using high field ^1H and ^{13}C n.m.r. and u.v./visible spectroscopic techniques.

"End-group" analyses by way of the high field ^1H n.m.r. spectra provided us with more quantitative results. These analyses were carried out by selecting two peaks in the ^1H spectrum of each of the aliquots, one corresponding to one or more equivalent protons of an end-group (H^1, Scheme 3.3) and the other to one or more equivalent protons of the repeating unit (H^2, Scheme 3.3). The ratio of their relative integrals provides an estimate of the number of repeating units (n) at any one time (Table 3.1), though it must be borne in mind that one is always dealing with a molecular weight distribution.

Time/Hours	4	8	12	16	21	25	29	45
n	2.30	2.89	3.54	4.08	3.46	3.00	2.39	1.58

Table 3.1

Figure 3.4 shows the absorbances at the λ_{max} values for each of the aliquots (1 mg in 100 cm^3 H_2O). Close examination of these
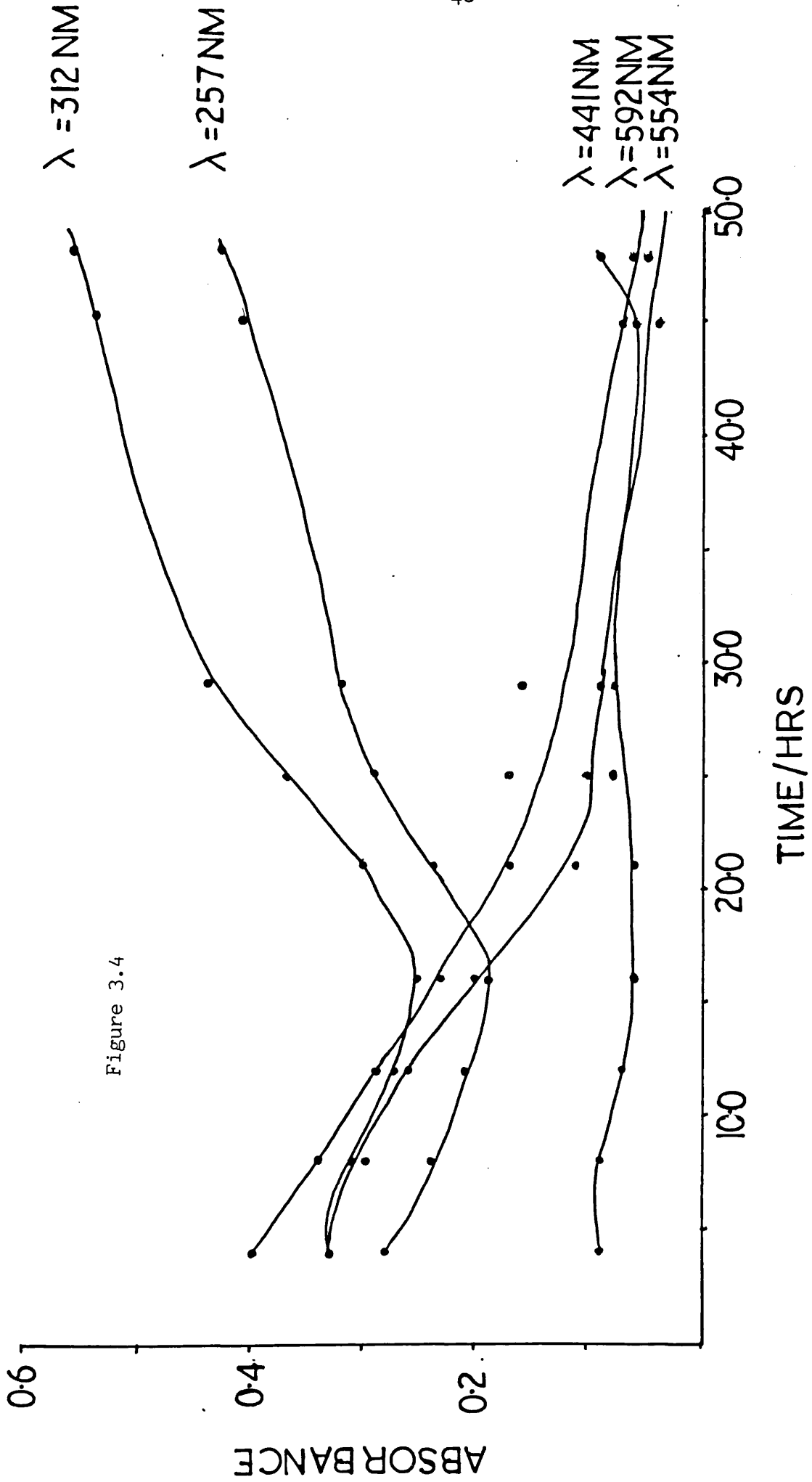
Figure 3.4

results in conjunction with their [1]H n.m.r. spectra shows

(a)   0 - 16 hours; (i) a gradual decrease in absorbances at 592, 554 and

441 nm coupled with a decrease at 312 and 257 nm;

and

(ii) a steady shift to a higher molecular weight distribution.

(b)   16 - 48 hours; (i) a gradual increase in absorbances at 257 and

312 nm coupled with a decrease at 592, 554 and 441 nm.

and

(ii) a steady shift to a lower molecular weight distribution.

The absorbances at 592, 554 and 441 nm are essentially due to the

lower molecular weight, water soluble species, monomeric and dimeric

material in the main. The absorbances at 257 and 312 nm correspond to the

bis-hydroxypyridone (II, Scheme 3.3). The results then suggest that

between 0 - 16 hours we are observing a consumption of the

bis-hydroxypyridone and the formation of higher molecular weight, water

insoluble, material. Between 16 - 48 hours we are seeing an increase in

residual bis-hydroxypyridone resulting possibly from the gradual

decomposition of oligomeric material.

It thus became apparent that the most promising material was the

low molecular weight oligomeric material formed after only four hours. It

was water soluble and appeared to aggregate sufficiently well even at this

low molecular weight distribution to provide very good spectral coverage,

figure 3.5. Gelatin coatings on triacetate base have been made of this

material and it has undergone Ilford Ltd's standard evaluation tests for

substantivity (a) and bleachability (b) and (c), figure 3.5 (see section

10.2.3). The material is seen to be both highly substantive and bleachable.

(a)

(b)

(c)

WAVELENGTH/NM

350   450   550   650
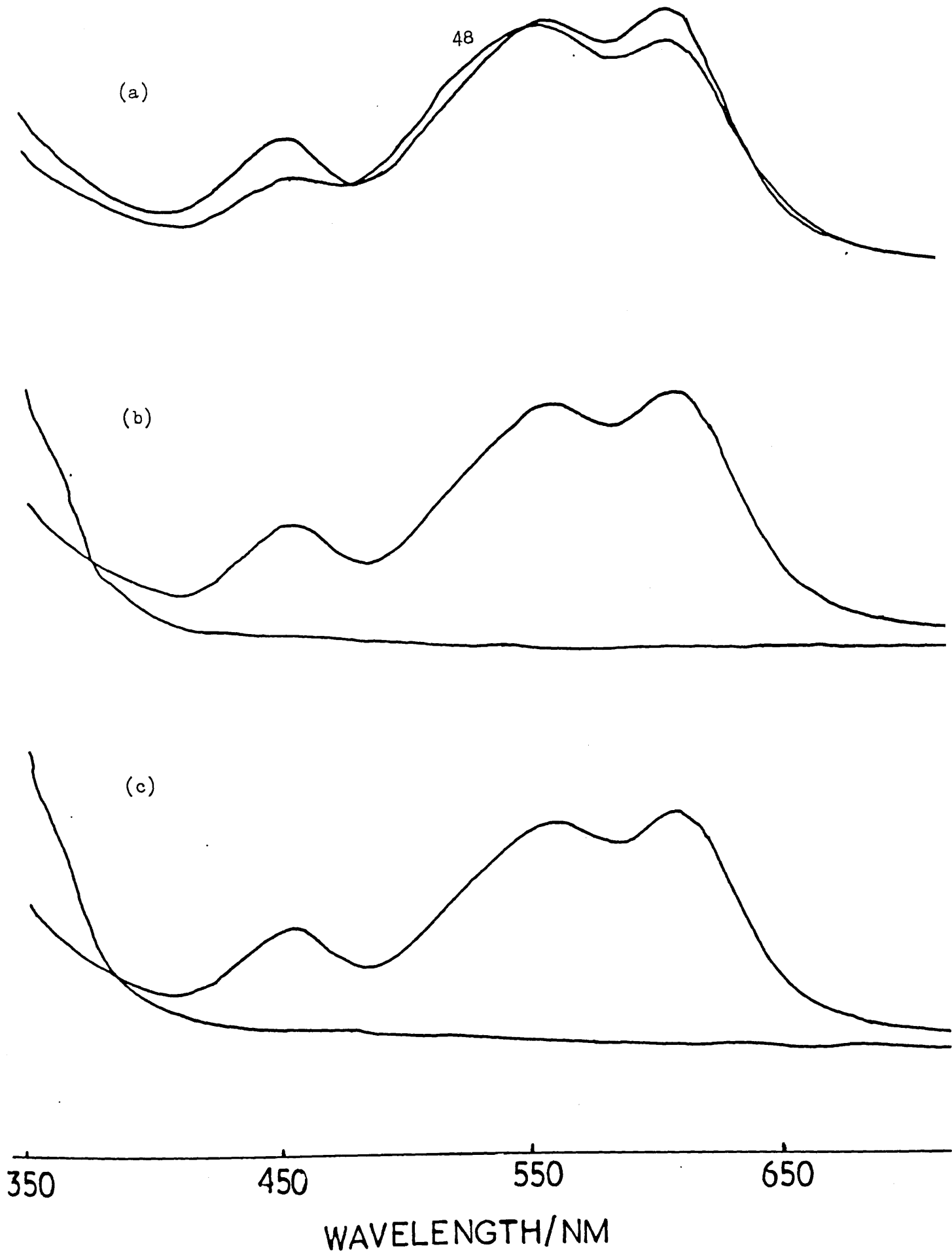
Figure 3.5

Thus, although the long chain "double bond" free-radical polymerised materials are not readily synthesised the oligomers obtained by condensation polymerisation appear to have the desired properties of an anti-halation underlayer and are easily prepared. Indeed the materials described here are currently undergoing further commercial evaluation.

CHAPTER 4

The Bleaching Reaction

4.1   Most bleachable dyes have the α, β-unsaturated carbonyl residue as part of their chromophore. This is susceptible to a Michael-type conjugate attack at the soft electrophilic centre on the methine bridge, Scheme 4.1.
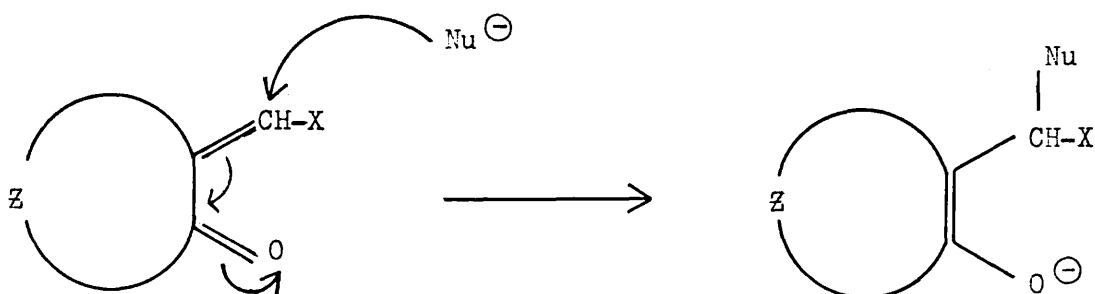
Scheme 4.1

This not only solubilises the dye, assisting its removal by washing out during aqueous processing, but also interrupts the chromophoric system (hence "bleaching" as a term). It may also, in aggregated systems disrupt the aggregand/crystal packing, making the aggregate as a whole less well held in the gelatin "fishing net".

Photographic folklore has always assumed the sulphite of the developer to be the major bleaching agent, but direct evidence for sulphite ion bleaching dyes of this type has been lacking. The so-called Stenhouse dyes have shown to undergo attack by sulphite ions[25] as shown in Scheme 4.2. The benzylidene dyes, which are also bleachable, have

$$PhNH - CH = CH - CH = \overset{\underset{|}{OH}}{C} - CH = \overset{\oplus}{N}HPh \quad Cl^{\ominus}$$

$\downarrow \quad SO_3^{2-}$

$$^{\ominus}O_3S - CH = CH - CH = \overset{\underset{|}{OH}}{C} - CH = NPh \quad + PHNH_2$$

(colourless stable crystals)
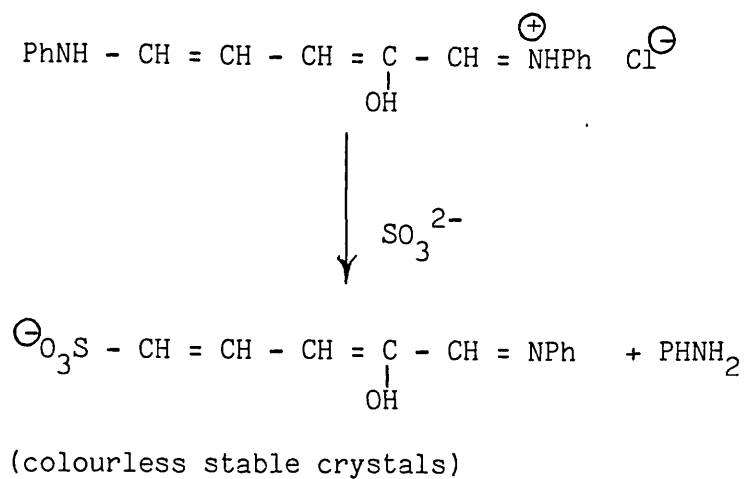
Scheme 4.2

been shown to undergo nucleophilic addition by the cyanide ion in a similar fashion, Scheme 4.3.
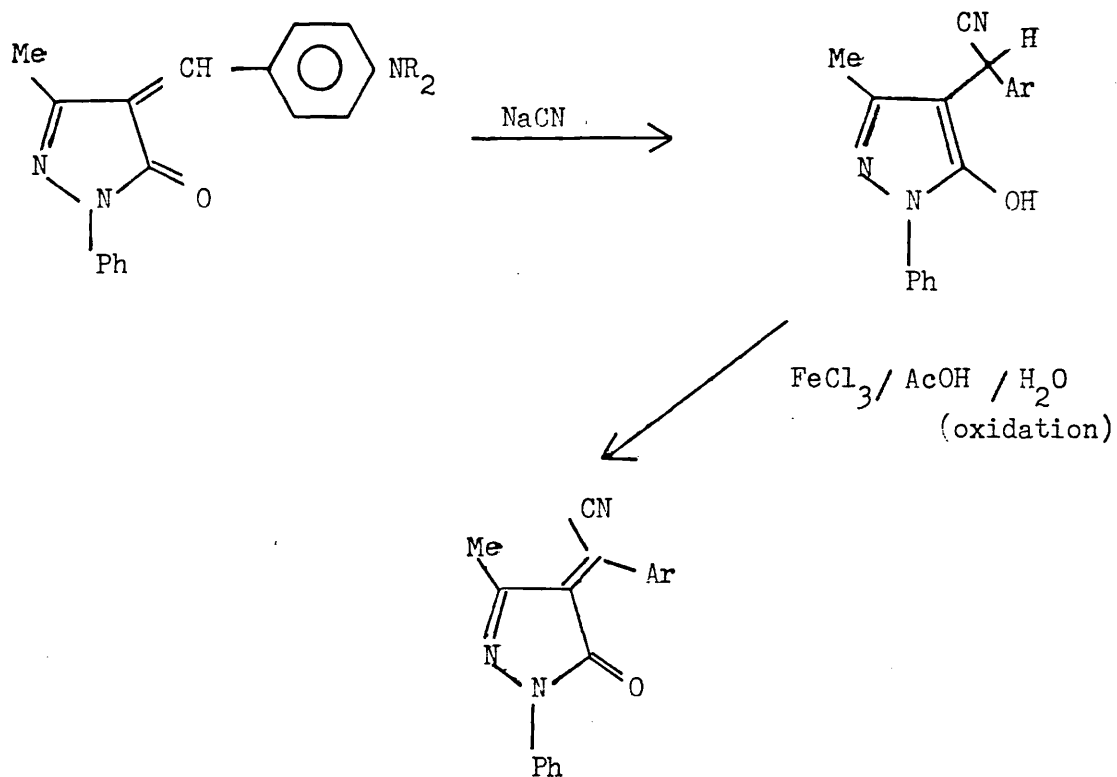
Scheme 4.3

We thus set out to investigate in more depth the bleaching of the

hydroxypyridone trimethine oxonols by a variety of nucleophiles using

visible and ^{1}H and ^{13}C n.m.r. spectroscopic techniques. Although the

sulphite ion was to be studied most extensively, reactions involving

ions such as OH$^-$, S^{2-}, CN$^-$, $\overline{O}Me$, NH$_3$ and EtNH$_2$ were also

examined. Dye (I) was chosen for our investigations as it had relatively

simple ^{1}H and ^{13}C n.m.r. spectra resulting from its metallic cation and

(I)
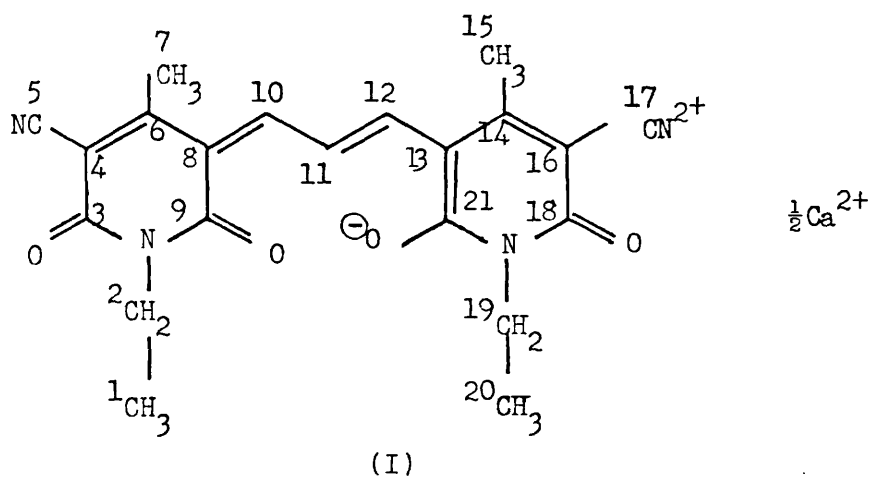
symmetry. Figure 4.1 shows its ^{1}H, ^{13}C-proton decoupled and

^{13}C fully proton coupled n.m.r. spectra, tables 4.1 and 4.2 their

respective assignments.

400.13MHz ^{1}H spectrum (d^{6}-DMSO)
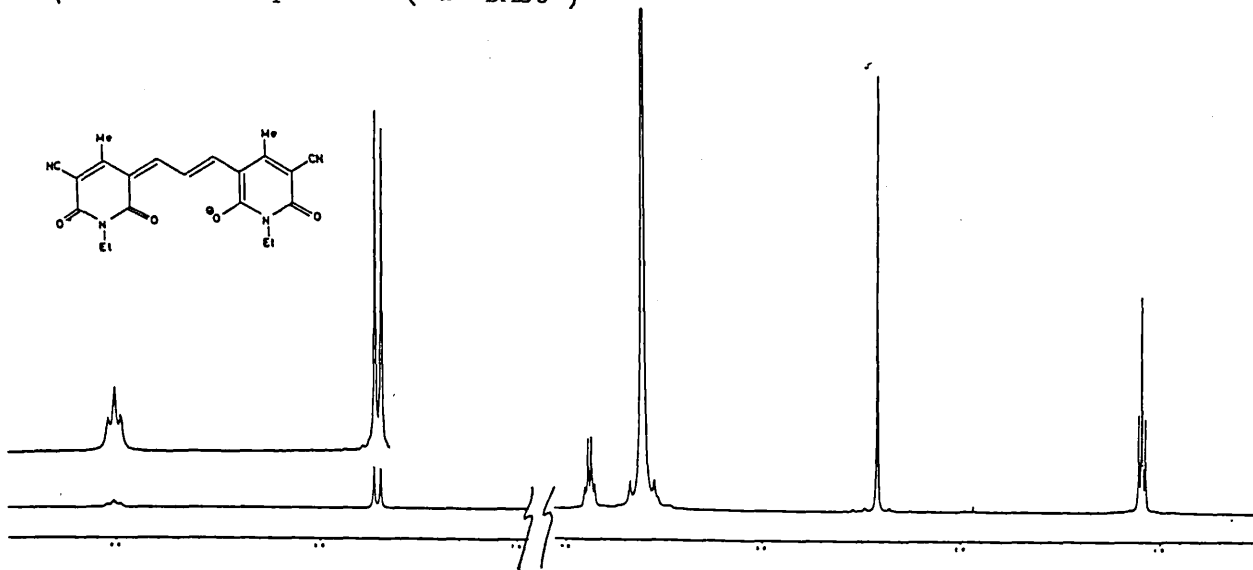
62.90 MHz ^{13}C-proton decoupled spectrum (d^{6}-DMSO)
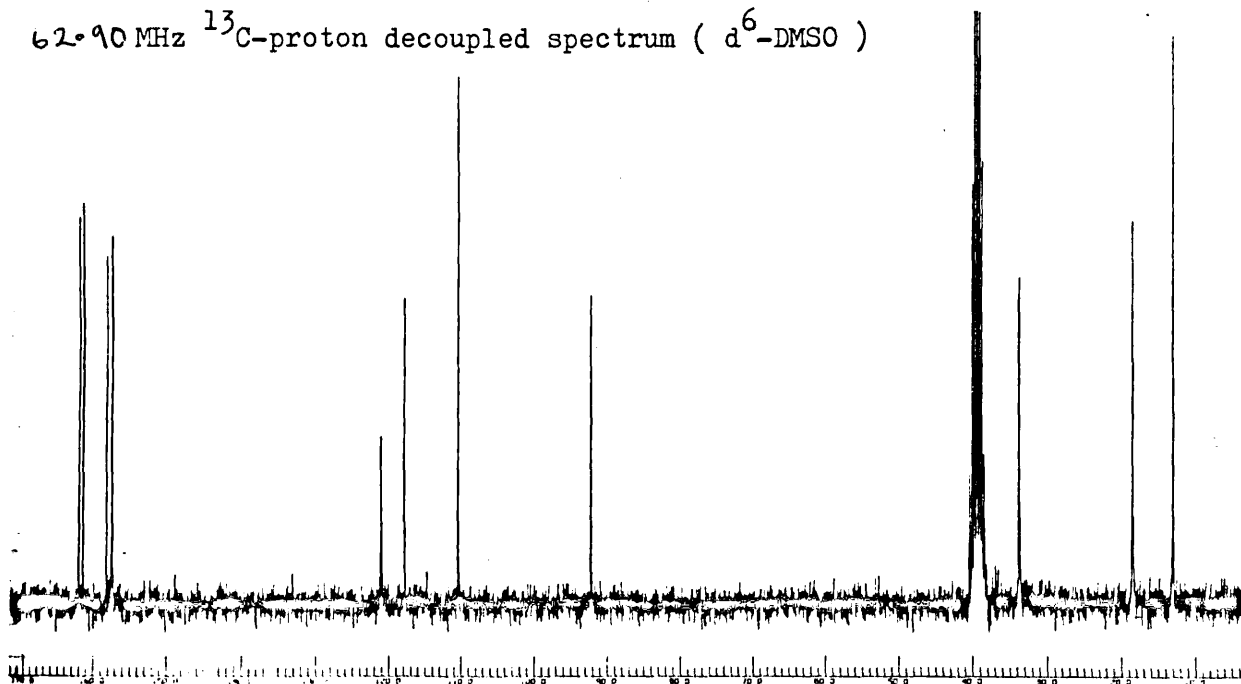
62.90 MHz ^{13}C-fully proton coupled spectrum (d^{6}-DMSO)
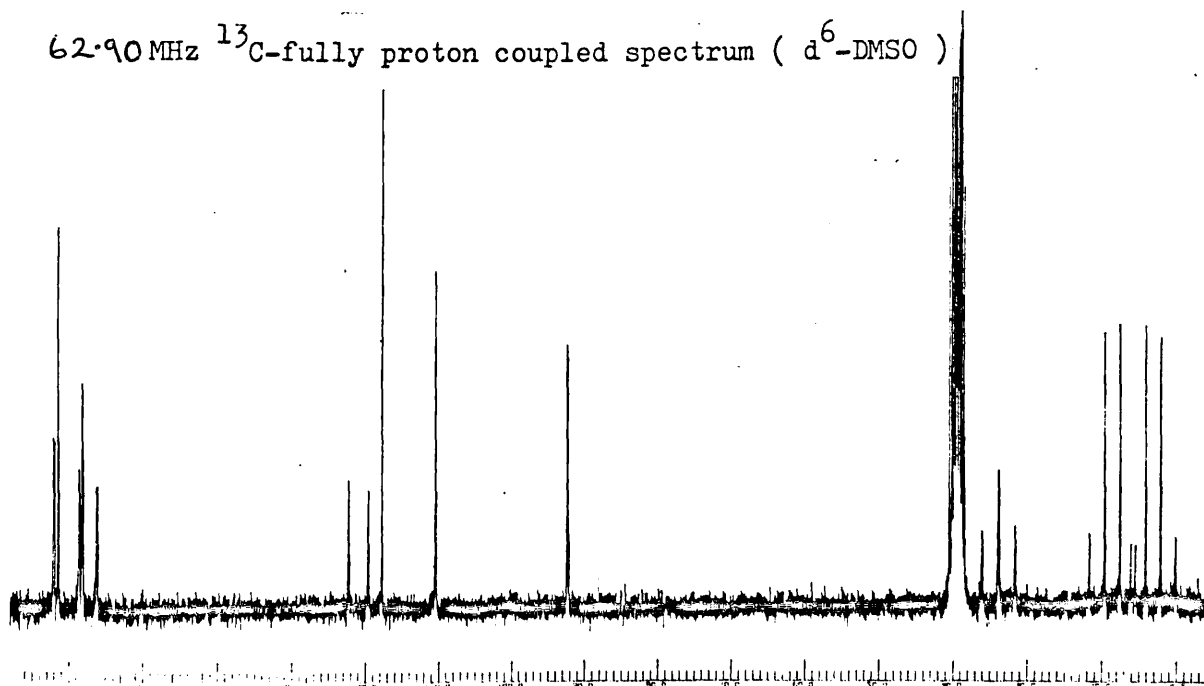
Figure 4.1

Table 4.1

$\delta(d^6\text{-DMSO, ppm})$	J, Hz	Assignment
1.09 (t)	7.0	$C^{1,20}H_3$
2.44 (s)	.	$C^{7,15}H_3$
3.90(qt)	7.0	$C^{2,19}H_2$
7.71 (d)	13.0	$C^{10,12}H$
9.01 (t)	13.0	$C^{11}H$

Table 4.2

$\delta(d^6\text{-DMSO, ppm})$	Assignment
13.08	C(1), C(20)
18.55	C(7), C(15)
33.82	C(2), C(19)
92.21	C(6), C(14)
110.40	C(8), C(13)
117.72	C(5), C(17)
120.93	C(11)
157.36	C(10), C(12)
158.13	C(4), C(16)
161.39 ⎫	C(3), C(9)
161.97 ⎭	C(18), C(21)

4.2. Sulphite Bleaching

4.2.1 Kinetic studies

The bleaching of (I) was studied in aqueous solution at $20^{\circ}C$, using large excesses of sodium sulphite ($[SO_3^{2-}]/[Dye] > 20$) to simplify the kinetics. Under these conditions (figure 4.2) the consumption of dye was first-order:

$$-d[Dye]/dt = k_1[Dye]$$

The pseudo first-order rate constant, k_1, was also linearly linked with the stoichiometric sulphite ion concentration (Table 4.3, figure 4.3), i.e.

$$-d[Dye]/dt = k_2[Dye][SO_3^{2-}]stoich.$$

Table 4.3

$$[Dye]_o = 1.0 \times 10^{-6}M$$

$[SO_3^{2-}]_o/M$	k_1/s^{-1}	$\ln[SO_3^{2-}]$	$\ln k_1$
3.32×10^{-5}	1.43×10^{-2}	−10.31	−4.25
6.62×10^{-5}	3.31×10^{-2}	−9.62	−3.41
1.32×10^{-4}	11.60×10^{-2}	−8.93	−2.15
1.96×10^{-4}	13.30×10^{-2}	−8.54	−2.02
2.60×10^{-4}	22.50×10^{-2}	−8.25	−1.49

$$k_2 = 921 \ M^{-1} \ s^{-1}$$
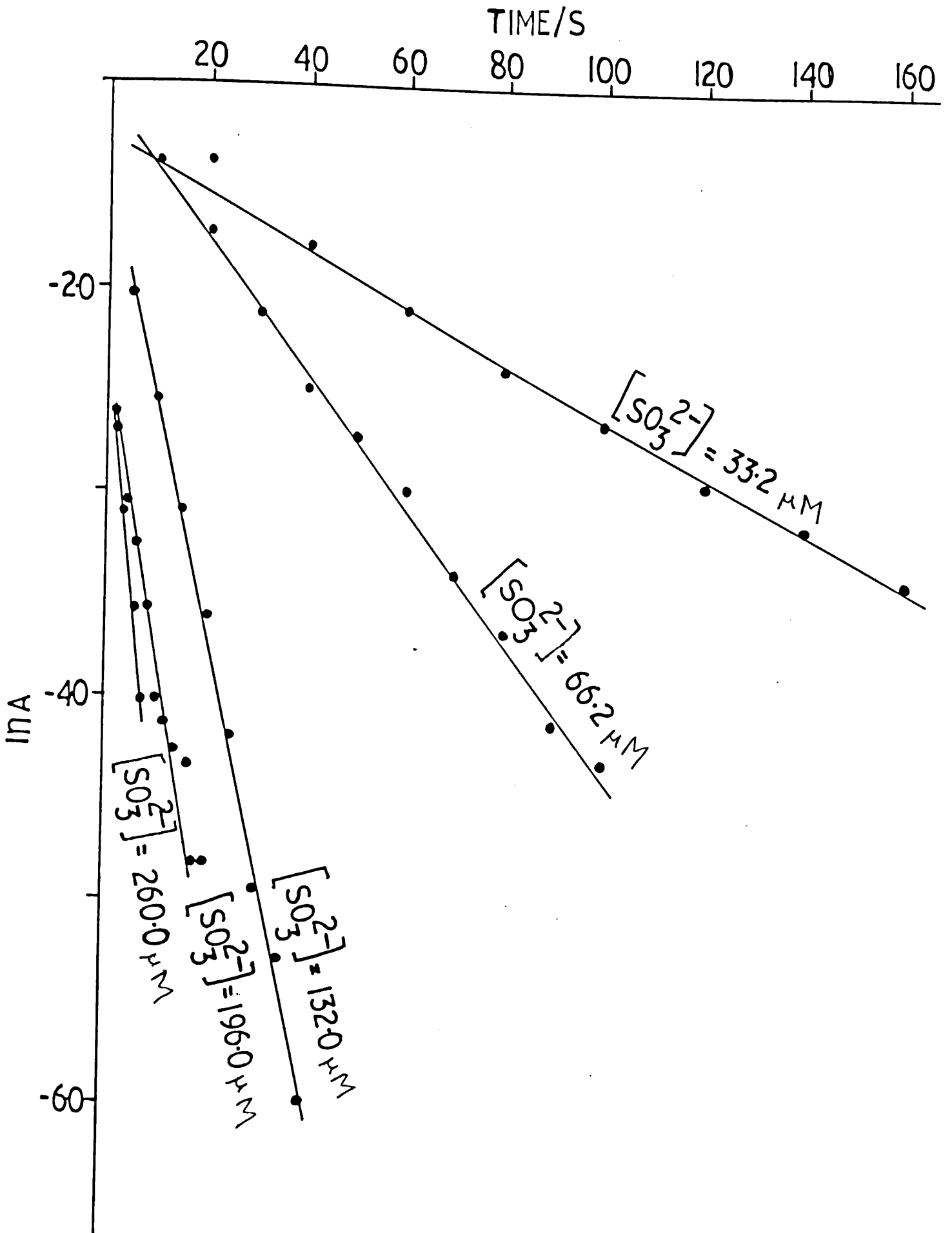
Figure 4.2
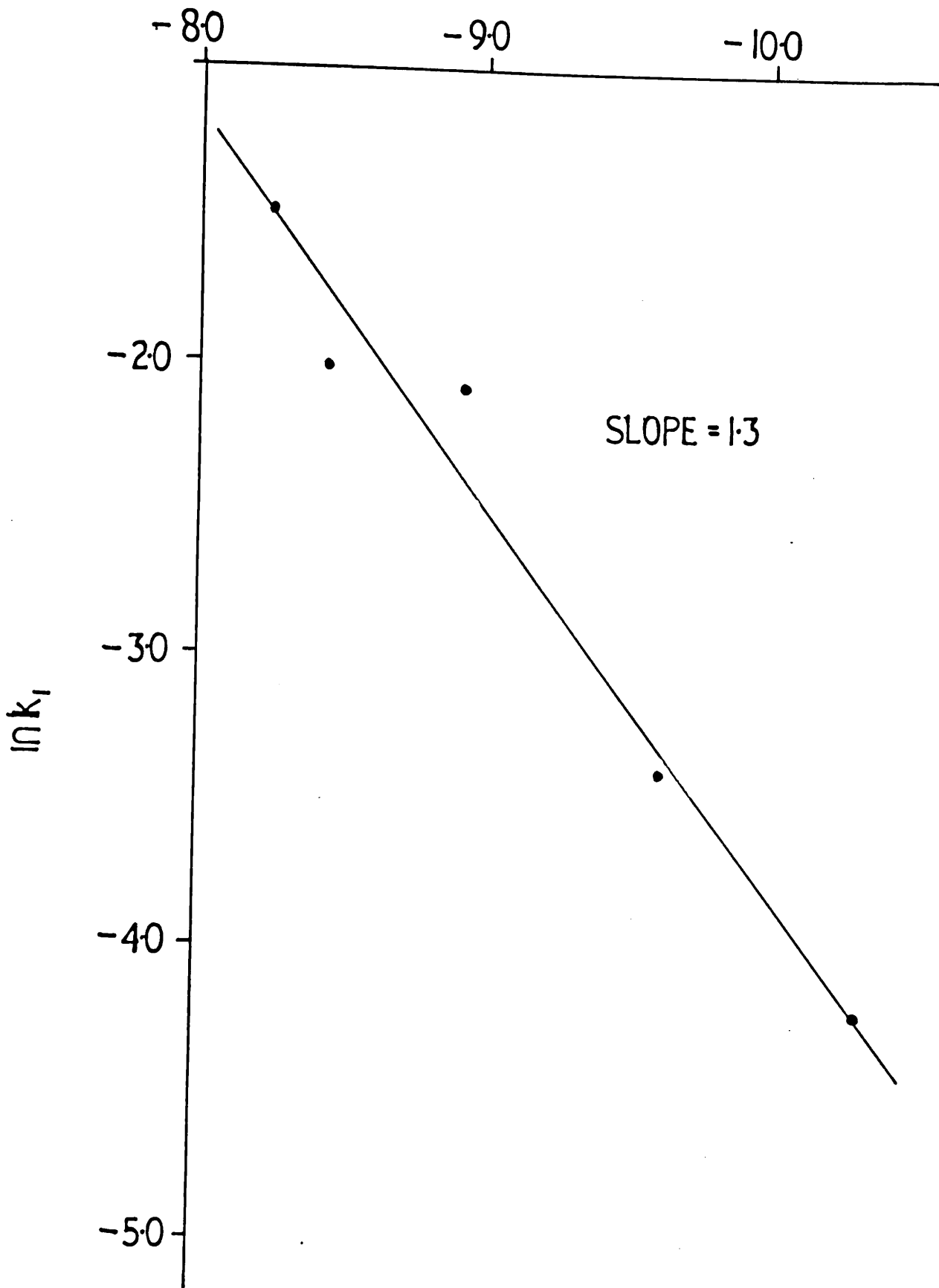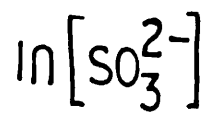
Figure 4.3

The kinetic form with respect of sulphite ion suggests

$$\text{Rate } \alpha \ [SO_3^{2-}]^{1.3}$$

and this implies two contributions of different kinetic order.

Other possible bleaching reagents in this system included sulphur dioxide, bisulphite ions or even hydroxide ions. The effect of changing the pH of the solution upon the observed rate of reaction (Table 4.4, figure 4.4) shows that neither sulphur dioxide nor hydroxide ions could possibly have been the bleaching reagents. Although the bisulphite ion

Table 4.4

pH	2.13	3.15	4.04
k^1/s^{-1}	2.87×10^{-3}	4.77×10^{-3}	18.82×10^{-3}
$[H+]/M$	7.40×10^{-3}	7.08×10^{-4}	9.12×10^{-5}
$[HSO_3^-]/M$	4.22×10^{-3}	5.98×10^{-3}	6.21×10^{-3}
$[SO_3^{2-}]/M$	5.80×10^{-8}	8.62×10^{-7}	69.50×10^{-7}
$[SO_2]/M$	2.03×10^{-3}	0.82×10^{-3}	0.04×10^{-3}

concentration is seen to increase with increasing pH and observed rate of reaction, the extent to which it increases is very slight. This leaves us then with the most probable bleaching reagent being the sulphite ion.

The reaction can thus be separated into

$$k^1[\text{Dye}][SO_3^{2-}] = k_a[\text{Dye}][SO_3^{2-}] + k_b[\text{Dye}][SO_3^{2-}]^2$$

$$\Rightarrow k^1 = k_a + k_b[SO_3^{2-}]$$

thence

$$\frac{-d[\text{Dye}]}{dt} = 2.88 \times 10^{-3}[\text{Dye}][SO_3^{2-}] + 2100[\text{Dye}][SO_3^{2-}]^2$$

in which the kinetic order of the second contribution has not been rigorously defined.
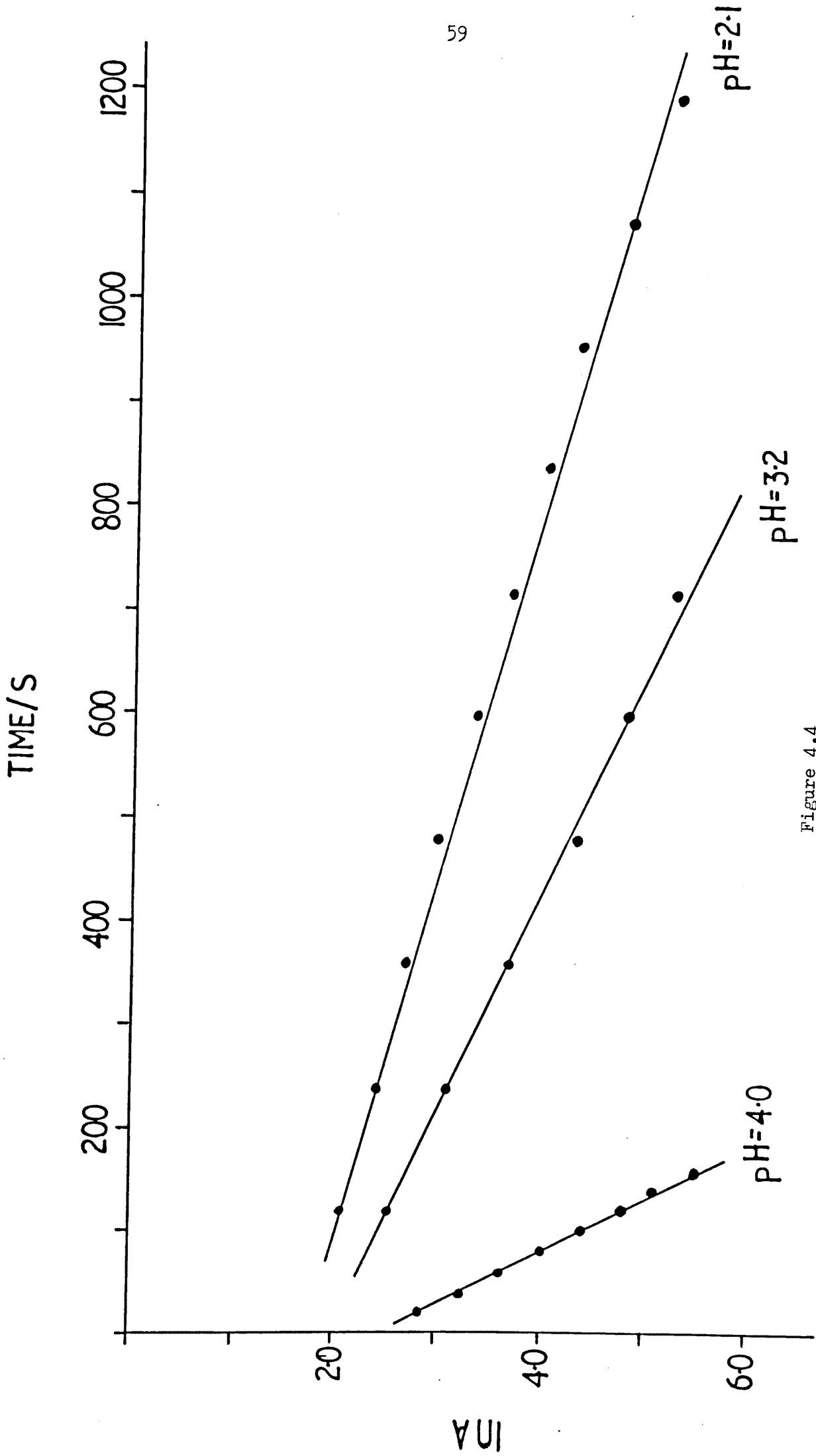
Figure 4.4

4.2.2. N.m.r. studies

The disymmetry introduced into the dye molecule by the addition of sulphite ion is reflected in both the ^{1}H and ^{13}C n.m.r. spectra (figure 4.5).

Tables 4.5 and 4.6 show the assignments of the ^{1}H and ^{13}C n.m.r. spectra, respectively. The double up on signals, the shift in

Table 4.5.

$\delta(\text{d}^6\text{-DMSO/D}_2\text{O, ppm})$	J,Hz	Assignment
0.96 (t)	7.2	C^1H_3
0.99 (t)	7.0	$C^{20}H_3$
2.12 (s)		C^7H_3
2.31 (s)		$C^{15}H_3$
3.79 (qt)	7.3	C^2H_2
3.83 (qt)	7.2	$C^{19}H_2$
5.50 (qt)	1.3	$C^{10}H$
	8.3	
6.24 (qt)	1.3	$C^{12}H$
	15.6	
6.68 (qt)	8.3	C^{11}
	15.6	
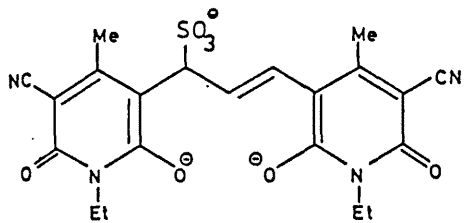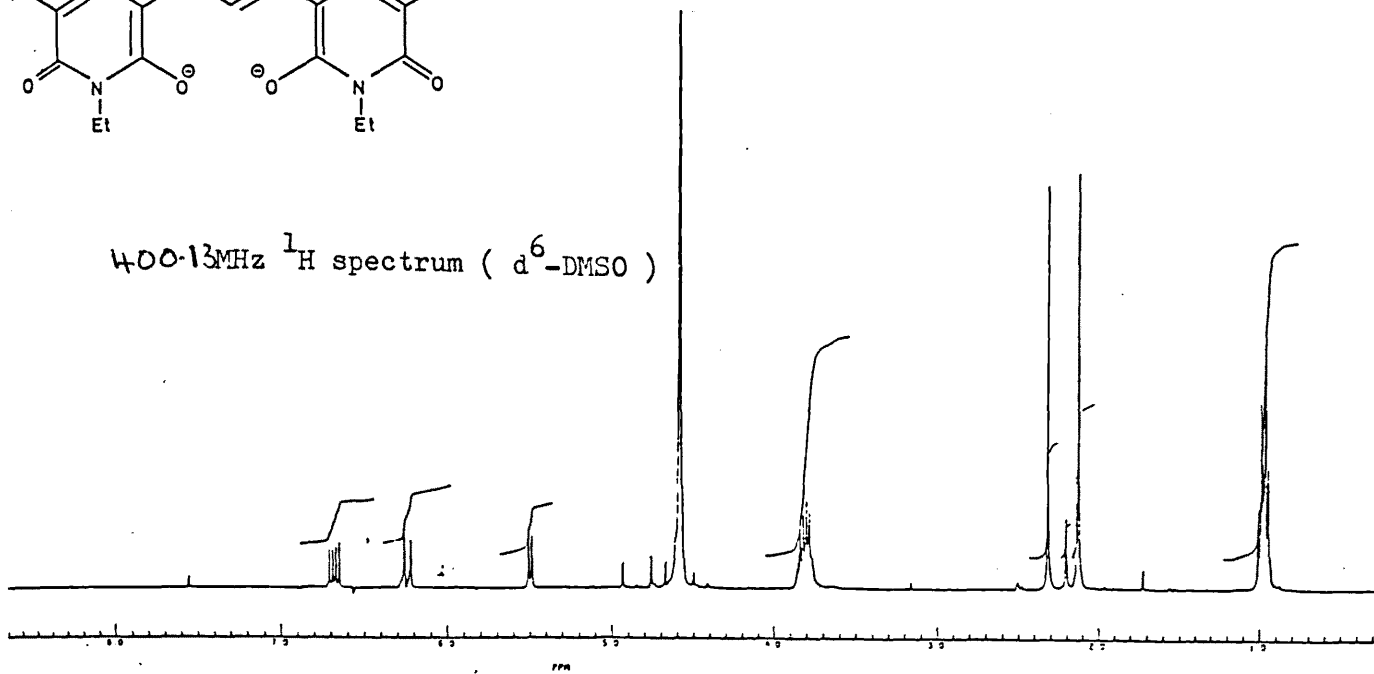
Figure 4.5   61

400·13MHz ^{1}H spectrum (d^6-DMSO)

62·90MHz ^{13}C-proton decoupled spectrum (d^6-DMSO)
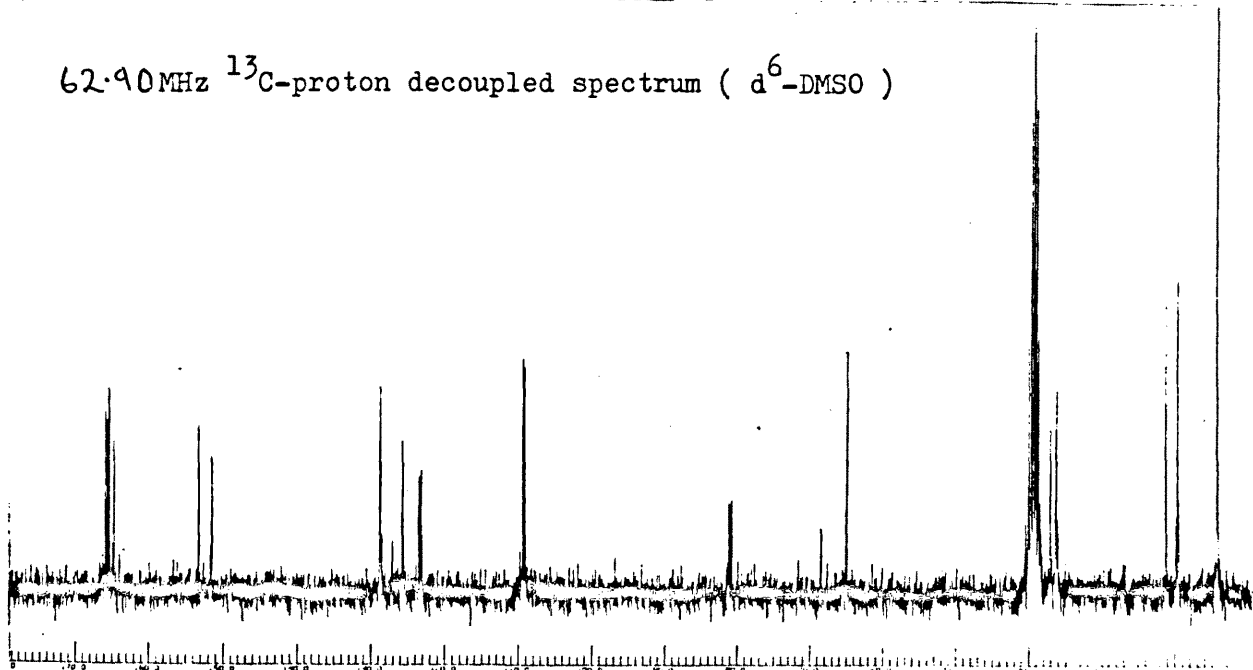
62·90 MHz ^{13}C-fully proton coupled spectrum (d^6-DMSO)
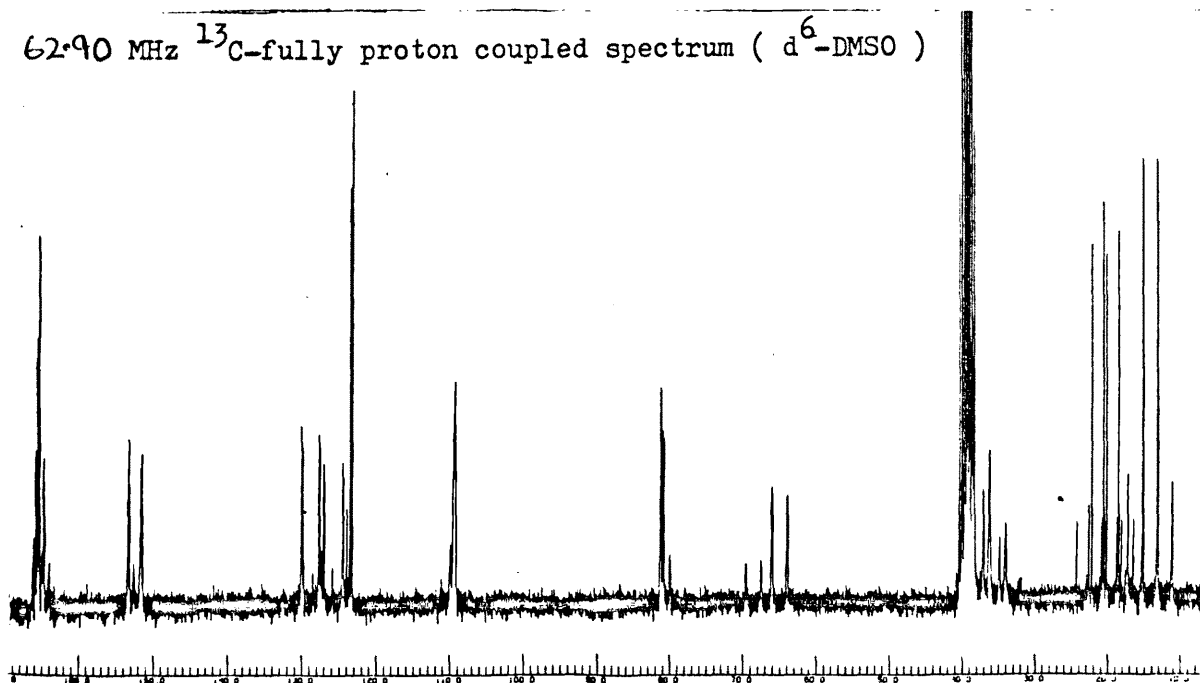
Table 4.6

$\delta(d^6\text{-DMSO/D}_2\text{O, ppm})$	Assignment
14.32	C(1), C(20)
19.69 ⎱	C(7), C(15)
21.31 ⎰	
36.34 ⎱	C(2), C(19)
37.15 ⎰	
65.02	C(10)
80.88 ⎱	C(6), C(14)
81.18 ⎰	
109.26 ⎱	C(5), C(17)
109.44 ⎰	
123.27 ⎱	C(8), C(13)
123.53 ⎰	
125.79	C(11)
128.79	C(12)
151.55 ⎱	C(4), C(16)
153.29 ⎰	
164.74 ⎫	
165.41 ⎬	C(3), C(9)
165.60 ⎪	C(18), C(21)
165.88 ⎭	

position of the C(10) peak from 157.4 to 65.0 ppm and the region of the ^{1}H spectrum corresponding to the methine bridge protons (shown expounded in figure 4.6) all suggest the existence of a Michael-type adduct.
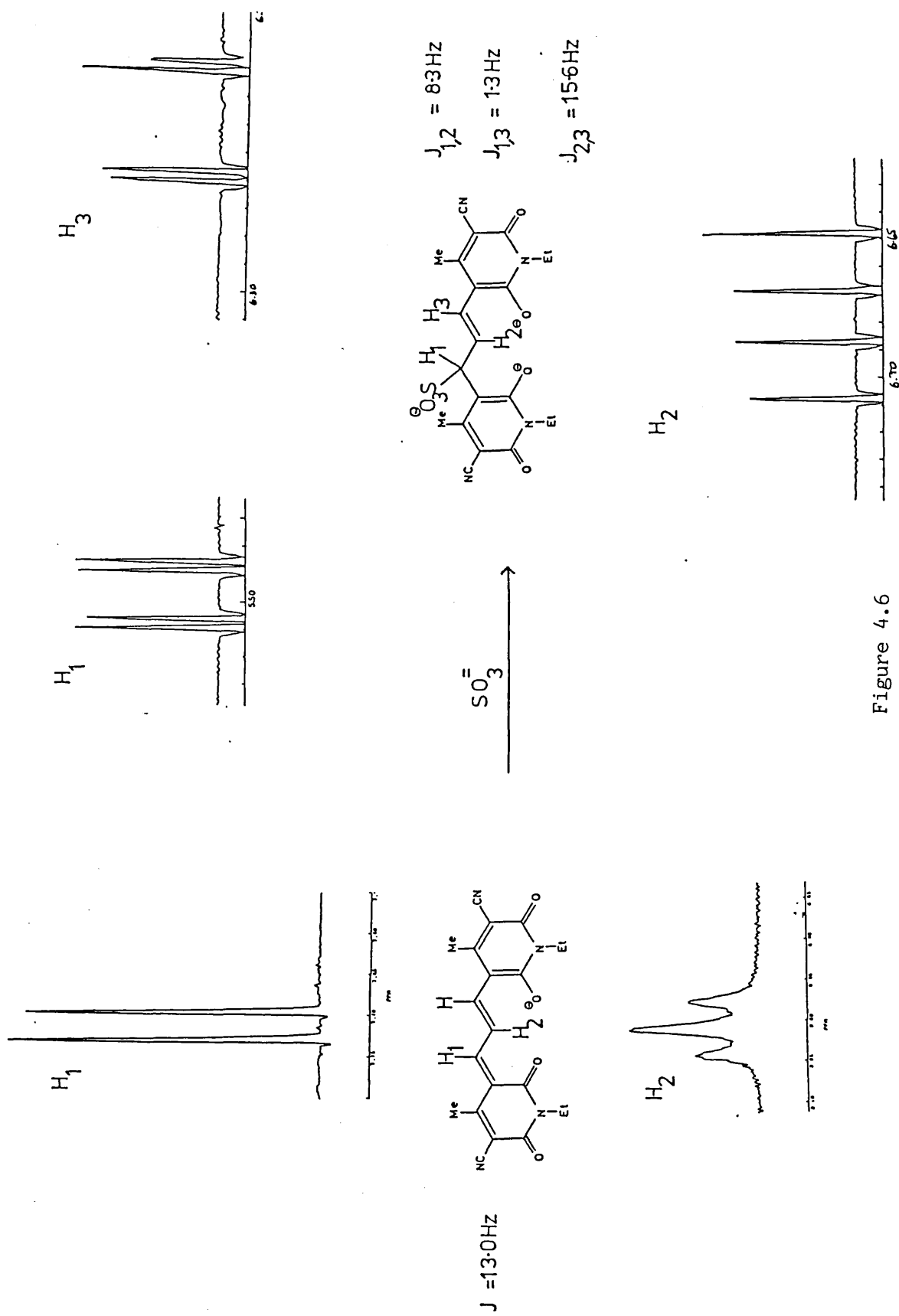
Figure 4.6

4.3 Other Nucleophiles

4.3.1 Initial qualitative studies revealed CN^-, MeO^-, S^{2-}, NH_3, Et_3N, OH^-, SH^- and $EtNH_2$ like SO_3^{2-} to be effective in bleaching dye I. The additions of OH^-, SH^-, NH_3, and $EtNH_2$ being reversible (that is the acidification of the bleached solution, in each case, regenerated the original dye chromophore, figure 4.7).
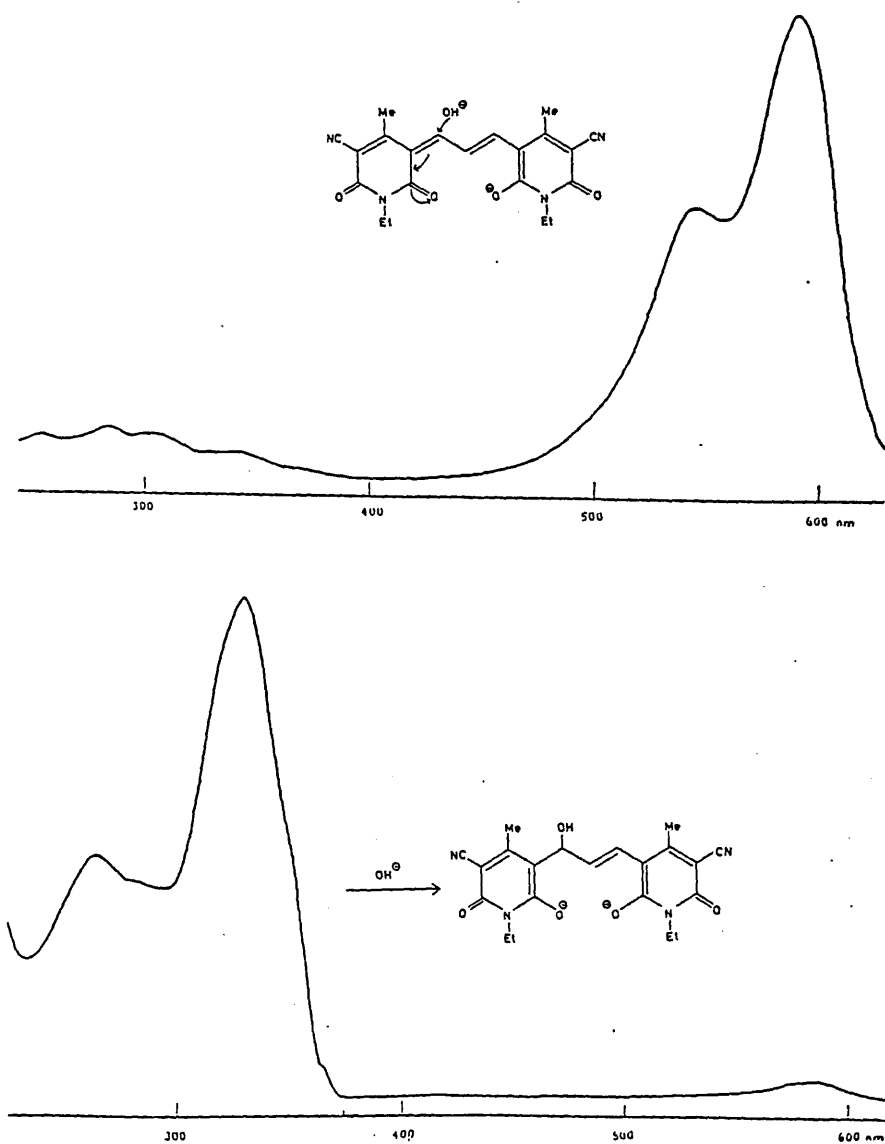
Figure 4.7

Nucleophiles such as N_3^-, $PhNH_2$, SCN^-. Ph_3P and $S_2O_3^{2-}$ were found to be ineffective bleaching agents.

4.3.2 N.m.r. studies

Of the nucleophiles investigated, the ^1H and ^{13}C n.m.r. spectra of the CD_3O^-, S^{2-} and $EtNH_2$ bleached adducts resembled most closely those of the SO_3^{2-} case, figure 4.8.

The spectra of the NH_3 bleached adduct were highly complex, figure 4.9 (possibly as a result of the equilibrium;

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^-).$$

50.31 MHz ^{13}C-proton decoupled spectrum: NH_3-bleached adduct (D_2O/d^6-DMSO)
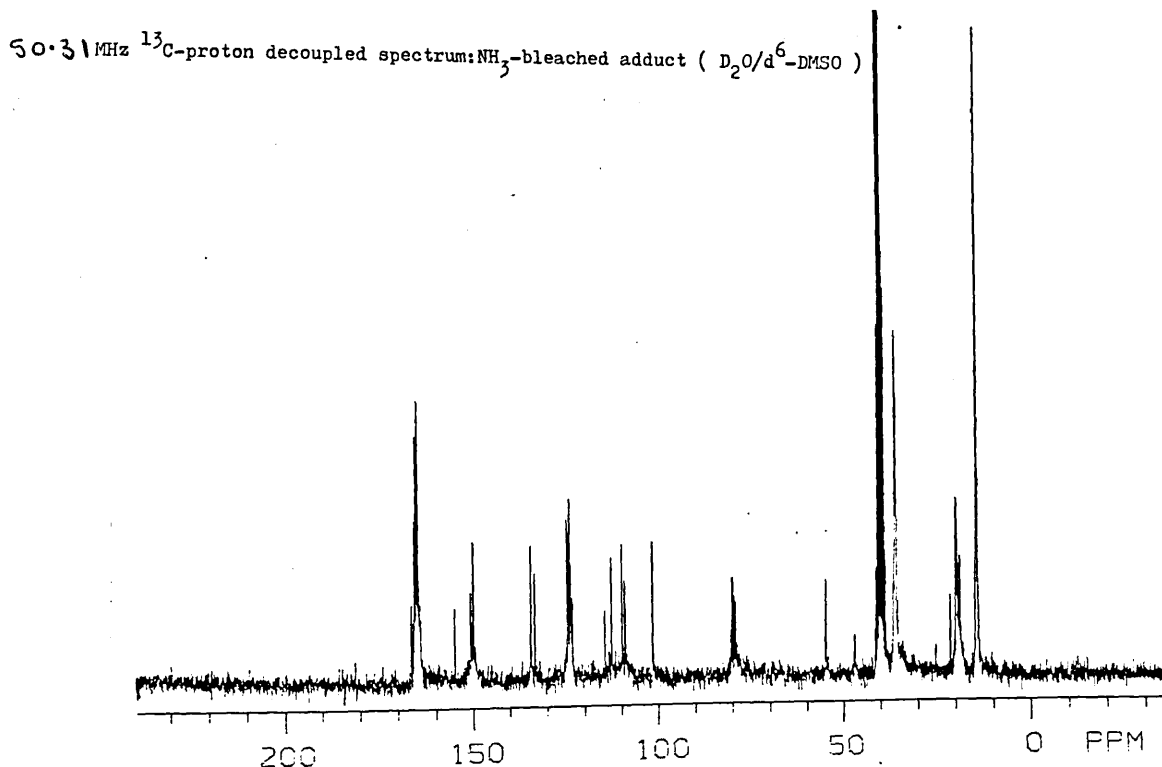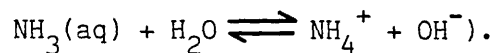
Figure 4.9

400·13MHz ^{1}H spectrum: CD_3O^--bleached adduct (d^4-MeOH/d^6-DMSO)
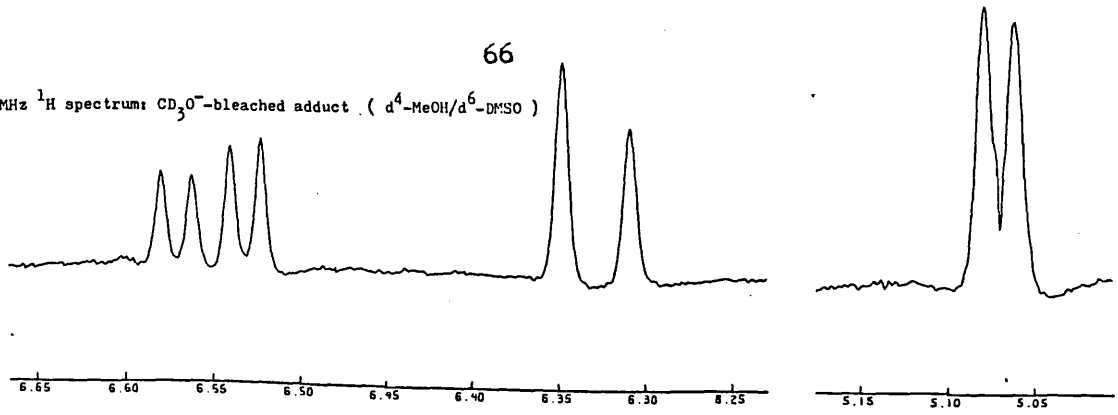
50·31 MHz ^{13}C-proton decoupled spectrum: CD_3O^--bleached adduct (d^4-MeOH/d^6-DMSO)
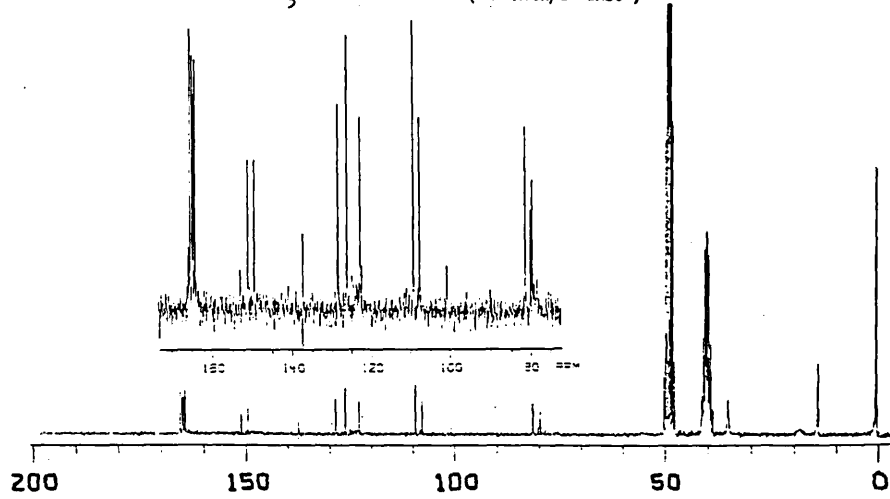
400·13 MHz ^{1}H spectrum: S^{2-}-bleached adduct (D_2O/d^6-DMSO)
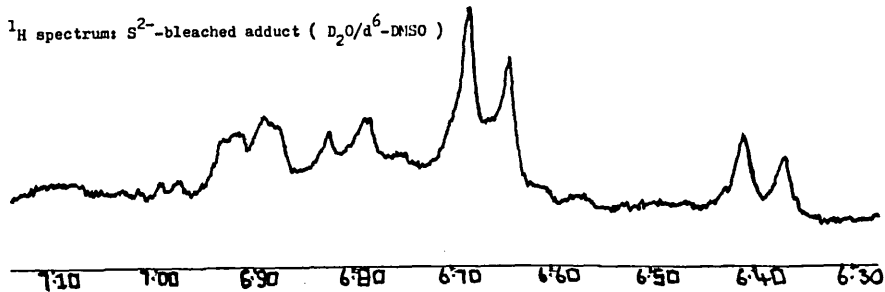
50·31 MHz ^{13}C-proton decoupled spectrum: $EtNH_2$-bleached adduct (d^6-DMSO)
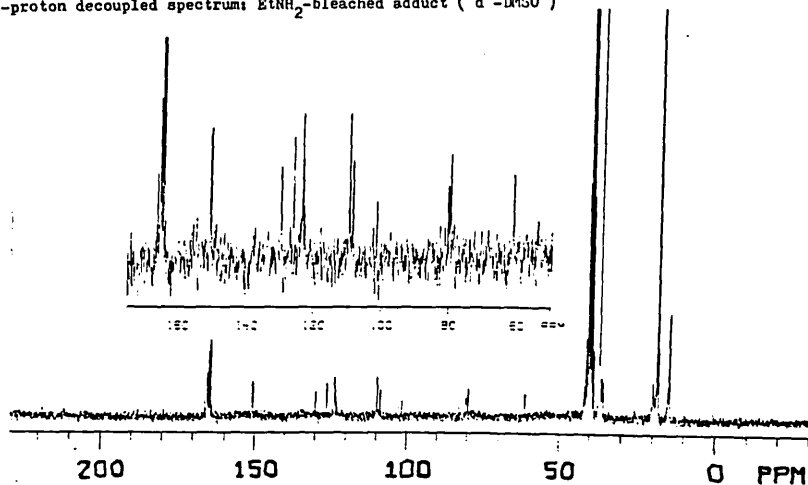
Figure 4.8

For the CN⁻ case the coupling of the methine bridge protons

changed drastically, figure 4.10 (i). The most probable explanation

being that the C(10) proton had deuterium exchanged leaving just the two

non-equivalent bridge protons on carbons (11) and (12). The

carbon-deuterium coupling is, however, not readily identifiable from the

^{13}C-proton decoupled spectrum, figure 4.10 (ii).

400·13 MHz ^{1}H spectrum: CN⁻-bleached adduct (D_2O/d^6-DMSO)
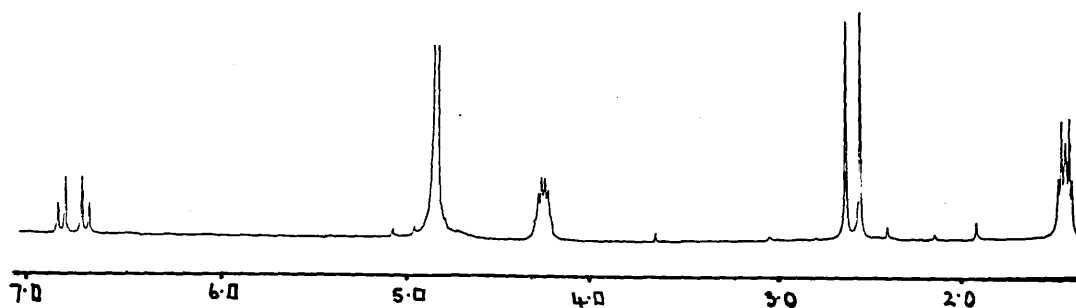
100·60 MHz ^{13}C-proton decoupled spectrum: CN⁻-bleached adduct (D_2O/d^6-DMSO)
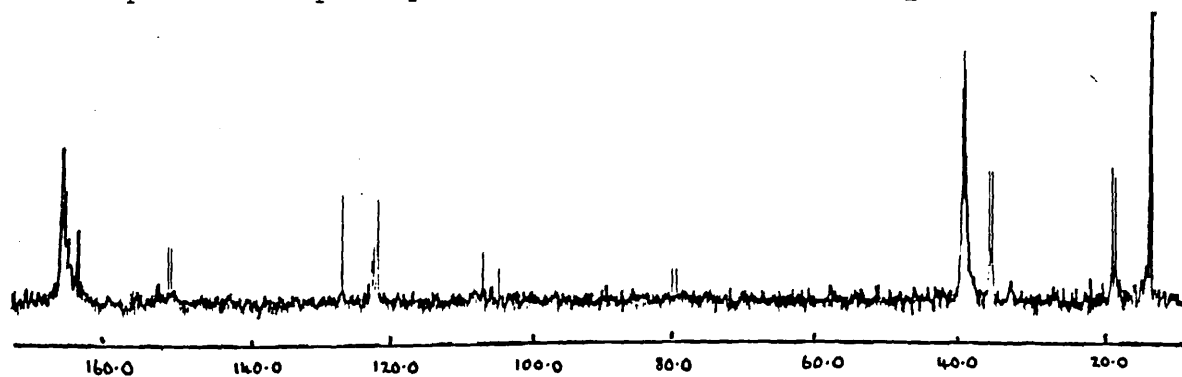
Figure 4.10

4.4   Trapping a Bleached Adduct

After many different approaches to trapping a bleached adduct we
eventually had some success using o-phenylenediamine as the attacking
nucleophile, Scheme 4.4. The pale blue adduct precipitated from a hot

(II)   (III)
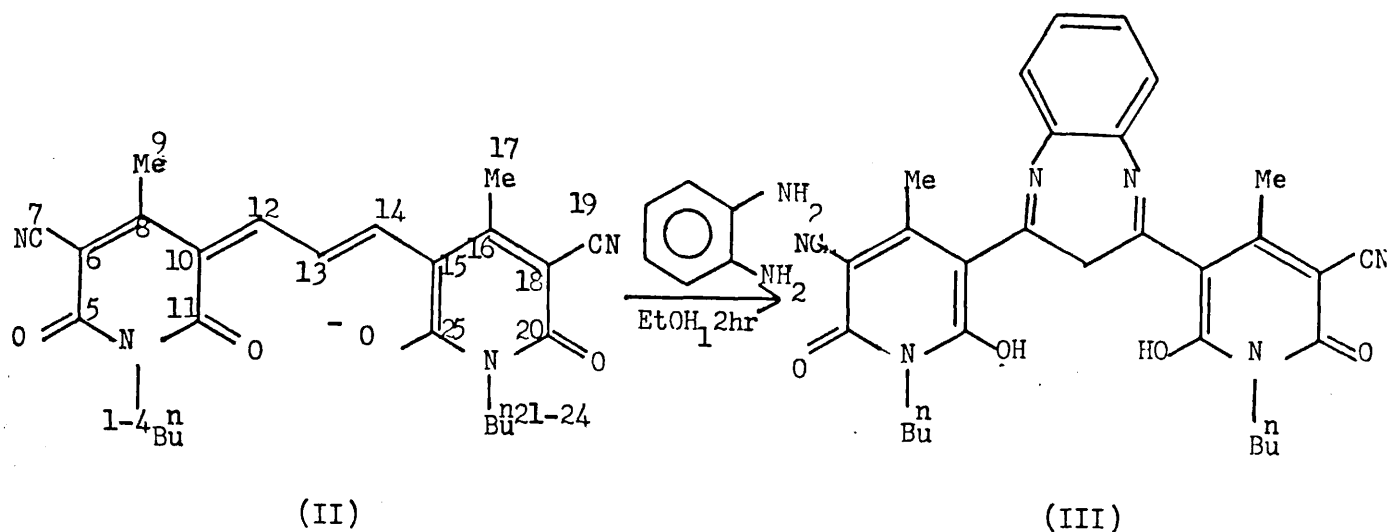
ethanolic solution (see 10.3.5). It was however found to be totally
insoluble in all of the available deuterated n.m.r. solvents. Solid-state
^{13}C n.m.r. spectra of dye II and its o-phenylenediamine bleached adduct
(III) were of limited use, however, addition peaks in the aromatic region
are clearly visible, figure 4.11. Table 4.7 lists the assignment of the
solution ^{13}C n.m.r. spectrum of dye II. The accurate top mass of 553

O-phenylenediamine bleached adduct (III) -solid state
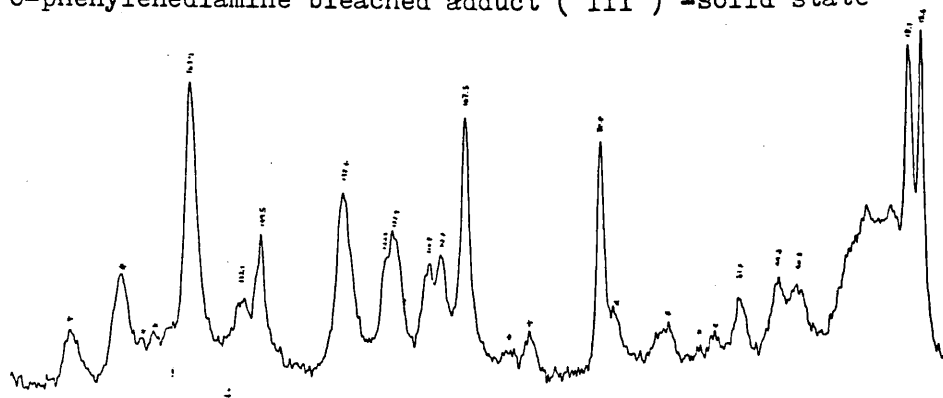
Dye II-solid state
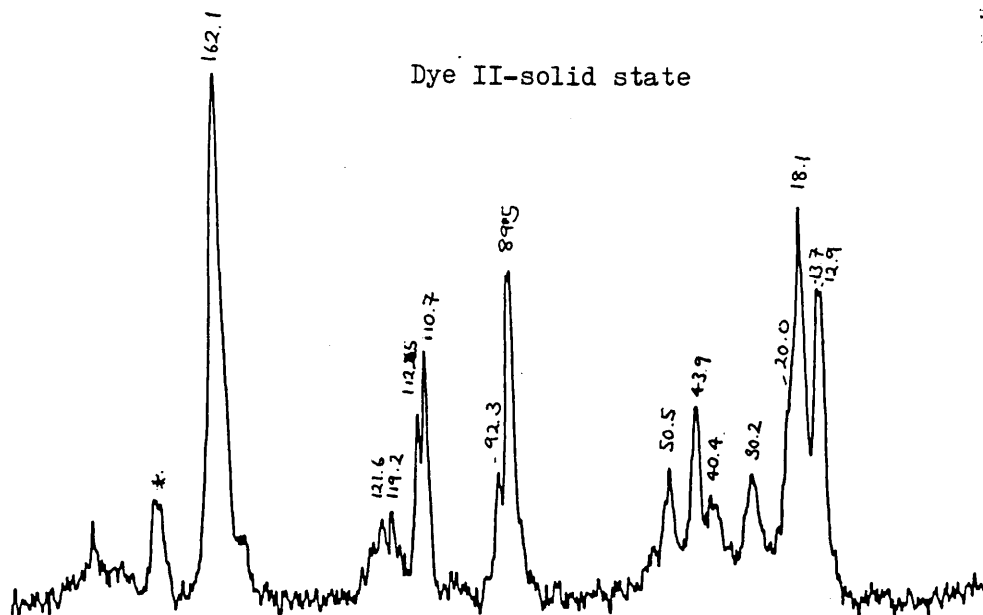
Dye II-22·5 MHz ^{13}C-proton decoupled spectrum (d^6-DMSO)
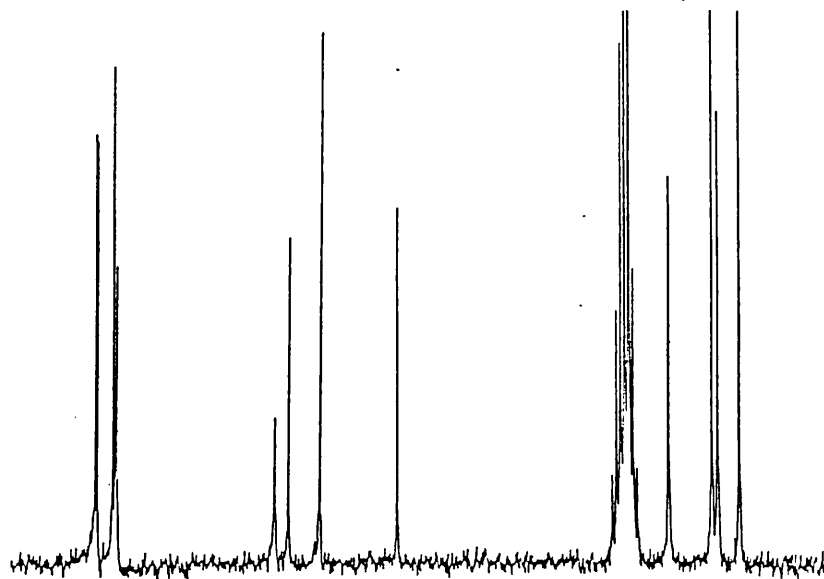
Figure 4.11

Table 4.7

$\delta(d^6\text{-DMSO, ppm})$	Assignment
13.58	C(1), C(24)
18.40	C(9), C(17)
19.76	C(2), C(23)
29.52	C(3), C(22)
38.49	C(4), C(21)
92.08	C(8), C(16)
110.22	C(10), C(15)
117.63	C(7), C(19)
120.82	C(13)
157.24	C(12), C(14)
157.95	C(6), C(18)
161.46	C(5), C(11)
161.92	C(20), C(25)

from mass spectrometry was consistent with a monoprotonated species of III. The elemental analysis was not wholly satisfactory however, attempts to further purify the adduct failed.

Michael-type addition at the methine bridge does appear to be the major process involved in the bleaching of these oxonol dyes. The kinetic and n.m.r. data, however, suggests that to consider this the only process is an over-simplification. A far more detailed investigation is obviously required to give a fuller understanding of this reaction.

CHAPTER 5

Electrical Properties of Semi-insulating and

and Semiconducting Materials

5.1 Basic Classification[27].

From the electrical standpoint a material may be classified as a

metal, a semiconductor or an insulator, depending on its conductivity,

although the limits of conductivity which mark the boundaries between

these classes are somewhat arbitrary. At room temperature, if the

conductivity lies in the range $10^6 - 10^3 \ \Omega^{-1} \ cm^{-1}$, the material

is said to be a metal, and if it is lower than $10^{-12} \ \Omega^{-1} \ cm^{-1}$ it is

an insulator. Semiconductors have conductivities lying in the range

$10^3 - 10^{-7} \ \Omega^{-1} \ cm^{-1}$, although not all materials having

conductivities within this range are semiconductors. Substances with

conductivities in the range $10^{-7} - 10^{-12} \ \Omega^{-1} \ cm^{-1}$ may be regarded

as "poor" or "semi-insulators".

5.2 Band Theory[27,28,29].

To differentiate between various elements and compounds, in

respect of their electrical conduction properties one needs only to

consider electrons with energies in two bands - the "valence" and

"conduction" bands. The valence band is the uppermost band which is

filled or partially filled with electrons; the conduction band is the

next higher band, which may be either empty or partially filled.

Electrons in deeper lying levels, which are normal.ly filled, play no

part in the conduction process. Representative energy band diagrams for

a metal (a), an insulator (b) and a semiconductor (c) are shown in figure

5.1.
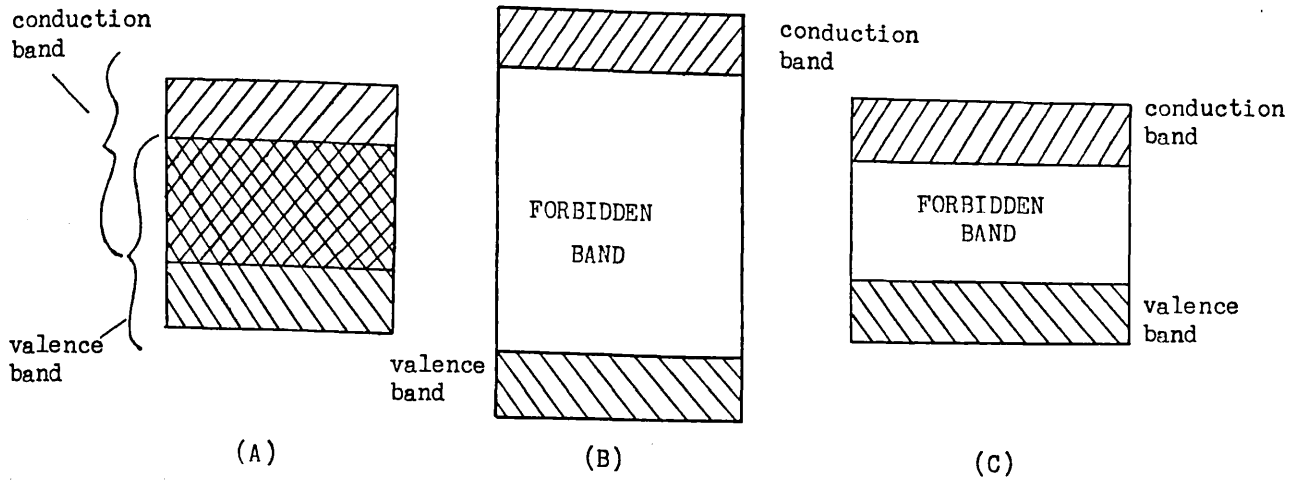
Figure 5.1

5.2.1 Metals

Metals are characterised by an upper energy band which is approximately half-filled. Such a band can originate for two reasons; (i) overlap can occur between the valence and conduction bands; (ii) the atoms may have insufficient valence electrons to fill the available states in the valence band (e.g. alkali metals).

Since vacant electron energy levels exist in close proximity to the levels which are occupied, electrons can be readily excited to higher levels when an electric field is applied and current can flow. The high conductivity of metals arises because of the large number of electrons with energies in the topmost partially filled band (approximately one per atom).

5.2.2 Insulators

If a material has a full valence band and an empty conduction band, which is separated by a forbidden band, then it is either an insulator or a semiconductor. An insulator is characterised by a conduction band which is virtually empty, both in thermal equilibrium and when an electric field is applied. This means that the forbidden gap separating the energy levels of the valence and conduction bands has to be so large that electrons cannot be excited from the valence to the conduction band. Such excitation could arise in thermal equilibrium if the forbidden gap was narrow enough. This is because the atoms of the solid are continually vibrating about their mean positions and some of this thermal vibrational energy is shared by the electrons. In the presence of an electric field valence electrons also absorb energy, but again, if this is less than the energy gap, they cannot be excited to the conduction band.

5.2.3   Intrinsic Semiconductors

If the valence and conduction bands are separated by a narrow forbidden energy gap, then at all temperatures above absolute zero there may be some electrons in the conduction band and some holes in the valence band of a pure crystal in thermal equilibrium i.e. even though no external exciting radiation or electric field is applied. Since the conduction band is then partially filled and the valence band partially empty, further energy can be absorbed from an external electric field by the electrons in the conduction band and the holes in the valence band. For such an "intrinsic" semiconductor the density n_i of electrons in the conduction band is equal to the density of p_i of holes in the valence band and both classes of carrier will contribute to the current.

5.2.4 Extrinsic Semiconductors

The usefulness of semiconductors in electronic devices is

ultimately bound up, not with the pure or "intrinsic" type of

semiconductor referred to above, but with the modifications brought about

in such materials by incorporating relatively small percentages of

selected impurities in the host crystal. The resulting material is known

as an impurity or "extrinsic" semiconductor. The basic features of

extrinsic semiconduction can be simply demonstrated with reference to

germanium, which in pure form is an intrinsic semiconductor.

Figure 5.2

Germanium is tetravalent. In single crystal form each germanium

atom is surrounded by four nearest neighbours at the corners of a regular

tetrahedron. Each of the four valence electrons combines with a similar

electron belonging to one of the near-neighbour atoms to form a covalent

bond. This arrangement is shown diagrammatically in two dimensions in

figure 5.2(a). Each pair of lines represents a covalent bond. In figure

5.2(b) the modification of this diagram is shown when one of the

germanium atoms is replaced by a pentavalent atom such as arsenic. Only

four of the five valence electrons of the arsenic atom can form covalent

bonds, the fifth revolves around the arsenic nucleus in a loosely bound

orbit. The microscopic energy band picture in the vicinity of the

arsenic atom is illustrated in figure 5.3. A potential well has been
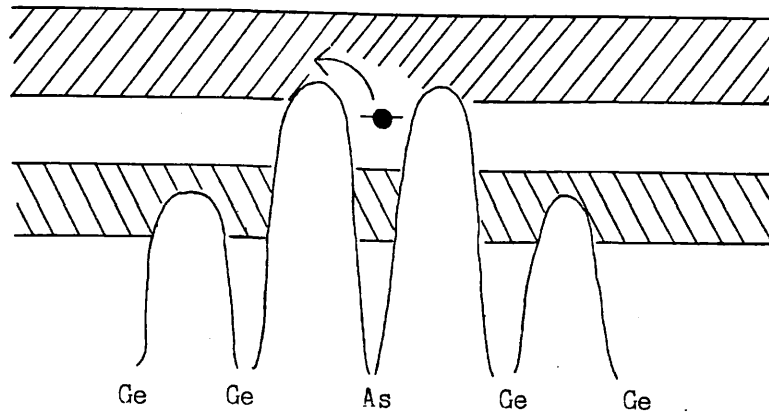
Figure 5.3

shown at the site of the arsenic atom, in which there is a localised

electron energy level just below the bottom of the conduction band. At

very low temperatures the fifth valence electron will occupy this level.

Since the level is very near the bottom of the conduction band, however,

only a small amount of thermal energy is required to excite this electron

into the conduction band. The arsenic atom is then positively ionised

and the liberated electron is free to move through the crystal.

A pentavalent atom like arsenic in the germanium lattice is called

a "donor" impurity, since it has in effect donated a conduction electron.

The associated name for the conductivity is "n-type" (electrons have a

negative charge) with a concentration "n" of free electrons in the

conduction band which exceeds the concentration p of holes in the valence

band.

Trivalent atoms such as indium replacing germanium atoms produce a

concentration of holes in the valence band which exceeds the
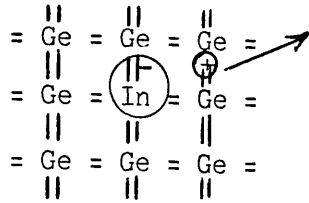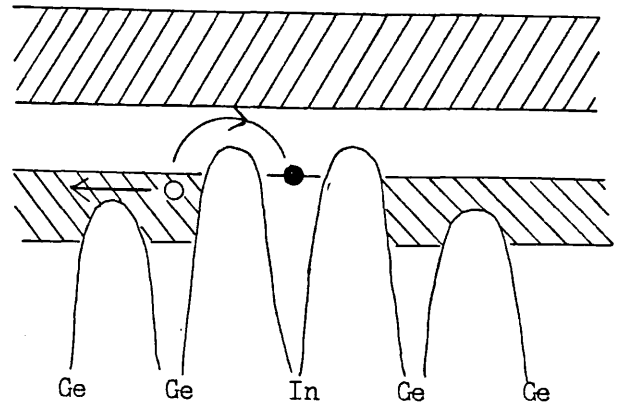
Figure 5.4   Figure 5.5

concentration of electrons in the conduction band. The resulting

conductivity is called "p-type" (holes have positive charge). Such

impurities are called "acceptors" since they accept an electron from the

valence band in their ionised state. The mechanism is illustrated by

figures 5.4 and 5.5.

In any practical semiconductor both donor and acceptor impurities

will be present although, by design one impurity type is usually

dominant. Since in thermal equilibrium the general tendency is for

electrons to occupy the lowest levels, one finds that the acceptors are

ionised as far as possible by the extra electrons available from donor

atoms. In consequence, as far as impurity carrier density is concerned,

this is of a type equivalent to the dominant impurity present. If the

densities of donors and acceptors are Nd and Na respectively then

material for which Nd > Na is n-type and if Na > Nd it is p-type. If Na

= Nd the material is said to be "compensated" and as far as free carrier

densities are concerned will behave like intrinsic material. Its

conduction properties will differ from intrinsic material, however,

because of the extra scattering of free charges introduced by the ionised

donor and acceptor atoms.

5.3 Distribution of Electrons and Holes in Energy States[27,28].

5.3.1 The Fermi-Dirac distribution function.

The Fermi-Dirac probability distribution function, $f(\varepsilon)$, specifies the probability that an electron energy state at energy ε is occupied by an electron. Its form is

$$f(\varepsilon) = \frac{1}{1 + \exp\left\{(\varepsilon - \varepsilon_F)/kT\right\}}$$

5.1

where ε_F is the "Fermi level"; when $\varepsilon = \varepsilon_F$, then $f(\varepsilon) = \frac{1}{2}$. An alternative interpretation of $f(\varepsilon)$ is that the product $f(\varepsilon)d\varepsilon$ represents the average value of the fraction of all the states in an energy range, between ε and $\varepsilon + d\varepsilon$, which are occupied. The form of the Fermi-Dirac distribution is shown in figure 5.6 for three different temperatures; $T_1 = 0$ and $0 < T_2 < T_3$.
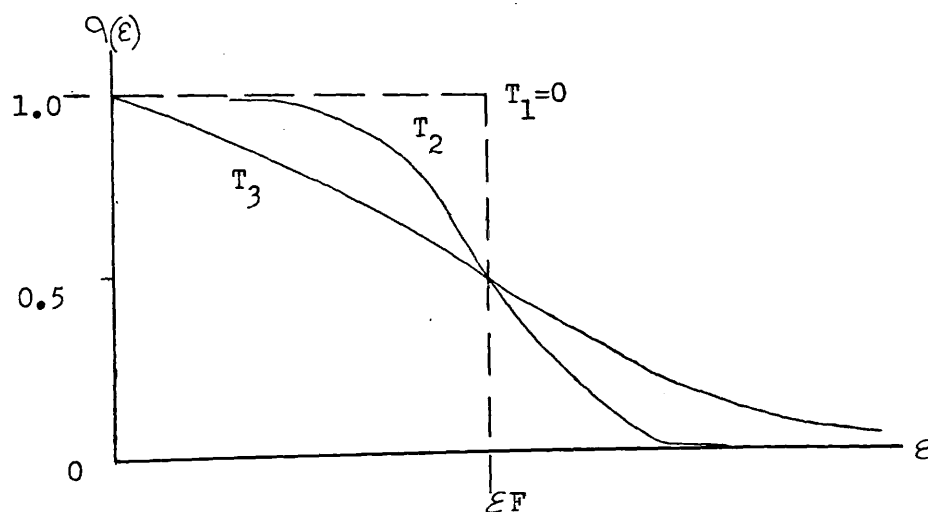
Figure 5.6

If ε is larger than ε_F by several times kT then the exponential term in the denominator is large compared with unity and $f(\varepsilon)$ has the appropriate form

$$f(\varepsilon) \simeq \exp \left\{ -(\varepsilon - \varepsilon_F)/kT \right\} \qquad 5.2$$

This approximate form is the same as the Maxwell-Boltzmann distribution, which applies to a gas. When applied to semiconductors it is referred to as the "classical approximation".

Clearly, if $f(\varepsilon)$ is the fraction of quantum states at ε occupied by electrons, $1 - f(\varepsilon)$ is the fraction left vacant or occupied by holes. Writing this as $f_h(\varepsilon)$ one has, from equation 5.1.

$$f_h(\varepsilon) = 1 - f(\varepsilon) = \frac{1}{1 + \exp \left\{ (\varepsilon_F - \varepsilon)/kt \right\}} \qquad 5.3$$

For $\varepsilon \ll \varepsilon_F$ by several units of kT this reduces to

$$f_h(\varepsilon) \simeq \exp \left\{ -(\varepsilon_F - \varepsilon)/kT \right\} \qquad 5.4$$

The functions $f(\varepsilon)$ and $f_h(\varepsilon)$ discussed above simply indicate the probabilities that a quantum state at energy ε is occupied by an electron or a hole. The actual density of electrons or holes in a range of energy $d\varepsilon$ at ε is given by the product of the appropriate probability function and the density of states function $N(\varepsilon)$ at ε.

5.3.2 Density of energy states.

The electrons and holes which contribute significantly to conduction have energies near the bottom of the conduction band and near the top of the valence band, respectively. For most purposes it suffices therefore to determine the density of available states only in the vicinity of the edges of these bands. The energy versus wavenumber (k) relationships in these regions have the form

$$\varepsilon_k = \frac{h^2 k^2}{8\pi^2 m} \tag{5.5}$$

(where h is the Planck constant and m is the mass of the charge carrier) and are parabolic. If states specifically near the bottom of the conduction band are considered, at which the energy datum is taken as ε_c, then one can write

$$\varepsilon - \varepsilon_c = \frac{h^2 k^2}{8\pi^2 m_e^*} \tag{5.6}$$

where m_e^* is the effective electron mass. If the incremental volume of k-space between k-values of k and k + dk is considered; in the first Brillouin zone this is $4\pi k^2 dk$ if spherical symmetry is assumed. Since each electron state (not allowing for spin) occupies $8\pi^3/V$ of k-space where V is the volume of the crystal it follows that the number of energy states in this incremental volume of k-space, per unit volume of the

crystal is given by

$$dN = 2 \times \left\{ \frac{4\pi k^2 dk/(8\pi^3/V)}{V} \right\} = \frac{k^2 dk}{\pi^2} \qquad 5.7$$

where the multiplying factor 2 takes account of the two possible directions of spin associated with each state. This equation may be rewritten

$$dN = \frac{k(kdk)}{\pi^2} \qquad 5.8$$

and substitutions may be made for k and kdk (by differentiation) from equation 5.6. Hence, one obtains

$$dN = \left(\frac{4\pi}{h^3} \right)(2\, {}_e{}^{*})^{\frac{3}{2}} (\varepsilon - \varepsilon_c)^{\frac{1}{2}} d\varepsilon \qquad 5.9$$

as the number of energy states in the range of energy from ε to $\varepsilon + d\varepsilon$, per unit volume of the crystal. It follows that the number of electron energy states, per unit energy, per unit volume of the crystal can be specified as

$$N(\varepsilon) = \frac{dN}{d\varepsilon} \qquad 5.10$$

so that from equation 5.9

$$N(\epsilon) = \left(\frac{4\pi}{h^3}\right)(2m_e{}^*)^{\frac{3}{2}} (\epsilon - \epsilon_c)^{\frac{1}{2}} \qquad 5.11$$

A similar expression is obtained for the density of available electron states near the top of an energy band starting with

$$\epsilon - \epsilon_v = \frac{-h^2 k^2}{8\pi^2 m_h{}^*} \qquad 5.12$$

and hence,

$$N(\epsilon) = \left(\frac{4\pi}{h^3}\right)(2m_h{}^*)^{\frac{3}{2}} (\epsilon_v - \epsilon)^{\frac{1}{2}} \qquad 5.13$$

Here ϵ_v is the energy at the top of the valence band and $m_h{}^*$ is the effective mass of a hole.

By combining the results of the two preceding sections it is possible to calculate the densities, i.e. numbers of electrons and holes per unit volume, having energies in the range ϵ to $\epsilon + d\epsilon$. The respective expressions are:

$$n(\epsilon) = f(\epsilon)N(\epsilon)d\epsilon \qquad 5.14a$$

$$p(\epsilon) = f_h(\epsilon)N(\epsilon)d\epsilon \qquad 5.14b$$

5.3.3 Intrinsic semiconductor

Figure 5.7 shows how, by applying the results of the above sections, the actual density distributions, $n(\epsilon)$ and $p(\epsilon)$, of electrons and holes respectively, can be determined from the Fermi-Dirac distribution function

and the density of states functions. The Fermi-Dirac function is

plotted in part (a), the density of state functions in part (b) and the

resultant curves, obtained by multiplying these, in part (c). The areas

under the upper and lower curves of part (c) give the total electron and

hole densities n and p respectively.

Electron
energy ;

$\mathcal{E}_c$

$\mathcal{E}_F = \mathcal{E}_i$

$\mathcal{E}_v$

(a)   (b)   (c)

$\longrightarrow q(\mathcal{E})$ $\longrightarrow N(\mathcal{E})$ $\longrightarrow \begin{matrix} n(\mathcal{E}) \\ p(\mathcal{E}) \end{matrix}$
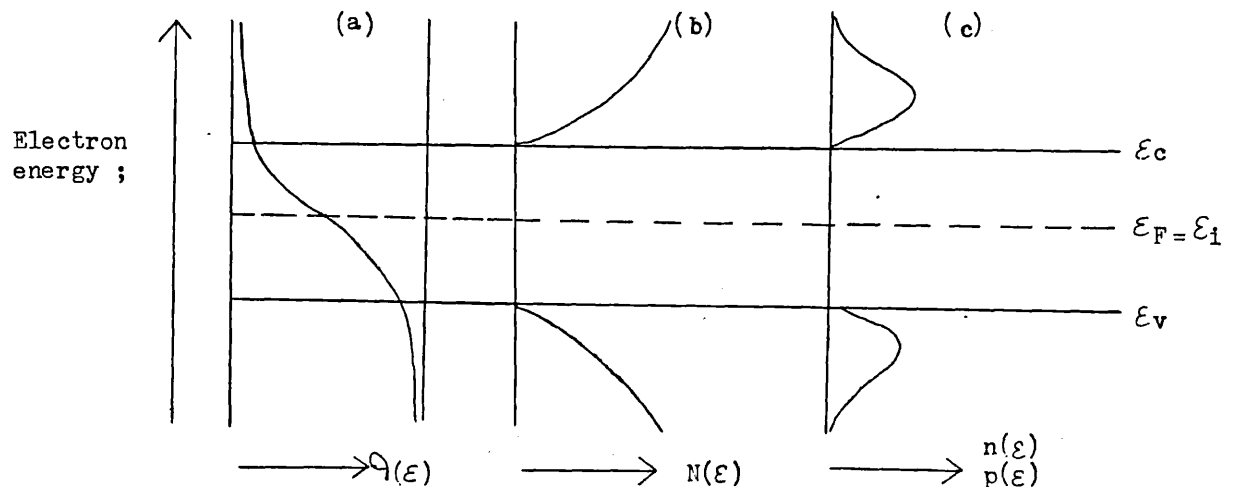
Figure 5.7

Expressions for n and p may be obtained analytically from

equations 5.1 and 5.11 and 5.3 and 5.13 by integrating equations 5.14a

and 5.14b respectively. Since intrinsic material contains equal

densities of electrons and holes it can be assumed that the Fermi level

is near the centre of the forbidden gap so that the energies of electrons

in the conduction band are several units of kT higher than ε_F, provided

that the energy gap, $(\varepsilon_c - \varepsilon_v) \gg kT$. In this case the classical

approximation for $f(\epsilon)$ can be used and

$$n_o = \exp(\epsilon_F/kT) \int_{\epsilon_C}^{\epsilon_2} [4\pi(2m_e^*)^{\frac{3}{2}}/h^3](\epsilon - \epsilon_C)^{\frac{1}{2}} \exp(-\epsilon/kT)d\epsilon$$

$$= \left\{ \exp[(\epsilon_F - \epsilon_C)/kT]4\pi(2m_e^*)^{\frac{3}{2}}/h^3 \right\} \int_{0}^{\epsilon_2-\epsilon_C} \exp(-\epsilon_1/kT)\epsilon_1^{\frac{1}{2}}d\epsilon_1 \qquad 5.15$$

where $\epsilon_1 = \epsilon - \epsilon_C$ and ϵ_2 is an energy level in the conduction band

several units of kT above ϵ_C, at which the parabolic distribution for

$N(\epsilon)$ is still valid and the suffix o is used to indicate the value of a

quantity, in thermal equilibrium. The integral converges rapidly,

because the exponential term in the integrand is dominant. Physically,

this means that the probability of finding an electron in any state

decreases rapidly the higher is the energy of the state. Hence ϵ_2 -

ϵ_C can be replaced by ∞, whereby it is converted to a standard form,

with a value $(\pi kT)^{\frac{1}{2}}kT/2$. Hence

$$n_o = 2(2\pi m_e^* kT/h^2)^{\frac{3}{2}} \exp\left\{ -(\epsilon_C - \epsilon_F)/kT \right\} \qquad 5.16$$

This is frequently written as

$$n_o = N_C \exp\left\{ -(\epsilon_C - \epsilon_F)/kT \right\} \qquad 5.17$$

where

$$N_C = 2(2\pi m_e^* kT/h^2)^{\frac{3}{2}} \qquad 5.18$$

N_C is interpreted as the "effective density of states" in the

conduction band. The reason for this becomes clear when it is recognised that exp $\{-(\epsilon_c - \epsilon_F)/kT\}$ is the value of the Fermi-Dirac function at the bottom of the conduction band. N_c can therefore be regarded as a localised density of states at this level.

A similar calculation may be carried out for hole density, and it is found that

$$p_o = N_v \exp \{ -(\epsilon_F - \epsilon_v)/kT \} \qquad 5.19$$

where

$$N_v = 2(2\pi m_h^* kT/h^2)^{\frac{3}{2}} \qquad 5.20$$

Here N_v is the effective density of states for holes at the top of the valence band.

For intrinsic material $p_o = n_o$ and both are usually represented by the symbol n_i so that, from equations 5.18 and 5.20, one obtains

$$p_o n_o = n_i^2 = N_c N_v \exp \{ -(\epsilon_c - \epsilon_v)/kT \} \qquad 5.21$$

and therefore

$$n_i = \sqrt{N_c N_v} \exp \{ -(\epsilon_c - \epsilon_v)/2kT \} \qquad 5.22$$

Now d.c. conductivity (σ_o) for an intrinsic material is given by

$$\sigma_o = n_i e (\mu_e + \mu_h) \qquad 5.23$$

where μ_e and μ_n are the mobilities of the electron and hole respectively, and e is the electronic charge.

Thus

$$\sigma_0 = [\sqrt{N_c N_v}\ e\ (\mu_e + \mu_h)]\exp\left\{-(\varepsilon_c - \varepsilon_v)/2kT\right\}$$ 5.24

Now [   ] varies slowly with temperature compared with the exponential term of equation 5.24 and it can be regarded as substantially constant for some purposes. Therefore, in general, for an intrinsic material,

$$\sigma_0 = A\ \exp\left\{- \Delta\varepsilon/2kT\right\}$$ 5.25

where $\Delta\varepsilon = \varepsilon_c - \varepsilon_v$ and is referred to as the "activation energy" or "band gap energy" (for an intrinsic material).

5.4   Conduction Mechanisms in Insulating Materials

Sections (5.2) and (5.3) have essentially discussed semiconductor theory and hence electronic conduction. Conduction is, however, neither solely specific to metals, and semiconductors nor restricted to being electronic in nature. A variety of conduction mechanisms exist which could be effective in insulators (dielectrics).

These are of particular interest to us, since many of our materials fall into the semi-insulating class.

5.4.1   Ionic conduction[30].

It is known that carriers, in insulators, have an inherently low mobility and move by some form of hopping. Ionic conduction is an extreme form of hopping and it occurs when the carriers (ions) jump through sites which are vacancies.

5.4.2   Space charge limited conduction[31]

Space charge limited conduction arises when the supply of carriers
is electrode controlled and a copious injection of charges takes place
from an electrode, regardless of the mobility of the charge carriers in
the material. Space charge limited conduction can have a pronounced
effect on the transport of charge in insulators at room temperature.
This is particularly the case in the presence of an ohmic contact which
facilitates the injection of charge into the insulator[32]. SCL
conduction is characterised by a quadratic voltage-current response
i.e. $I \propto (V^2/d^3)$.

5.4.3   Impurity conduction[30].

In impure insulators the wave function of the charge associated
with the impurity centre is localised in the region of the centre. The
wave functions of electrons of neighbouring impurity atoms overlap if
there is a moderate concentration of impurities. In such cases a
conduction process is possible in which the electrons move between centres
without activation into the conduction band. This is known as impurity
conduction.

5.4.4   Tunnelling[33].

There can arise situations when an energy barrier is too large for
a charge carrier to surmount. In such cases carriers may prefer to pass
through the material without changing their potential energies. This
process is called tunnelling and requires the barrier thickness to be of
the order of a localised wave function length.

5.4.5   Schottky Effect[30].

In the presence of high fields electron emission is possible from an electrode, which has a negative potential into the conduction band of the insulator. The high fields lower the metal-insulator interface barrier such that a thermally activated electron can easily pass over the barrier. The current density for such an emission is given by the Richardson-Schottky equation:

$$J = AT^2 \exp\left\{- \Phi/kT \right\}\exp\left\{\beta_s E^{\frac{1}{2}}/kT \right\}$$ 5.26

where A is a constant, Φ is the barrier height, T is the temperature and β_s is the Schottky barrier lowering coefficient with e the electronic charge.

5.4.6   Poole-Frenkel conduction.

The Poole-Frenkel mechanism is commonly used to explain high field currents in amorphous materials and in impure semiconductors[34]. The effect is based on the lowering of the effective ionisation energy of a donor by the applied field. For an ionisation energy E_1, the field-lowered value is $E_1 - \beta F^{\frac{1}{2}}$, where β is called the Poole-Frenkel constant. The current is given by

$$J = J_o \exp\left\{(\beta F^{\frac{1}{2}}/kT)-(E_1/kT)\right\}$$ 5.27

Theoretically[35],

$$\beta = \left\{ q^3/\pi\varepsilon_o\varepsilon_r \right\}^{\frac{1}{2}} \qquad\qquad 5.28$$

where ε_o is the permittivity of free space and ε_r the relative permittivity for low or high frequencies depending on whether the medium surrounding the donor can or cannot polarise within the emission time. At very low temperatures the carriers are emitted at constant energy by direct tunnelling into the conduction band, and at moderate temperatures carriers are emitted by thermally assisted tunnelling through the top of the potential barrier.

The Poole-Frenkel effect requires the presence of donor sites which may co-exist[35] with traps present in the forbidden gap. In general it is assumed that the potential surrounding a site is coulombic in nature and does not contain a screening factor, i.e. it falls off as the inverse distance measured from the site under consideration. This assumption gives a decrease in the potential barrier proportional to $E^{\frac{1}{2}}$ in the single site case.

The appearance of a linear region in a log I vs $V^{\frac{1}{2}}$ (or $E^{\frac{1}{2}}$) graph is considered[36] to be evidence for the presence of a Poole-Frenkel mechanism.

5.5   Organic semiconductors to organic metals[37,38,39,40,41,42]

The electrical conductivity of most organic materials (when purified) is extremely low . However, strong π-molecular donor (D) and acceptor (A) molecules often react to form radical-ion salts ($X^+A^{\overline{}}$

and $D^{+\cdot}X^-$) and charge-transfer compounds (DA and $D^{+\cdot}A^{-\cdot}$) which have

considerably higher conductivities. As may be seen in Table 5.1, the

conductivities of some of the organic compounds resemble those of metals.

Table 5.1

Material	σ	n	μ
Ag	6.6×10^5	5.8×10^{22}	70
Cu	6.4×10^5	8.5×10^{22}	47
Hg	4.4×10^4	4.2×10^{22}	6.6
InSb	3.5×10^2		6.5×10^4
Si(n-type)	4×10^1	1×10^{18}	240
TCNQ salts	$1 - 1000$	$\simeq 10^{21}$	4
Perylene I_3	2×10^1	1.3×10^{20}	$\simeq 1$
Anthracene	$\ll 10^{-14}$	$\ll 10^5$	$\simeq 1$
Teflon	$\ll 10^{-14}$		

(All values at room temperature, σ = conductivity in Ω^{-1} cm^{-1},

n = density of carriers in cm^{-3}, and μ = mobility in

cm^2 V^{-1} s^{-1}).

Charge-transfer complexes are formed from closed-shell molecules, are

neutral in their ground state, and are characterised by weak van der Waals

interactions. In the crystalline CT complexes, the donor and acceptor

molecules stack in the order DA DA DA DA, as shown in figure 5.8 for

perylene-fluoranil[43]. These stacks are called "mixed" or
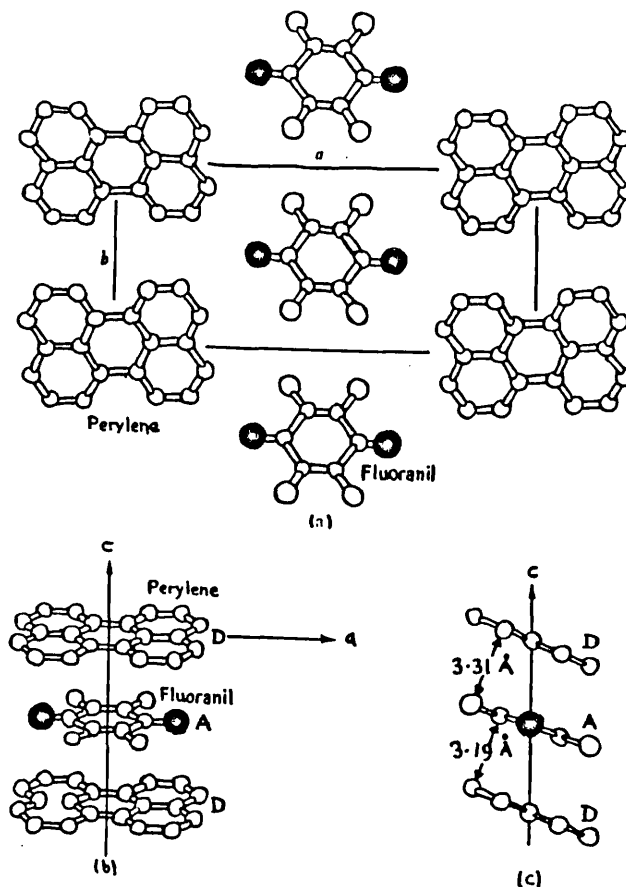
Fig. 5.8

"intercalated" stacks. The intermolecular spacing between the D and A

molecules in the same stack is less than the 3.4 - 3.6 $\overset{\text{o}}{\text{A}}$ spacing that is

characteristic of van der Waals solids.

The other class of D-A complexes consists of the radical-ion salts,

e.g. the alkali metal-TCNQ salts and TTF-TCNQ (tetrathiafulvalene-

tetracyanoquinodimethane) type salts[44-48], shown in figure 5.9. In many
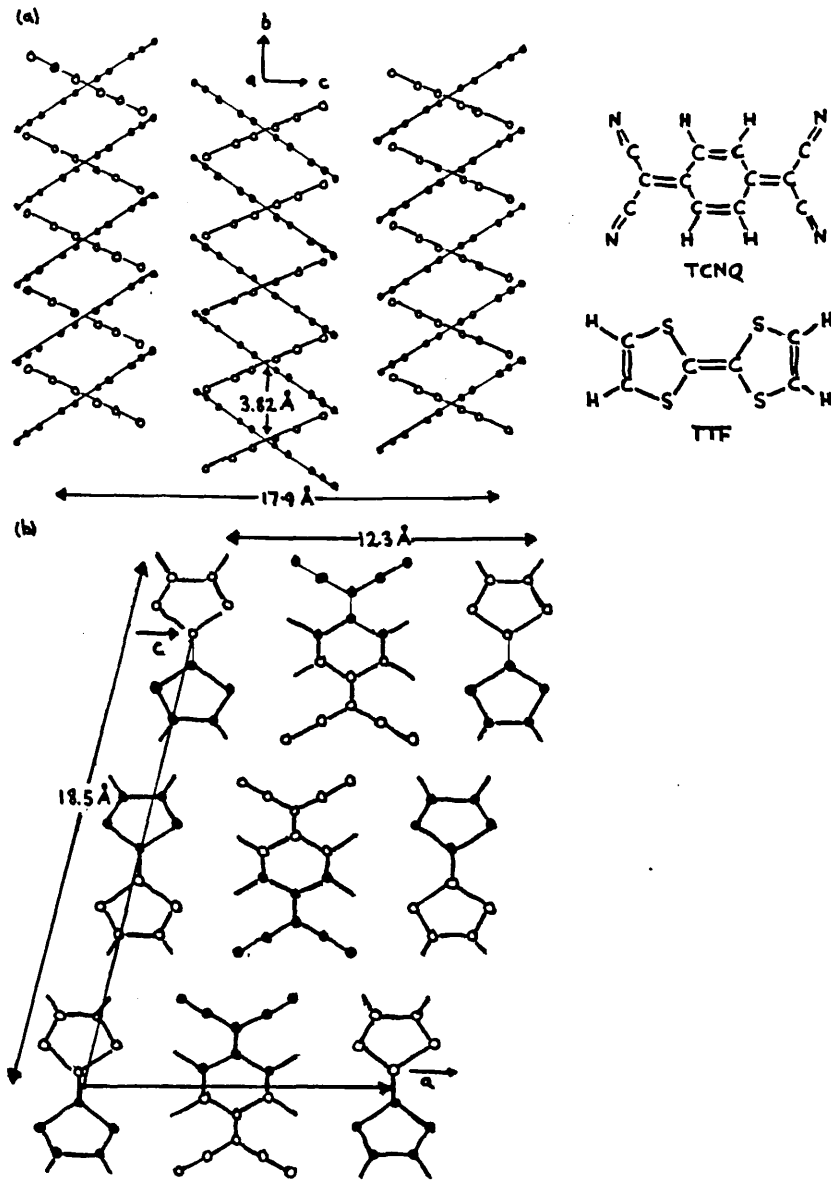
Figure 5.9

of the radical salts, the donors and acceptors are arranged in separate stacks, as shown in Figure 5.10.

$$
\begin{array}{cccc}
D & A & D & A \\
D & A & D & A \\
D & A & D & A \\
- & - & - & -
\end{array}
$$

Figure 5.10

In crystalline TTF-TCNQ the molecules in each stack are tilted with

respect to the axis of the stack, and adjacent columns are arranged to

form a herringbone pattern. A common feature of all radical ion salts and

complexes is the planarity of the individual molecules. The metallic

conductivities referred to in Table 5.1 appear only in those compounds in

which D and A are in separate stacks. TTF-TCNQ, for example, has been

referred to as an organic metal, and $(TMTSF)_2PF_6(di-(\Delta^{2,2'}-bi-$

4,5-dimethyl-1,3-diselenole)-hexafluorophosphate) is a superconductor[39].

Organic radical-ion salts are of practical interest because they

have already demonstrated superconductivity, and they are interesting

theoretically because they exhibit a quasi-one-dimensional behaviour. As

has been mentioned, the D and A molecules in single crystals of the

radical-ion salts are often arranged in separate and parallel stacks, and

the carrier motion seems to be confined mostly to the particular stack in

which the carrier is generated. Occasionally, the carrier will hop out of

its stack. If there were no forces of interaction between neighbouring

stacks, this system would be truly 1-D and the conductivity would be zero

in two directions; since there must be forces of attraction in order to

form the crystal in the first place, the radical-ion salts are quasi-1-D

systems. Nevertheless, these salts provide a convenient and challenging

testing ground for 1-D theories.

In particular, the research in quasi-1-D crystals has been spurred

by the hope of finding high-temperature superconductivity or high

conductivity produced by some collective mechanism other than the

quasi-Bose-Einstein condensation of Cooper-pairs[49]. The idea that

superconductivity might be found in conjugated aromatic compounds first

appeared in the work of London[50] who looked upon the motion of the

electrons in the half-filled π-orbitals of the benzene molecule as being non-dissipating: the magnetic field generated by this motion had an appropriately diamagnetic character. Pursuing this concept, he then suggested that superconductivity is a manifestation of quantum behaviour on a macroscopic scale; he viewed the superconductivity as a gigantic molecule over which the charge was delocalised in unsaturated orbitals.

This idea was taken up and given greater relevance by Little[51], who proposed that an attractive potential between conduction electrons could be mediated by an intramolecular polarisability, producing an effect similar to that of lattice phonons in the creation of Cooper-pairs. Little envisaged the constitution of a polymer-like molecule, consisting of a conducting spine and polarisable side groups; an electron travelling along the spine would polarise the side groups, and this polarisation could act as an attractive potential to the next electron coming along the spine. Figure 5.11 illustrates the superconducting backbone of a polymer chain and cyanine dye side groups initially suggested by Little.
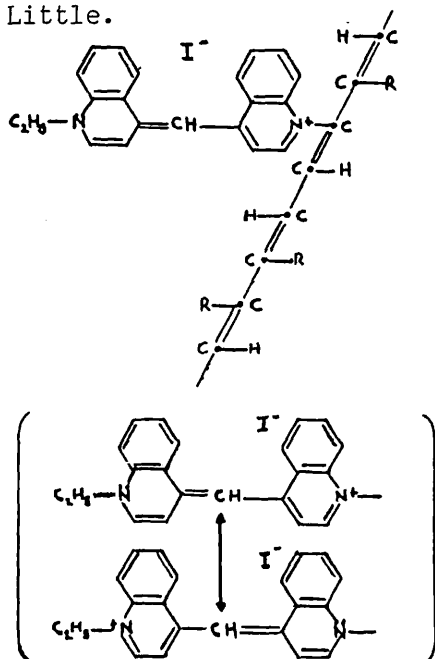
Figure 5.11

Although this material has not been made, several analogs of this
polymer have been synthesised[52], but unfortunately, none displays
superconductivity.

The TCNQ salts which have a 1:1 composition ratio of cations to
TCNQ (i.e. simple salts) and which have separate (segregated) cations and
TCNQ stacks comprise ≃ 25% of the known TCNQ compounds. Figure 5.12
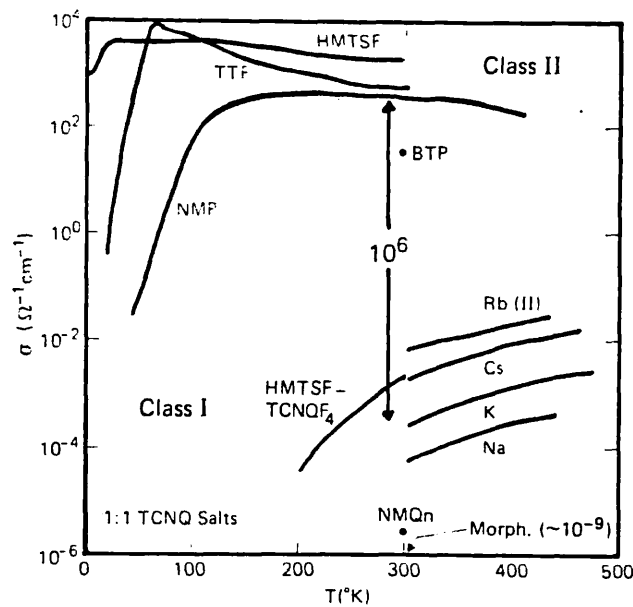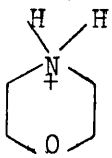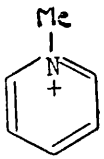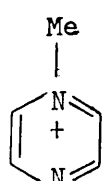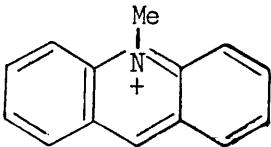
Figure 5.12
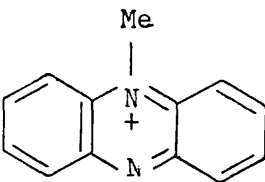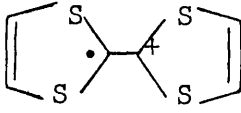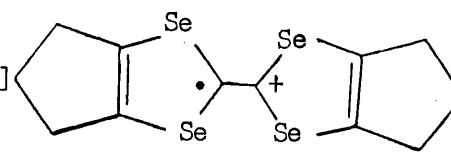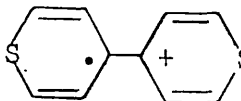
shows the dc conductivity data taken along the stacking axis of single
crystals of a number of simple (1:1) TCNQ salts known to form segregated
stacks. The cations of these salts are listed in Tables 5.2 and 5.3 along
with a number of other examples[38].

Table 5.2

$\sigma(\Omega^{-1}cm^{-1})$

Na^+		3×10^{-5}
(Li^+, K^+, Cs^+, Rb^+)		$(10^{-4} - 10^{-6})$
Triethylammonium [TEA]	$Et_3\overset{+}{N}H$	10^{-9}
Ammonium	NH_4^+	2×10^{-5}
Morpholinium [Morph]		10^{-9}
N-methylpyridinium [NMPy]		10^{-5}
(pyridinium)		(10^{-6})
(4-cyano-NMPy)		(10^{-6})
N-methylpyrazinium [NMPyz]		3×10^{-8}
N-methylacridinium (NMAd)		2×10^{-5}

(Cations of Class I TCNQ salts with their 300 K powder conductivities).

Table 5.3

$$\sigma(\Omega^{-1}cm^{-1})$$

N-methylphenazinium [NMP]	2
Tetrathiafulvalinium [TTF]	10
(tetraselenafulvalinium [TSeF]	(18)
hexamethylene-TSeF[HMTSF]	25
Δ 4,4' bithiopyranium [BTP]	1

(Cations of Class II TCNQ salts with their 300 K powder conductivities).

On the basis of the magnitude of the conductivity, at say, 300 K, these salts separate into two distinct groups Class I salts are semiconducting and Class II salts have a very high conductivity, which initially increases with decreasing temperature below 300° K, hence they are called "metallic" (even though they are generally not metallic at low temperatures).

There are many differences between, for example, K^{+} (Class I) and TTF^{+} (Class II) that could be responsible for the large difference in the conductivities of their TCNQ salts. The differences, however, are not so easily found for the N-methylacridinium (NMAd) vs. the N-methylphenazinium (NMP) salts of TCNQ where the cations differ only by one heterocyclic nitrogen.

Salts in both classes contain face-to-face stacks of TCNQ molecules with strong π-molecular overlap along the stacking direction, resulting in a large tight-binding charge-transfer integral, t. Both theoretical and experimental estimates of the electronic bandwidth, 4t, are about 0.5 eV. One would think that, with one unpaired electron per TCNQ molecule in a simple non-interacting electron (or molecular orbital) theory, the band (or orbital) would be only half-filled and that, with such a large overlap, all of these materials should be potentially highly conducting. For this reason, some workers have approached the problem by asking; why are Class I salts poorer conductors?

It has been suggested[53,54] that distortions in the TCNQ stacks play an important role in the conductivity of these salts. Indeed, the X-ray crystal structures of K-, Na-, and Rb (phase I) - TCNQ show[55] that the spacing between the molecules in the stacks strongly alternates at 300 K while that in NMP- and TTF-TCNQ is uniform[56]. Such a pairing of molecules or dimerisation would be expected for a simple Peierls transition and would be expected to make the distorted salts far less conducting than those with uniform stacks. Furthermore, the alkali-TCNQ salts have a phase transition at T_c, below which they are dimerised, but above which the stacks are uniform[55] . For example, for K, Na and Rb (phase II), T_c = 395, 345 and 227 K, respectively, and yet above T_c, where the stacks are uniform, the conductivity is still at least four orders of magnitude lower than that of typical class II salts.

Thus, class I salts are semiconducting even when they have uniform stacks, and hence stack distortions cannot account fully for the large differences in conductivity.

In these materials, Coulomb interactions have important effects. The magnitude of the Coulomb repulsion energy between two electrons separated by a distance r is given by $e^2/r = 14.3$ eV/r (r is in $\overset{\circ}{A}$). In these salts r is typically about 3 -4 $\overset{\circ}{A}$, and therefore the characteristic Coulomb energies are large, i.e., about 3 - 4 eV. If these repulsive interactions are not appreciably reduced in the solid, they will be larger than the bandwidth associated with delocalising the electrons on to adjacent molecules; the bandwidth, 4t, is about 0.5 eV. The ground state of the $(TCNQ^-)_2$ dimer, for example, will then have the unpaired electrons localised on each $TCNQ^-$. The lowest excitation will be a charge-transfer excitation with an energy U given by

$$U = h\nu_{CT} = U_o - V_1 \qquad\qquad 5.29$$

U is thus the difference between the Coulomb repulsion energy (U_o) when two electrons are on the same TCNQ molecule and the repulsion (V_1) when they are on adjacent molecules. U_o may also be viewed as the disproportionation energy of the reaction

$$TCNQ^- + TCNQ^- \xrightarrow{U_o} TCNQ + TCNQ^{2-} \qquad\qquad 5.30$$
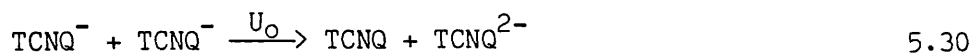
Similarly, the unpaired electrons on a stack of $TCNQ^-$ anions will be localised if the Coulomb interactions are large. The lowest excitation will also be a charge-transfer band, at an energy $h\nu_{CT} \simeq U$ given by equation 5.29. Since the conductivity along the stack is achieved by exciting an electron down the stack, the conductivity will be limited by a large activation energy, $\simeq U$. If the energy U is large (compared to 4t), the material will be an insulator.

In close analogy with the mechanism for organic superconductivity proposed by Little[51], Le Blanc[57] proposed that the excitonic polarisability of the cations of class II sufficiently reduces (screens) the repulsion interactions (U) on the TCNQ stacks so the U becomes small compared to the band width 4t. In this event, the 300 K conductivity would become metallic for class II salts, while those of class I would remain semiconducting with large unreduced Coulomb energies U.

The differences in polarisability between $NMAd^+$ and NMP^+, however, cannot be large enough to be the most important difference between these salts. Therefore, the cations in Table 5.3 are apparently neither polarisable enough nor close enough to the TCNQ stack[58] to substantially decrease U.

On the basis of optical experiments, it was suggested[59] that the difference between classes was caused by a difference in the amount of charge, ρ, transferred from donor to TCNQ, i.e. that in class I salts this charge transfer is complete ($\rho = 1$) and the TCNQ molecules are completely reduced to $TCNQ^-$. For class II salts, on the other hand, it is suggested that the charge transfer is incomplete ($\rho < 1$), hence the TCNQ molecules are only partially reduced. For class I salts there is $\rho = 1$ unpaired electron on each TCNQ molecule and the lowest excitation coresponds to exciting an electron from $TCNQ^-$ to a neighbouring (occupied) $TCNQ^-$ molecule. This charge-transfer transition requires an energy $h\nu_{CT} \approx U$, as discussed earlier.

In class II salts, on the other hand, there are only electrons (with $\rho < 1$) transferred from the donor. Hence on a short time scale,

the stack may be viewed as containing both neutral TCNQ^O and ionic

TCNQ$^-$ molecules. In such a mixed-valence stack, it is possible to

excite an electron from TCNQ$^-$ to a neigbouring neutral TCNQ^O molecule,

hence not having to overcome the strong Coulombic repulsion energy, U, as

$$\text{TCNQ}^- + \text{TCNQ}^O \longrightarrow \text{TCNQ}^O + \text{TCNQ}^-$$
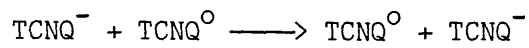
shown schematically in figure 5.13.
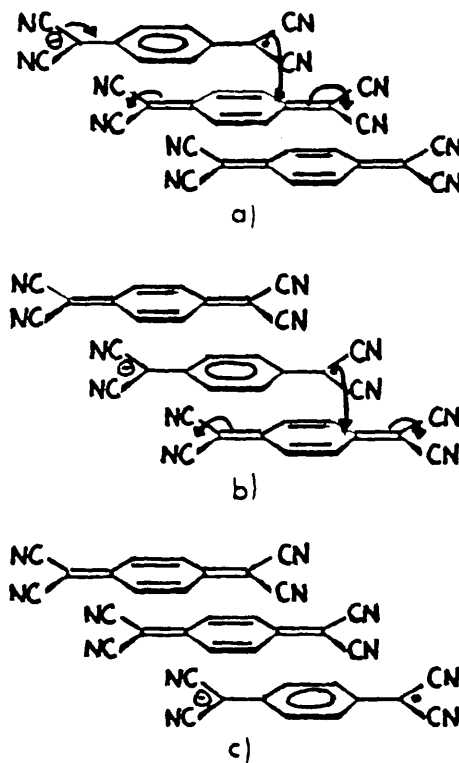
Figure 5.13

5.6. Aims and Objectives (electrically)

The crystal structure of the hydroxypyridone trimethine oxonol MI1579[2] showed the anions to be planar and ordered one above the other along the b axis with an interplanar separation of 3.67 $\overset{\circ}{A}$, figure 5.14.
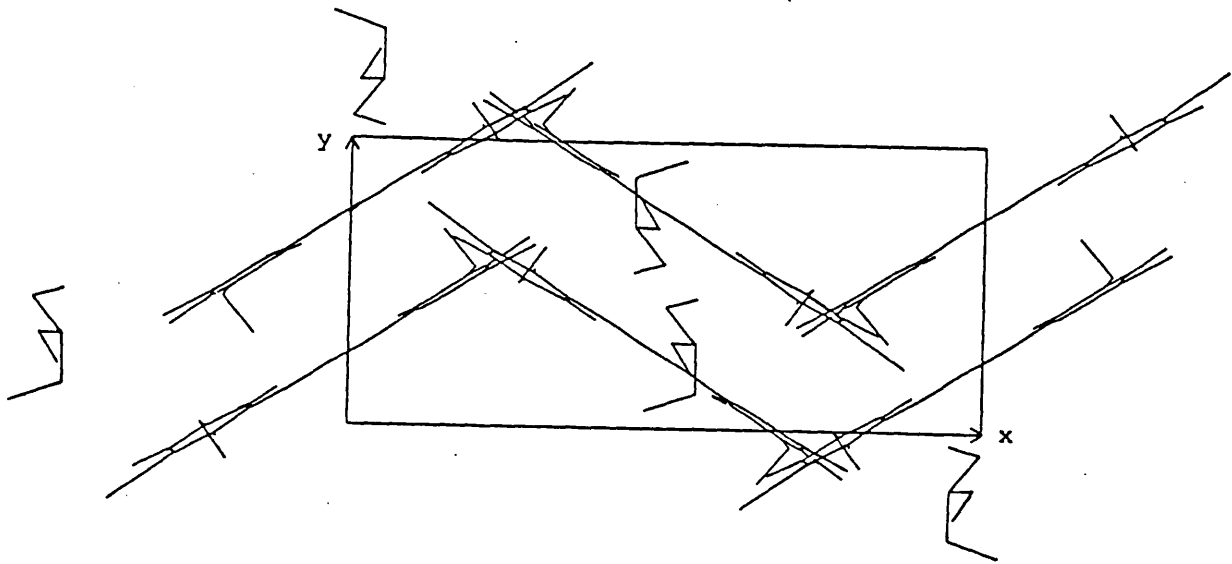
Figure 5.14

MI1579 was found to have a dc conductivity $\sigma = 5.75 \times 10^{-11} \Omega^{-1}$ cm^{-1} at 373 K (compacted powder). The insulating nature of MI1579, however, was not altogether suprising as in order for efficient electronic migration to occur an interplanar distance of less than or equal to van der Waals spacing (3.4 A) would be required.

The result did, however, encourage us to look for ways of modifying the dye structure to improve the dc conductivity.

(a)   In the short term this might have been achieved by:

i.   shortening the N-alkyl substituent. From figure 5.14, the N-ethyl group did appear to hinder closest packing of the anions;
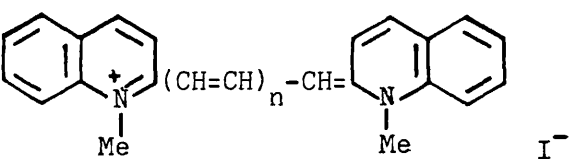
ii.   introducing additional potential charge carriers. This would involve enriching the structures with π-electrons either via the cation e.g.
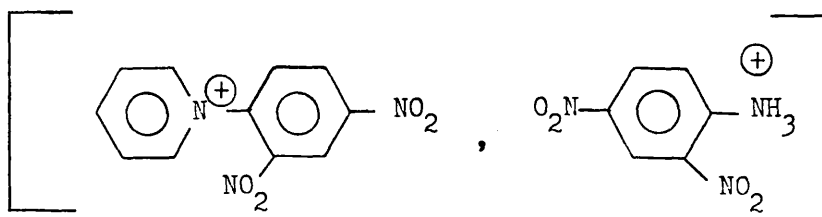
or via the anion by introducing N-aryl substituents or by increasing the methine chain length. Increasing methine chain lengths had been shown to decrease thermal activation energies and increase dc conductivities in the cyanine dyes[60,61], Table 5.4.

Table 5.4

n	N	λmax/nm	$\Delta\varepsilon$/eV	$\sigma/\Omega^{-1}cm^{-1}$
1	8	605	1.8	2×10^{-13}
2	10	710	1.3	10^{-11}
3	12	817	0.69	1.3×10^{-8}

(N is the number of π electrons, $\Delta\varepsilon$ the thermal activation energy and σ the conductivity).

iii. Introducing cations or anions with their own inherent conductivity; this would involve the synthesis of radical cation-oxonol dye salts.

(b)   In the longer term we hoped to elucidate a general relationship between packing in the crystal and substituent and counter-ion changes. This would involve X-ray crystal structure determination and solid-state n.m.r. spectroscopy.

(c)   It was also our intention to investigate conduction in insulating and semi-insulating materials as well as in the semiconductors using dielectric spectroscopy.

(d)   The preparation of a range of solids by cocrystallisation of different anionic (oxonol) and cationic (cyanine) dyes, of similar molecular dimensions, in the hope of forming charge transfer complexes was also planned.

CHAPTER 6

Structural Studies in the Solid State

6.1.   X-ray Crystal Structure Analyses

6.1.1. To our knowledge only two other oxonol dye crystal

structures are known[62]. This, recent publication concerns co-crystals

of cyanine and oxonol dyes. They show multiple morphology and have

potentially interesting electrical and magnetic properties.

The most extensively studied photographic dyes, in terms of

structure, are the cyanines and their analogues [63]. The cyanines are

spectral sensitizers, that is, their addition sensitize·s silver halides

to regions of the spectrum other than just the blue and violet. Their

general formula is given in Figure 6.1. The molecular packing in
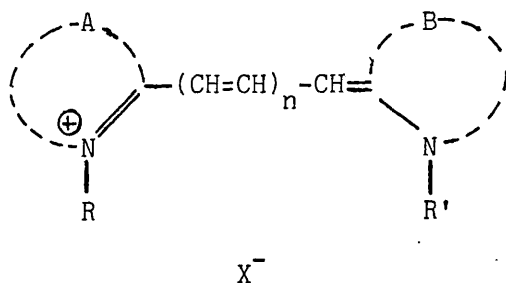
Figure 6.1

(A and B complete heter·ocyclic nuclei, which may be the same or

different)

many of these crystals involves planar dye cations, with angles of less

than 15° between planes defined by the two heterocyclic rings, packed

plane to plane and end to end in layers. Examples include thiacyanine (I)

(bromide[64] or TCNQ complex[65]), phosphathiacyanine (II)

perchlorate[66], 5,5',6,6'-tetrachlorobenzimidazolocarbocyanine (III)

iodide[67] and the acetylenic dye IV 5,6-di-chloro-1,3-diethyl-

2[(5,6-dichloro-1,3-diethyl-2-benzimidazolinylidene)-1-propynyl]-

benzimidazolium p-toluenesulphonate[68], Figure 6.2 shows average bond

lengths and angles for these four planar dyes and for the nonplanar

imidazo[4,5,-b]-quinoxalinocyanine V iodide[69].

Steric interactions are often relieved by twisting about the

central methine carbon. In V, for example, the reported angle of twist is

55°. Nearly equivalent bond lengths in the two heterocyclic rings for

almost every symmetrical cyanine, even in the presence of significant

distortion of the methine bridge, suggests that the charge on the dye is

delocalised over the chromophore. The cation-cation arrangements of most

interest have been those for 1,1'-diethyl-2,2'-quinocyanine chloride[70],

5,5',6,6'-tetrachloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine

iodide[67] and 5,5'-dichloro-3.3',9-tri-ethylthiacarbocyanine bromide[71].

The heterocyclic rings of these three dyes have plane-to-plane

orientations, and interplanar distances of 3.3 to 3.6 A. The lateral

shift of adjacent dye chromphores in the benzimidazole dye is 12 to 13 A

(Figure 6.3A). The atoms in the quinocyanine dye exhibit a more complex

relationship, where the highly twisted chromophore introduces an

inversion centre relating atoms of adjacent chromophores. In contrast

Figure 6.2

A

B
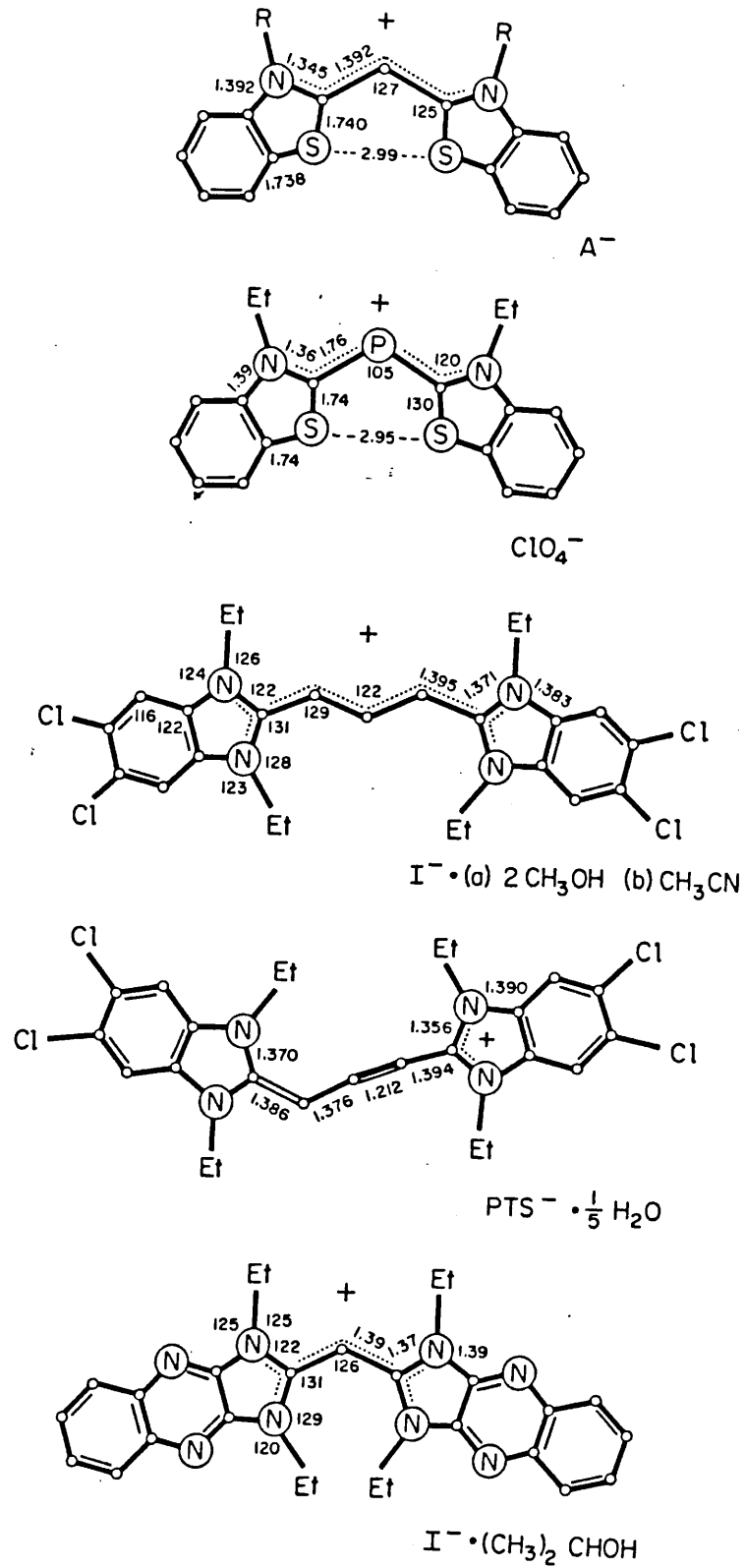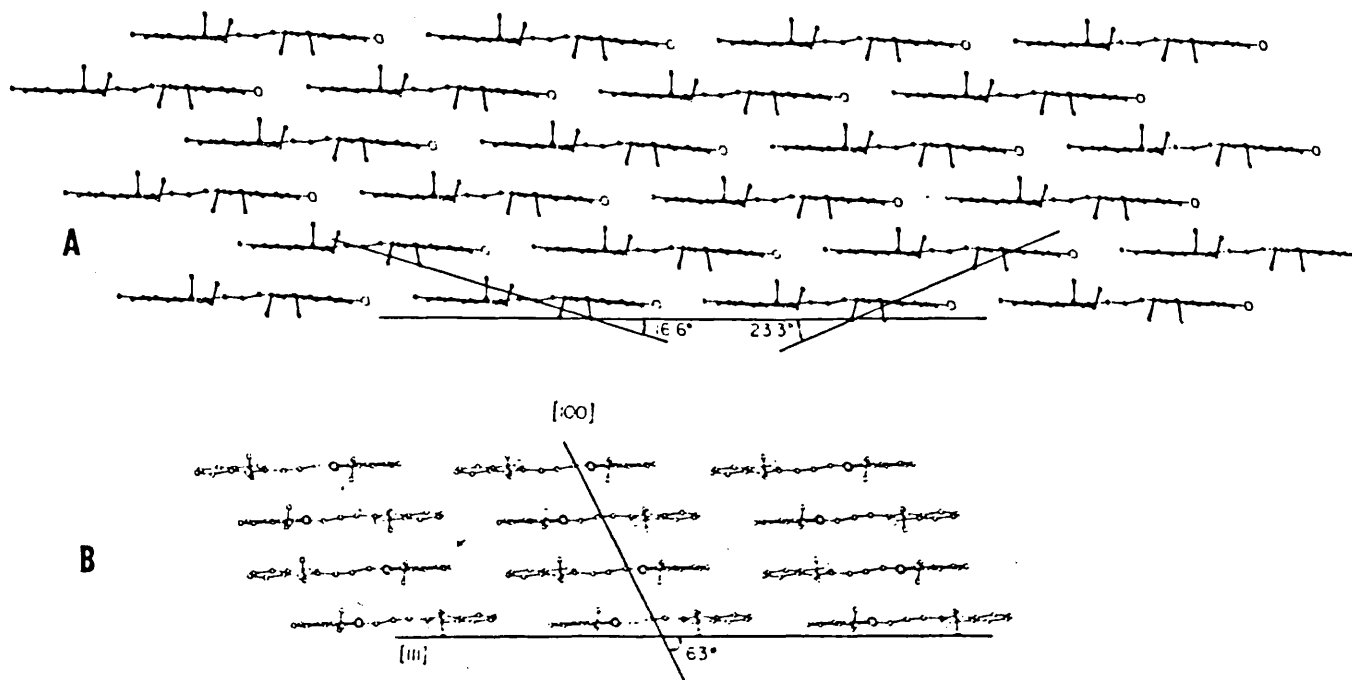
Figure 6.3

to this, 3,3'-diethylthiacarbocyanine[72,73] (Fig. 6.3B) with similar

interplanar distances ($\simeq$ 3.6 A) exhibits a lateral shift of adjacent

chromophores of only 4.05 A. This lateral displacement of adjacent

chromophores is highly influenced by substituents[63].

The structure determination of the hydroxypyridone trimethine

oxonol (Ia), Fig. 6.4, carried out by Cheetham, Grossel and Johnson

(unpublished results) reveals the anion to be highly planar (angle of
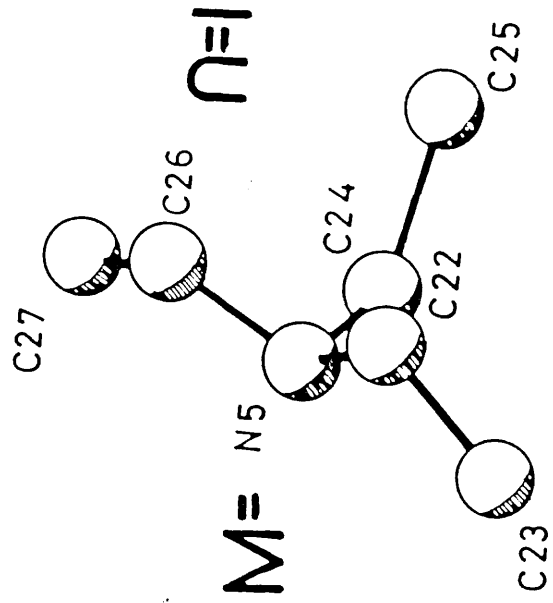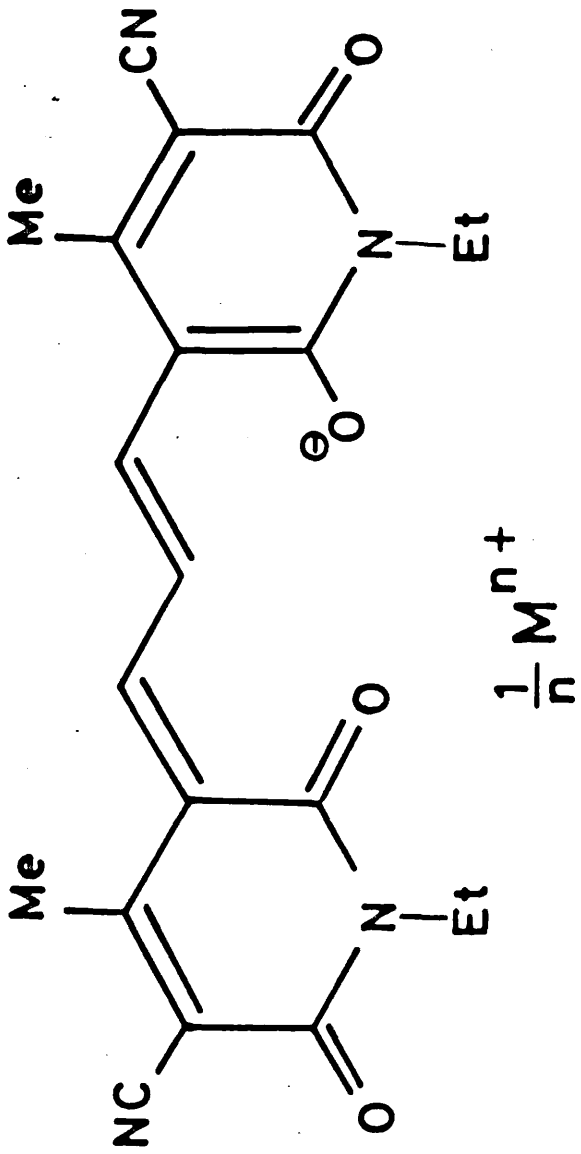
Figure 6.4
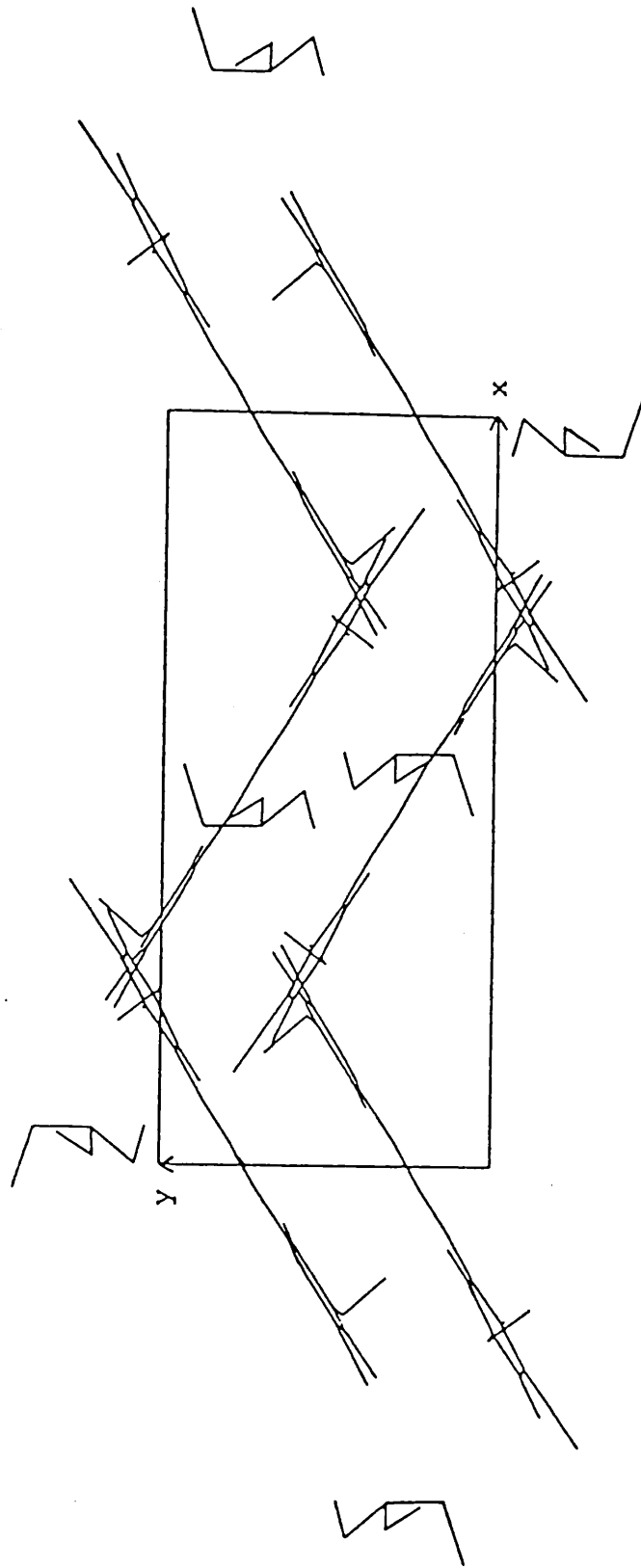
Figure 6.5

twist between planes defined by the two hydroxypyridone rings = 12°),

Figure 6.5. This figure also shows the closest approach of the

triethylammonium cation to the anion molecule. The interaction of the

external hydroxypyridone ring oxygen and the nitrogen of the cation is

presumably supplemented by hydrogen bonding, Fig. 6.6. It is also
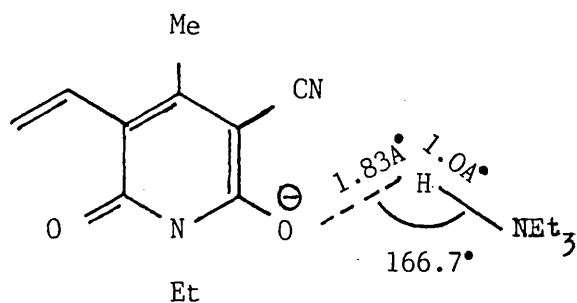
Figure 6.6

apparent that the anions stack in such a way as to minimise electrostatic

repulsions between them and this is supported by the positions adopted by

the associated cations, Fig. 6.7.
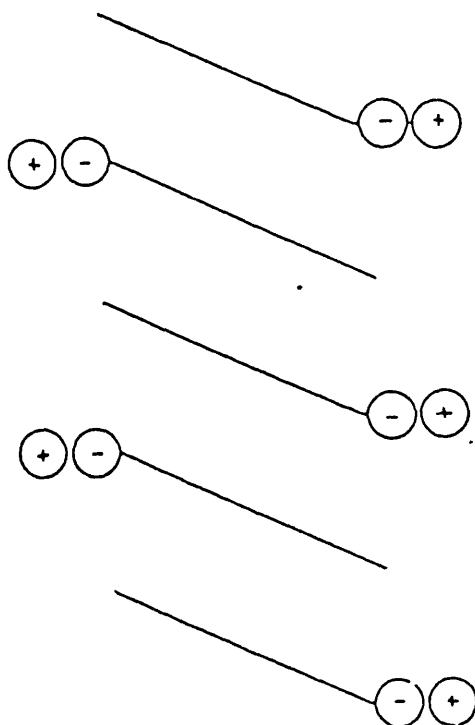
Figure 6.7

The perpendicular distance between the planes of two adjacent

anions in the stack is 3.67 A.

Like many of the cyanine dye structures this planar stacking

arrangement lends itself to the possibility of intermolecular electronic

charge transfer (van der Waals spacing in solids $\simeq$ 3.4 A). The

semiconductivity of many of the simple cyanine dyes[60,61] and the almost

metallic conductivity of some of their TCNQ complexes[74] is well known.

We therefore set out to investigate how we might modify the mode of

packing in the hydroxypyridone oxonols. Our crystallographic studies, due

to limited access to diffractometer facilities, were concentrated on the

effects of cation variation on anionic stacking.

6.1.2   The structure of tetraphenylphosphonium 1-ethyl-3-cyano-6-

hydroxy-4-methyl pyrid-2-one trimethine oxonol

(Ib), Fig. 6.8.
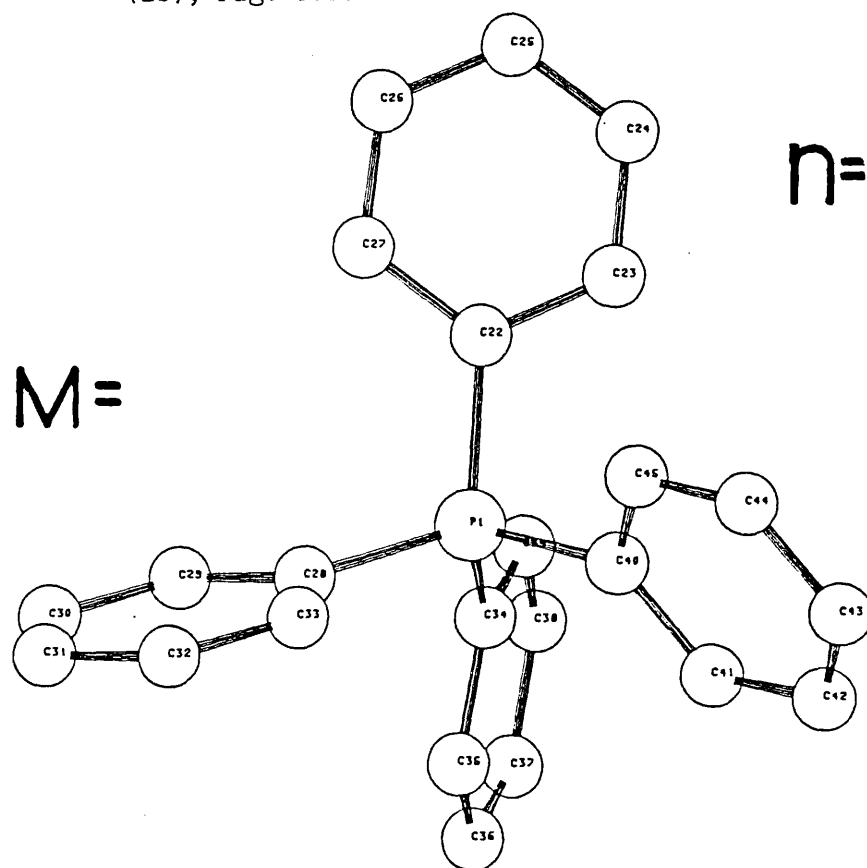
Figure 6.8
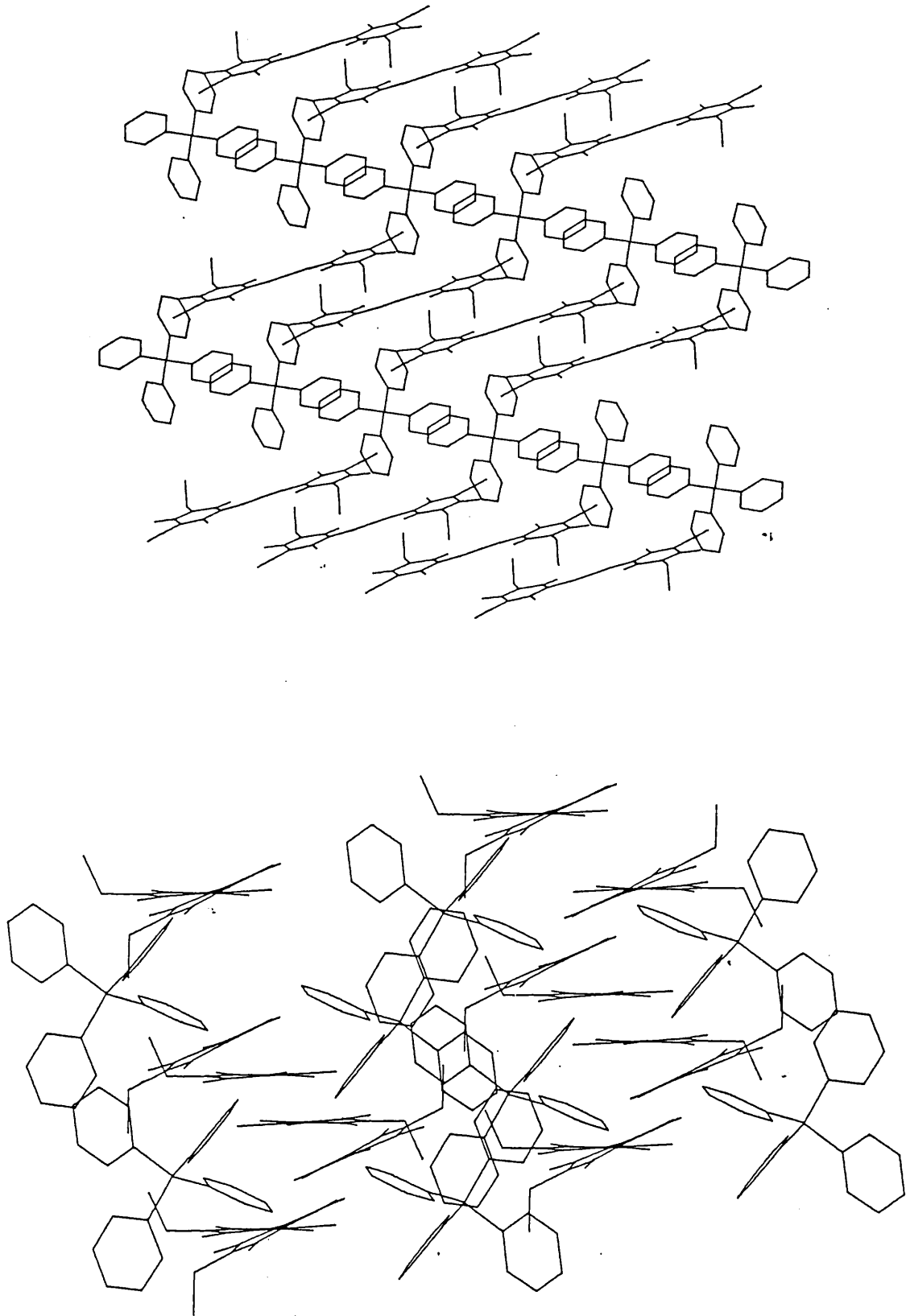
Figure 6.9

The anion is seen to be far less planar (angle of twist about methine bridge = 40.37°), Figure 6.9. Also the molecules of the anionic stack are infinitely parallel in contrast to the herringbone type arrangement in Ia. The interplanar distance has also increased to 4.06 A.

The fractional atomic coordinates, anisotropic temperature factors, bond lengths and bond angles are listed in Tables 6.1, 6.2, 6.3 and 6.4 respectively.

Table 6.1.

Fractional atom co-ordinates for I(b), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	0.0091(6)	0.3888(7)	0.1045(6)
C(2)	0.1192(5)	0.3626(5)	0.0838(5)
C(3)	0.1868(4)	0.1726(4)	0.1332(4)
C(4)	0.2000(3)	0.0565(4)	0.1018(3)
C(5)	0.2600(4)	-0.0120(5)	0.1793(4)
C(6)	0.1558(3)	0.0129(4)	0.0062(3)
C(7)	0.1659(5)	-0.1116(5)	-0.0176(5)
C(8)	0.1007(3)	0.0866(4)	-0.0690(3)
C(9)	0.0947(3)	0.2070(4)	-0.0455(3)
C(10)	0.0506(3)	0.0430(4)	-0.1649(3)
C(11)	0.0000(0)	0.1027(6)	-0.2500(0)
C(22)	0.4898(3)	0.2984(4)	0.1337(4)
C(23)	0.5594(4)	0.2093(5)	0.1280(4)
C(24)	0.5539(5)	0.1414(5)	0.0377(5)
C(25)	0.4774(5)	0.1615(5)	-0.0466(5)
C(26)	0.4081(5)	0.2487(6)	-0.0396(4)
C(27)	0.4128(4)	0.3182(5)	0.0489(4)
C(28)	0.6117(4)	0.4798(4)	0.2536(4)
C(29)	0.6901(4)	0.4644(5)	0.1879(4)
C(30)	0.7750(4)	0.5403(5)	0.1972(5)
C(31)	0.7804(5)	0.6269(6)	0.2697(6)
C(32)	0.7009(6)	0.6408(6)	0.3345(6)
C(33)	0.6157(5)	0.5685(5)	0.3259(5)
N(1)	0.1342(3)	0.2428(3)	0.0575(3)
N(2)	0.3103(4)	-0.0656(5)	0.2400(4)
O(1)	0.2182(3)	0.2099(3)	0.2223(3)

Table 6.1 (continued)

O(2)	0.0547(3)	0.2804(3)	-0.1062(2)
P(1)	0.5000(0)	0.3872(1)	0.2500(0)
H(1)	-0.041(5)	0.376(7)	0.043(5)
H(2)	0.004(5)	0.476(6)	0.126(5)
H(3)	-0.017(5)	0.336(6)	0.162(5)
H(4)	0.167(4)	0.379(5)	0.150(4)
H(5)	0.149(4)	0.417(4)	0.029(4)
H(6)	0.208(4)	-0.123(5)	-0.101(4)
H(7)	0.091(5)	-0.154(5)	-0.023(5)
H(8)	0.210(5)	-0.149(6)	0.019(5)
H(9)	0.053(3)	-0.053(4)	-0.177(3)
H(10)	0.000(0)	0.188(5)	-0.250(0)
H(20)	0.611(4)	0.190(5)	0.187(4)
H(21)	0.609(4)	0.074(5)	0.028(4)
H(22)	0.487(4)	0.112(5)	-0.121(5)
H(23)	0.343(5)	0.259(5)	-0.099(5)
H(24)	0.359(4)	0.382(4)	0.053(4)
H(25)	0.691(3)	0.395(4)	0.136(3)
H(26)	0.830(4)	0.525(5)	0.145(4)
H(27)	0.850(4)	0.692(5)	0.269(4)
H(28)	0.691(5)	0.710(6)	0.390(5)
H(29)	0.558(5)	0.585(5)	0.377(4)

Table 6.2
The anisotropic temperature factors for the atoms of I(b),
with estimated standard deviations in parentheses

Atom	u[1,1]	u[2,2]	u[3,3]	u[2,3]	u[1,3]	u[1,2]
C(1)	0.0975(51)	0.0718(46)	0.0698(43)	-0.0126(38)	0.0053(39)	0.0237(40)
C(2)	0.0792(38)	0.0455(31)	0.0528(33)	-0.0105(21)	-0.0199(29)	0.0058(27)
C(3)	0.0459(27)	0.0522(30)	0.0422(25)	0.0021(22)	-0.0096(20)	0.0016(22)
C(4)	0.0381(24)	0.0486(27)	0.0371(24)	0.0071(21)	-0.0087(19)	0.0028(21)
C(5)	0.0568(30)	0.0596(33)	0.0468(28)	0.0040(26)	-0.0142(24)	0.0062(27)
C(6)	0.0361(23)	0.0435(25)	0.0367(23)	0.0055(20)	-0.0018(18)	0.0030(20)
C(7)	0.0600(32)	0.0451(29)	0.0547(31)	0.0018(25)	-0.0086(25)	0.0109(26)
C(8)	0.0351(22)	0.0399(25)	0.0308(22)	0.0031(18)	-0.0038(17)	0.0016(19)
C(9)	0.0408(24)	0.0417(25)	0.0349(22)	-0.0001(20)	-0.0030(18)	-0.0013(20)
C(10)	0.0402(23)	0.00396(26)	0.0360(23)	0.0005(20)	-0.0025(18)	-0.0002(20)
C(11)	0.0404(33)	0.0435(38)	0.0325(31)	0.0000(0)	-0.0045(25)	0.0000(0)
C(22)	0.0420(24)	0.00433(26)	0.0419(26)	-0.0010(21)	-0.0037(20)	0.0003(21)
C(23)	0.0475(29)	0.0515(31)	0.0633(33)	-0.0130(26)	-0.0149(25)	0.0108(24)
C(24)	0.0584(35)	0.0567(35)	0.0789(40)	-0.0233(30)	-0.0067(29)	0.0068(29)
C(25)	0.0734(38)	0.0696(39)	0.0541(34)	-0.0166(30)	-0.0029(28)	-0.0093(31)
C(26)	0.0730(38)	0.0787(42)	0.0455(30)	-0.0017(29)	-0.0173(27)	0.0009(33)
C(27)	0.0501(29)	0.0589(33)	0.0495(29)	0.0033(25)	-0.0084(23)	0.0131(26)
C(28)	0.0401(25)	0.0449(28)	0.0526(30)	0.00030(23)	0.0029(22)	-0.0018(21)
C(29)	0.0459(27)	0.0531(32)	0.0553(31)	0.0121(26)	0.0029(23)	0.0038(24)
C(30)	0.0608(37)	0.0635(40)	0.1003(52)	0.0231(37)	-0.0110(34)	-0.0247(33)
C(32)	0.0834(47)	0.0637(42)	0.1024(53)	-0.0134(40)	0.0190(33)	-0.0206(30)
C(33)	0.0623(38)	0.0583(35)	0.0842(43)	-0.0149(32)	0.0190(33)	-0.0206(30)
N(1)	0.05009(23)	0.0409(22)	0.0359(20)	-0.0030(17)	-0.0142(17)	0.0223(32)
N(2)	0.0964(39)	0.0837(39)	0.0715(34)	0.0105(30)	-0.0363(29)	0.0223(32)
O(1)	0.0840(29)	0.0689(26)	0.0434(20)	-0.0087(19)	-0.0272(19)	0.0068(22)
O(2)	0.0778(25)	0.0405(19)	0.0385(18)	0.0045(16)	-0.0140(17)	0.0022(18)
P(1)	0.0368(8)	0.0385(9)	0.0457(9)	0.0000(0)	0.0005(7)	0.0000(0)

Table 6.3

Bond lengths (A), with estimated standard
deviations in parentheses for I(b)

C(1)-C(2)	1.499(9)
C(2)-N(1)	1.469(6)
C(3)-N(1)	1.389(5)
C(3)-O(1)	1.239(5)
C(3)-C(4)	1.441(6)
C(4)-C(5)	1.434(6)
C(4)-C(6)	1.383(6)
C(5)-N(2)	1.144(6)
C(6)-C(7)	1.508(7)
C(6)-C(8)	1.424(5)
C(8)-C(9)	1.456(6)
C(8)-C(10)	1.412(6)
C(9)-O(2)	1.236(5)
C(9)-N(1)	1.414(5)
C(10)-C(11)	1.393(5)
P(1)-C(22)	1.814(5)
C(1)-C(28)	1.773(5)
C(22)-C(23)	1.388(6)
C(22)-C(27)	1.406(6)
C(23)-C(24)	1.391(7)
C(24)-C(25)	1.397(7)
C(25)-C(26)	1.371(8)
C(26)-C(27)	1.383(7)
C(28)-C(29)	1.381(6)
C(29)-C(30)	1.409(7)
C(30)-C(31)	1.370(9)
C(31)-C(32)	1.382(9)
C(32)-C(33)	1.386(8)

TABLE 6.4

Bond Angles (°) for I(b)

C(1)-C(2)-N(1)	112.7(5)		C(22)-C(23)-C(24)	119.9(5)
C(2)-N(1)-C(3)	119.0(4)		C(22)-C(27)-C(26)	119.2(5)
C(2)-N(1)-C(9)	116.9(4)		C(23)-C(24)-C(25)	120.2(5)
C(3)-N(1)-C(9)	124.1(4)		C(23)-C(22)-C(27)	119.8(5)
N(1)-C(3)-C(4)	116.2(4)		C(24)-C(25)-C(26)	119.5(5)
N(1)-C(3)-O(1)	120.4(5)		C(25)-C(26)-C(27)	121.4(5)
C(4)-C(3)-O(1)	123.5(4)		C(28)-C(29)-C(30)	118.3(5)
C(3)-C(4)-C(6)	122.9(4)		C(28)-C(33)-C(32)	119.6(6)
C(3)-C(4)-C(5)	114.7(4)		C(29)-C(30)-C(31)	121.2(6)
C(5)-C(4)-C(6)	122.3(5)		C(29)-C(28)-C(33)	120.9(5)
C(4)-C(5)-N(2)	178.2(6)		C(30)-C(31)-C(32)	119.6(6)
C(4)-C(6)-C(8)	119.4(4)		C(31)-C(32)-C(33)	120.5(6)
C(4)-C(6)-C(7)	120.0(4)			
C(7)-C(6)-C(8)	120.6(4)			
C(6)-C(8)-C(9)	119.5(4)			
C(6)-C(8)-C(10)	120.3(4)			
C(9)-C(8)-C(10)	120.2(4)			
C(8)-C(9)-N(1)	117.3(4)			
C(8)-C(9)-O(2)	125.8(4)			
N(1)-C(9)-O(2)	116.9(4)			
C(8)-C(10)-C(11)	128.1(5)			
C(10)-C(11)-C(12)	119.2(6)			
C(22)-P(1)-C(28)	111.6(4)			
C(22)-P(1)-C(40)	104.2(4)			
C(28)-P(1)-C(34)	109.9(4)			
P(1)-C(22)-C(23)	119.5(4)			
P(1)-C(22)-C(27)	122.7(4)			
P(1)-C(28)-C(29)	121.9(5)			
P(1)-C(28)-C(33)	117.7(5)			

TABLE 6.4

Bond Angles ($^{\circ}$) for I(b)

C(1)-C(2)-N(1)	112.7(5)
C(2)-N(1)-C(3)	119.0(4)
C(2)-N(1)-C(9)	116.9(4)
C(3)-N(1)-C(9)	124.1(4)
N(1)-C(3)-C(4)	116.2(4)
N(1)-C(3)-O(1)	120.4(5)
C(4)-C(3)-O(1)	123.5(4)
C(3)-C(4)-C(6)	122.9(4)
C(3)-C(4)-C(5)	114.7(4)
C(5)-C(4)-C(6)	122.3(5)
C(4)-C(5)-N(2)	178.2(6)
C(4)-C(6)-C(8)	119.4(4)
C(4)-C(6)-C(7)	120.0(4)
C(7)-C(6)-C(8)	120.6(4)
C(6)-C(8)-C(9)	119.5(4)
C(6)-C(8)-C(10)	120.3(4)
C(9)-C(8)-C(10)	120.2(4)
C(8)-C(9)-N(1)	117.3(4)
C(8)-C(9)-O(2)	125.8(4)
N(1)-C(9)-O(2)	116.9(4)
C(8)-C(10)-C(11)	128.1(5)
C(10)-C(11)-C(12)	119.2(6)
C(22)-P(1)-C(28)	111.6(4)
C(22)-P(1)-C(40)	104.2(4)
C(28)-P(1)-C(34)	109.9(4)
P(1)-C(22)-C(23)	119.5(4)
P(1)-C(22)-C(27)	122.7(4)
P(1)-C(28)-C(29)	121.9(5)
P(1)-C(28)-C(33)	117.7(5)
C(22)-C(23)-C(24)	119.9(5)
C(22)-C(27)-C(26)	119.2(5)
C(23)-C(24)-C(25)	120.2(5)
C(23)-C(22)-C(27)	119.8(5)
C(24)-C(25)-C(26)	119.5(5)
C(25)-C(26)-C(27)	121.4(5)
C(28)-C(29)-C(30)	118.3(5)
C(28)-C(33)-C(32)	119.6(6)
C(29)-C(30)-C(31)	121.2(6)
C(29)-C(28)-C(33)	120.9(5)
C(30)-C(31)-C(32)	119.6(6)
C(31)-C(32)-C(33)	120.5(6)

6.1.3 The structure of tetrabutylammonium 1-ethyl-3-cyano-6-

hydroxy-4-methyl pyrid-2-one trimethine oxonol

(Ic), Figure 6.10.
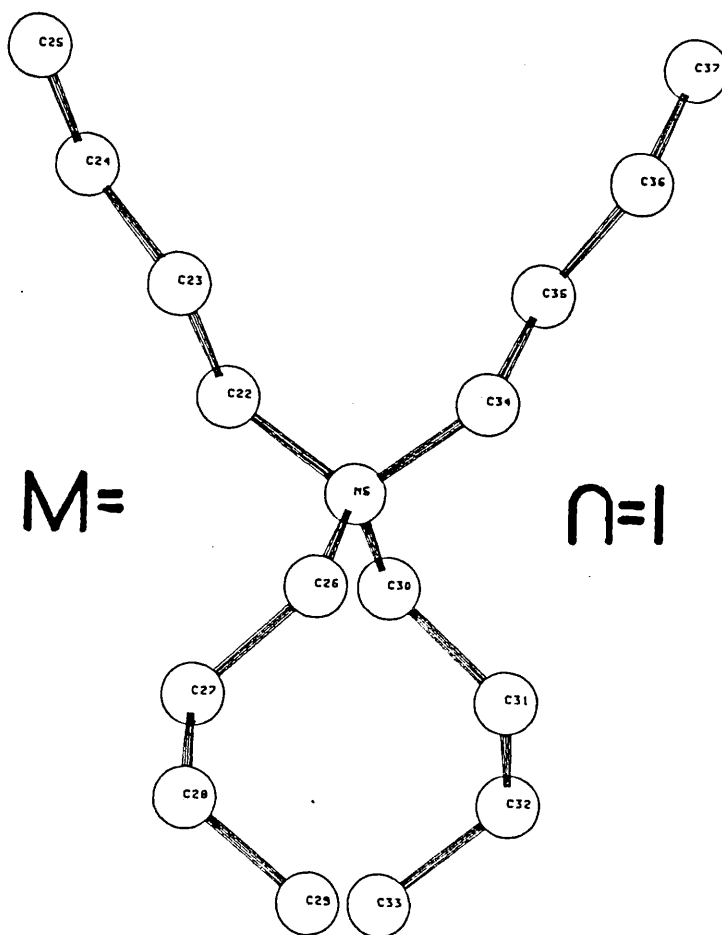
Figure 6.10

Here the anion is intermediate in planarity between Ia and Ib with an

angle of twist about the trimethine bridge of 25.62°. The arrangement

of the individual molecules within the stack is again different. We

observe a dimerisation of molecules within the stack reminiscent of the

class I type TCNQ radical anion salts. Two distinctly different

interplanar distances of 3.57 and 5.54 A are seen, Figure 6.11.
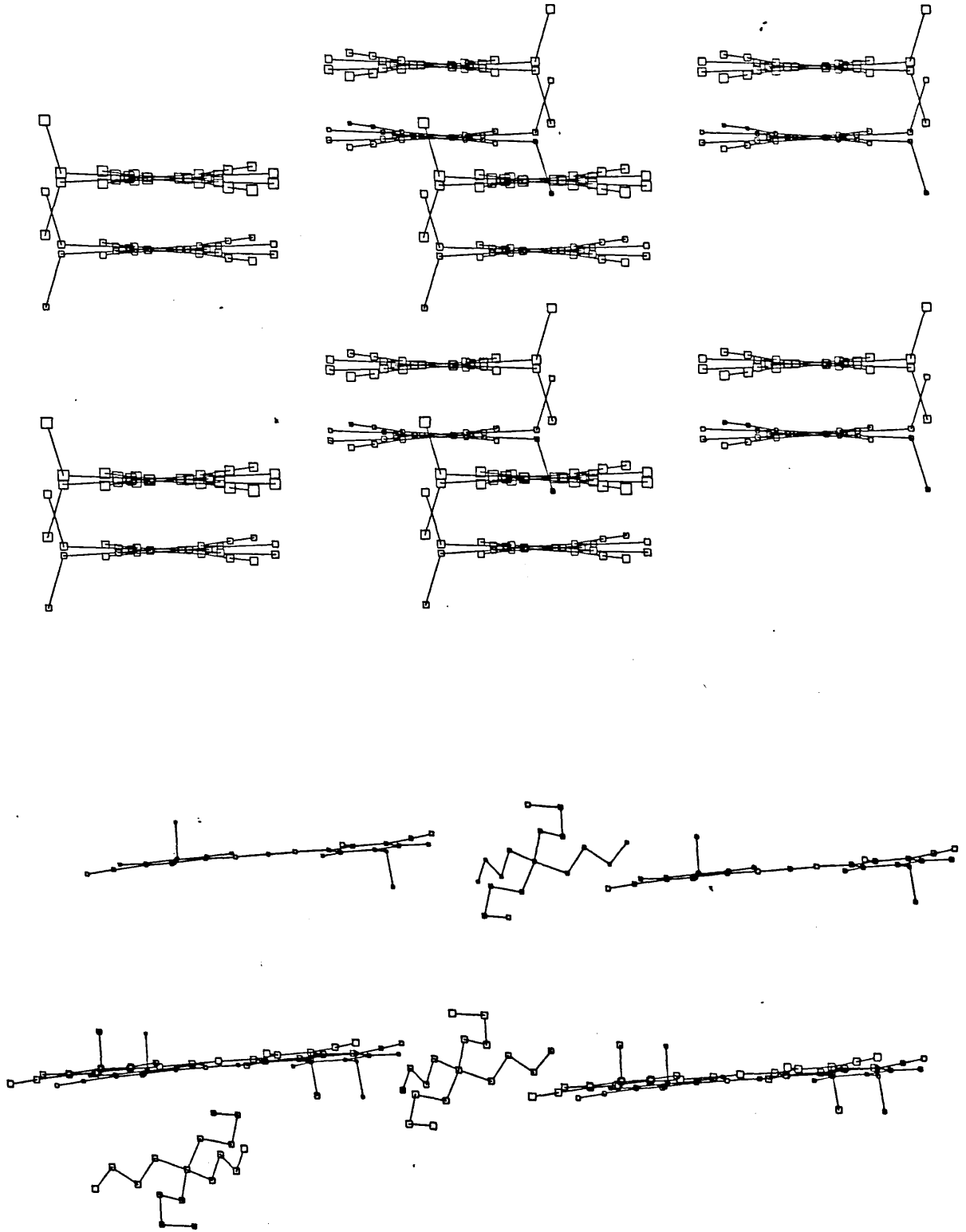
Figure 6.11

The fractional atomic coordinates, anisotropic temperature factors, bond lengths and bond angles are listed in Tables 6.5, 6.6, 6.7 and 6.8 respectively.

TABLE 6.5

Fractional atom co-ordinates for I(c), with estimated
standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	0.6109(9)	0.6684(6)	0.9669(3)
C(2)	0.7800(7)	0.6259(5)	0.9486(3)
C(3)	0.8084(6)	0.4078(5)	0.9896(2)
C(4)	0.8161(6)	0.2722(5)	0.9763(2)
C(5)	0.8440(6)	0.1928(5)	1.0299(3)
C(6)	0.8806(6)	0.2208(5)	0.9182(2)
C(7)	0.8068(8)	0.0775(5)	0.9104(3)
C(8)	0.7790(6)	0.3032(5)	0.8667(2)
C(9)	0.7699(6)	0.4413(5)	0.8771(2)
C(10)	0.7663(6)	0.2549(5)	0.8057(2)
C(11)	0.7500(0)	0.3190(7)	0.7500(0)
C(22)	0.7002(6)	0.5510(5)	0.3081(2)
C(23)	0.8248(8)	0.6484(6)	0.3250(3)
C(24)	0.7482(8)	0.7488(6)	0.3693(3)
C(25)	0.8536(10)	0.8502(7)	0.3864(4)
C(26)	0.8970(6)	0.3876(5)	0.2591(2)
C(27)	0.8731(8)	0.2897(6)	0.3118(3)
C(28)	1.0142(9)	0.1981(6)	0.3076(3)
C(29)	1.0192(9)	0.1082(7)	0.2531(4)
N(1)	0.7868(5)	0.4872(4)	0.9384(2)
N(2)	0.8683(8)	0.1341(5)	1.0728(2)
N(5)	0.7500(0)	0.4796(5)	0.2500(0)
O(1)	0.8178(5)	0.4541(4)	1.0419(2)
O(2)	0.7489(5)	0.5212(3)	0.8372(2)
H(1)	0.584(1)	0.635(1)	1.006(0)
H(2)	0.607(1)	0.763(1)	0.968(0)
H(3)	0.538(1)	0.636(1)	0.937(0)
H(4)	0.846(1)	0.647(1)	0.983(0)

H(5)	0.825(1)	0.669(1)	0.909(0)
H(6)	0.716(1)	0.049(1)	0.892(0)
H(7)	0.809(1)	0.038(1)	0.952(0)
H(8)	0.905(1)	0.053(1)	0.882(0)
H(9)	0.768(1)	0.160(1)	0.802(0)
H(10)	0.750(0)	0.414(1)	0.750(0)
H(20)	0.679(1)	0.493(1)	0.345(0)
H(21)	0.601(1)	0.598(1)	0.302(0)
H(22)	0.908(1)	0.605(1)	0.346(0)
H(23)	0.875(1)	0.688(1)	0.385(0)
H(24)	0.697(1)	0.707(1)	0.408(0)
H(25)	0.665(1)	0.792(1)	0.347(0)
H(26)	0.791(1)	0.912(1)	0.415(0)
H(27)	0.938(1)	0.811(1)	0.409(0)
H(28)	0.904(1)	0.896(1)	0.348(0)
H(29)	0.986(1)	0.445(1)	0.268(0)
H(30)	0.928(1)	0.341(1)	0.219(0)
H(31)	0.860(1)	0.335(1)	0.353(0)
H(32)	0.775(1)	0.240(1)	0.307(0)
H(33)	1.115(1)	0.248(1)	0.304(0)
H(34)	1.005(1)	0.147(1)	0.347(0)
H(35)	1.113(1)	0.050(1)	0.252(0)
H(36)	1.022(1)	0.154(1)	0.212(0)
H(37)	0.919(1)	0.058(1)	0.261(0)

Table 6.6

The anisotropic temperature factors for the atoms of I(ᴄ), with estimated standard deviations in parentheses.

Atom	u[1,1]	u[2,2]	u[3,3]	u[2,3]	u[1,3]	u[1,2]
C(1)	0.1179(60)	0.0767(45)	0.0947(49)	-0.0066(37)	-0.0366(42)	0.0093(40)
C(2)	0.0791(40)	0.0632(35)	0.0586(32)	-0.0036(26)	-0.0126(27)	0.0036(30)
C(3)	0.0538(32)	0.0655(33)	0.0511(29)	0.0054(25)	-0.0042(23)	0.0055(26)
C(4)	0.0540(32)	0.0566(32)	0.0536(30)	0.0087(23)	-0.0047(23)	0.0070(24)
C(5)	0.0700(41)	0.0808(32)	0.0605(30)	0.0140(31)	-0.0034(25)	0.0062(28)
C(6)	0.0511(32)	0.0525(30)	0.0598(32)	0.0070(24)	-0.0022(23)	0.0051(23)
C(7)	0.1005(48)	0.0634(36)	0.0681(36)	0.0084(28)	-0.0106(32)	0.0038(33)
C(8)	0.0505(30)	0.0514(28)	0.0471(27)	0.0025(22)	-0.0026(21)	0.0032(22)
C(9)	0.0629(34)	0.00558(31)	0.0461(26)	0.0055(24)	-0.0045(23)	0.0017(25)
C(10)	0.0538(30)	0.0515(28)	0.0575(29)	0.0027(25)	-0.0014(22)	0.0016(24)
C(11)	0.0576(46)	0.0527(41)	0.0530(40)	0.0000(0)	-0.0010(32)	0.0000(0)
C(22)	0.0630(32)	0.0522(32)	0.0603(28)	-0.0086(24)	0.0008(23)	0.0056(27)
C(23)	0.0774(42)	0.0810(41)	0.733(38)	-0.0197(31)	-0.0013(30)	-0.0111(33)
C(24)	0.1043(55)	0.0788(43)	0.0836(45)	-0.0193(36)	-0.0112(37)	-0.0019(38)
C(25)	0.1389(79)	0.0960(57)	0.1418(73)	-0.0272(53)	0.0122(58)	0.0039(53)
C(26)	0.0526(31)	0.0581(31)	0.0624(32)	-0.0023(24)	-0.0096(23)	0.0071(25)
C(27)	0.0868(45)	0.0749(38)	0.0618(34)	-0.0002(29)	-0.0176(29)	0.0154(33)
C(28)	0.0879(51)	0.0825(44)	0.1055(52)	-0.0008(40)	-0.0259(38)	0.0199(37)

Table 6.6. (continued)

C(29)	0.1221(64)	0.0916(54)	0.1268(64)	−0.0133(48)	0.0375(48)
N(1)	0.0660(28)	0.0543(26)	0.0498(24)	0.0003(19)	0.0047(21)
N(2)	0.1352(52)	0.0828(37)	0.0714(33)	0.0211(28)	0.0185(35)
N(5)	0.0488(34)	0.0562(33)	0.0463(30)	0.0000(0)	0.0000(0)
O(1)	0.0948(30)	0.0789(27)	0.0495(21)	−0.0050(19)	0.0056(22)
O(2)	0.1262(36)	0.0514(22)	0.0548(22)	0.0022(18)	0.0113(22)

| −0.0267(49) |
| −0.0065(20) |
| −0.0144(31) |
| −0.0034(24) |
| −0.0140(18) |
| −0.0148(21) |

TABLE 6.7

Bond lengths (A), with estimated standard deviations

in parentheses for I(c)

C(1)-C(2)	1.493(8)
C(2)-C(1)	1.466(6)
C(3)-N(1)	1.398(6)
C(3)-O(1)	1.224(6)
C(3)-C(4)	1.444(7)
C(4)-C(5)	1.432(5)
C(4)-C(6)	1.368(7)
C(5)-N(2)	1.155(5)
C(6)-C(7)	1.507(7)
C(6)-C(8)	1.423(6)
C(8)-C(9)	1.460(7)
C(8)-C(10)	1.405(6)
C(9)-O(2)	1.219(5)
C(9)-N(1)	1.408(6)
C(10)-C(11)	1.382(6)
C(22)-N(5)	1.518(5)
C(26)-N(5)	1.533(6)
C(22)-C(23)	1.531(8)
C(23)-C(24)	1.504(8)
C(24)-C(25)	1.454(9)
C(26)-C(27)	1.514(7)
C(27)-C(28)	1.517(8)
C(28)-C(29)	1.489(9)

TABLE 6.8

Bond Angles ($^{\circ}$) for I(c)

C(1)-C(2)-N(1)	110.7(5)
C(2)-N(1)-C(3)	118.5(4)
C(2)-N(1)-C(9)	117.9(4)
C(3)-N(1)-C(9)	123.6(4)
N(1)-C(3)-C(4)	115.9(4)
N(1)-C(3)-O(1)	120.1(5)
C(4)-C(3)-O(1)	123.9(5)
C(3)-C(4)-C(6)	123.7(4)
C(3)-C(4)-C(5)	114.3(4)
C(5)-C(4)-C(6)	122.1(4)
C(4)-C(5)-N(2)	178.3(4)
C(4)-C(6)-C(8)	119.6(5)
C(4)-C(6)-C(7)	119.3(5)
C(7)-C(6)-C(8)	121.1(5)
C(6)-C(8)-C(9)	119.2(4)
C(6)-C(8)-C(10)	121.5(5)
C(9)-C(8)-C(10)	119.3(4)
C(8)-C(9)-N(1)	118.0(4)
C(8)-C(9)-O(2)	125.3(5)
N(1)-C(9)-O(2)	116.7(4)
C(8)-C(10)-C(11)	129.9(5)
C(10)-C(11)-C(12)	121.9(7)
C(22)-N(5)-C(26)	111.1(3)
C(22)-N(5)-C(34)	105.4(3)
N(5)-C(22)-C(23)	115.5(4)
N(5)-C(26)-C(27)	115.5(4)
C(22)-C(23)-C(24)	110.8(5)
C(23)-C(24)-C(25)	115.9(6)
C(26)-C(27)-C(28)	110.3(5)
C(27)-C(28)-C(29)	113.3(6)

6.1.4 The structure of dimethylammonium ethyl methacrylate

1-Ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one trimethine

oxonol

(Id), Figure 6.12
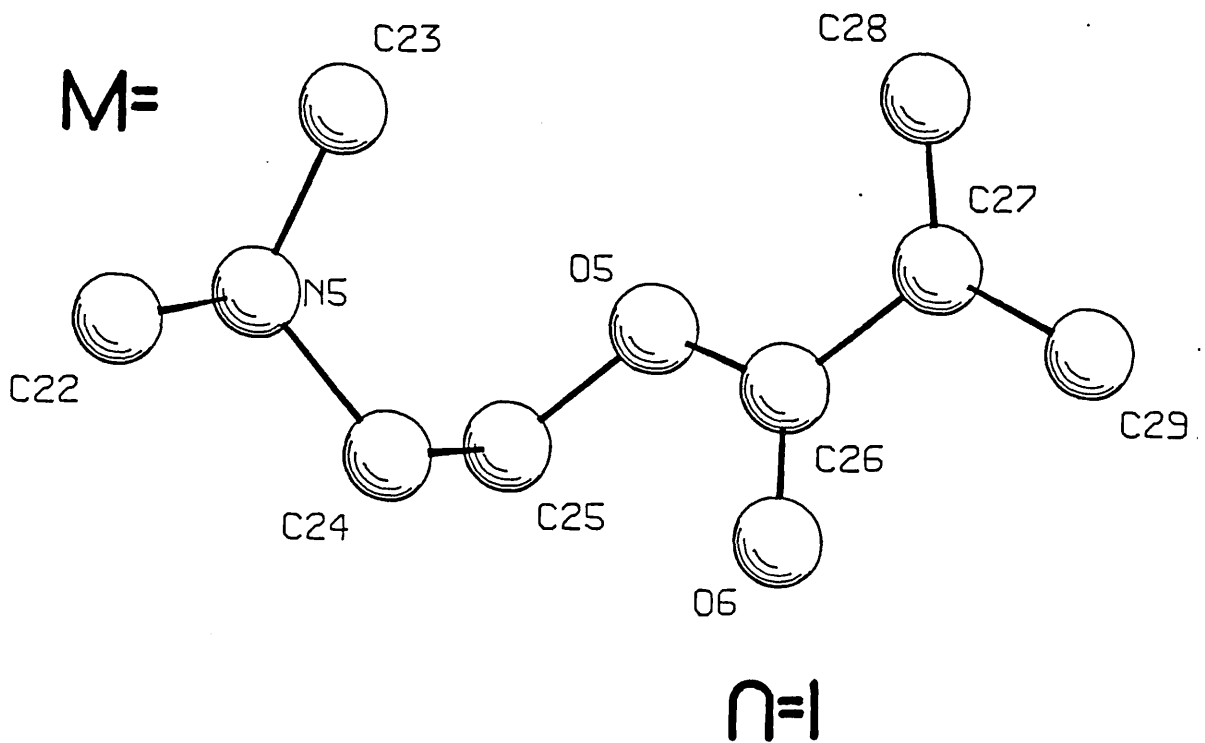
Figure 6.12

This structure is very similar to that of Ia. The anions are very

nearly planar (angle of twist about the methine bridge = 14°) and stack

in a herringbone type fashion, Figure 6.13. It also seems likely

that the ionic interaction between anion and cation is supplemented by

hydrogen bonding between the external hydroxypyridone ring oxygen atom and

the nitrogen of the cation (N5-O1 = 2.74 A; O1-H35 = 1.91 A; N5-H35 = 0.99 A).
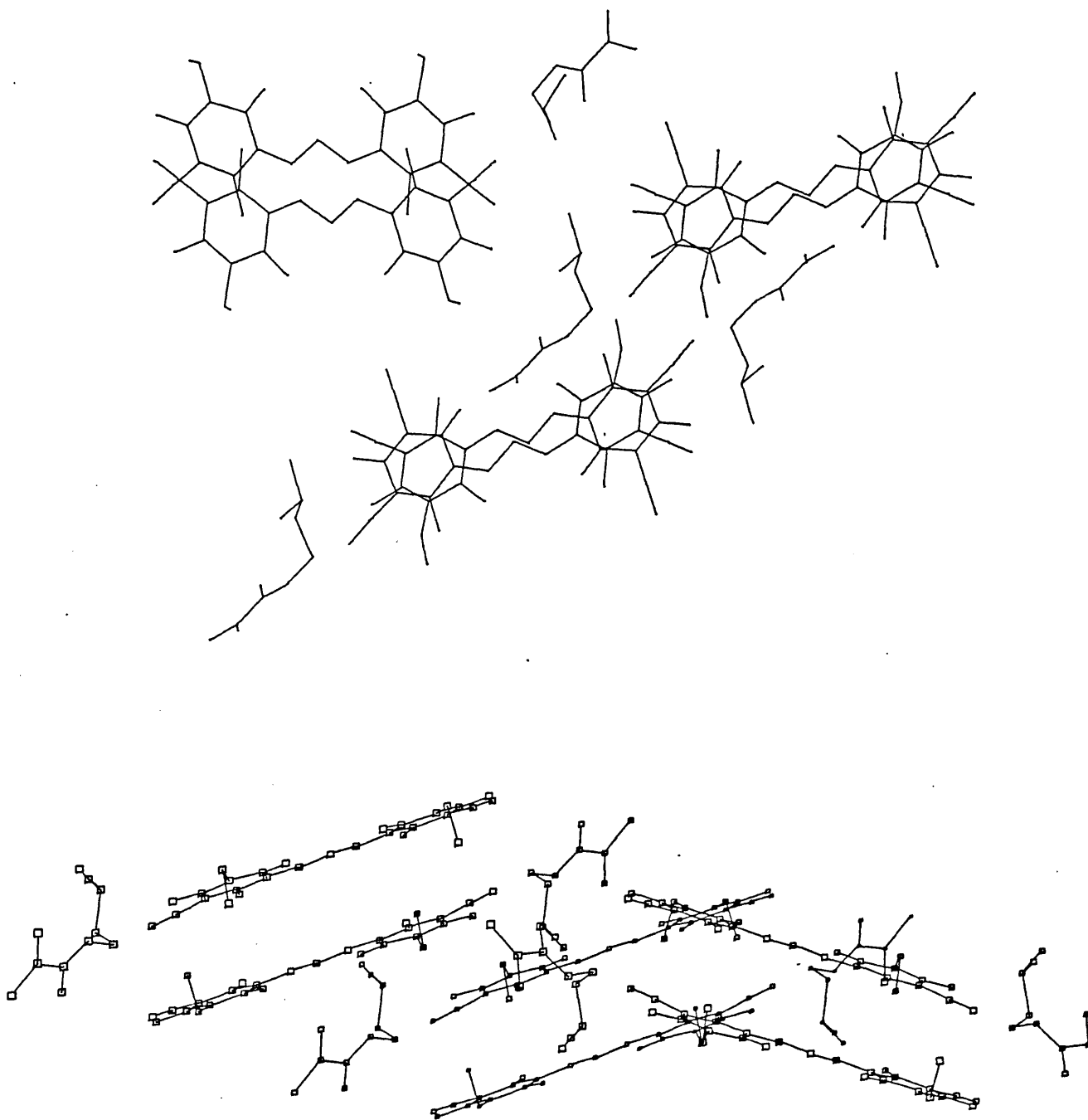
Figure 6.13

The interplanar distance, however, has increased to 4.53 A. The closest approach of the vinyl groups of the cation is 12.83 A.

One unique feature of this structure is that the terminal carbon atoms of the two N-ethyl substituents of the hydroxypyridone rings both point in the same direction.

The fractional atomic coordinates, anisotropic temperature factors, bond lengths and bond angles are listed in Tables 6.9, 6.10, 6.11 and 6.12 respectively.

TABLE 6.9

Fractional atom coordinates for 1(d), with estimated

standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	0.6909(5)	0.0387(21)	0.4699(6)
C(2)	0.6818(4)	0.1980(20)	0.4939(5)
C(3)	0.6615(3)	0.0872(14)	0.5791(5)
C(4)	0.6297(3)	0.0627(12)	0.6107(4)
C(5)	0.6455(4)	0.0120(14)	0.6629(5)
C(6)	0.5865(3)	0.1035(12)	0.5929(4)
C(7)	0.5556(3)	-0.0795(14)	0.6311(4)
C(8)	0.5724(3)	0.1652(11)	0.5398(4)
C(9)	0.6033(3)	0.1860(13)	0.5057(5)
C(10)	0.5276(3)	0.2068(12)	0.5215(5)
C(11)	0.5078(3)	0.2675(12)	0.4715(5)
C(12)	0.4622(3)	0.3050(13)	0.4668(5)
C(13)	0.4342(3)	0.3668(12)	0.4211(4)
C(14)	0.3893(3)	0.3931(12)	0.4243(5)
C(15)	0.3718(3)	0.3556(13)	0.4735(4)
C(16)	0.3617(3)	0.4549(13)	0.3786(5)
C(17)	0.3160(3)	0.4902(13)	0.3775(5)
C(18)	0.3754(3)	0.4913(13)	0.3293(5)
C(19)	0.4342(4)	0.4932(15)	0.2774(5)
C(20)	0.4371(4)	0.3188(17)	0.2479(5)
C(21)	0.4490(4)	0.4024(14)	0.3720(5)
C(22)	0.7561(3)	0.1676(14)	0.7217(4)
C(23)	0.8112(3)	0.2169(14)	0.6670(5)
C(24)	0.7792(3)	-0.0884(14)	0.6737(4)
C(25)	0.7900(3)	-0.1550(15)	0.6218(5)
C(26)	0.8624(3)	-0.2684(15)	0.6426(5)
C(27)	0.9089(4)	-0.2446(20)	0.6394(6)
H(21)	0.9276(4)	-0.5105(18)	0.6431(7)

H(22)	0.7085(4)	0.2419(20)	0.5174(5)
H(23)	0.6710(4)	0.2908(20)	0.4669(5)
H(24)	0.4635(4)	0.5477(15)	0.2857(5)
H(25)	0.4142(4)	0.5759(15)	0.2543(5)
H(26)	0.8046(3)	-0.1165(14)	0.7018(4)
H(27)	0.7532(3)	-0.1506(14)	0.6819(4)
H(28)	0.7810(3)	-0.2819(15)	0.6153(5)
H(29)	0.7728(3)	-0.0777(15)	0.5941(5)
H(30)	0.9532(4)	-0.0788(18)	0.6201(5)
H(31)	0.9004(4)	-0.0069(18)	0.6050(5)
H(32)	0.5079(3)	0.1959(12)	0.5476(5)
H(33)	0.5232(3)	0.2820(12)	0.4412(5)
H(34)	0.4502(3)	0.2859(13)	0.4997(5)
H(35)	0.7510(2)	0.1463(10)	0.6399(4)

Table 6.10

The anisotropic temperature factors for the atoms of I(d),
with estimated standard deviations in parentheses

Atom	u[1,1]	u[2,2]	u[3,3]	u[2,3]	u[1,3]	u[1,2]
C(1)	0.1176(146)	0.1381(168)	0.1438(189)	0.0166(139)	0.0309(140)	-0.0368(119)
C(2)	0.0970(114)	0.1532(160)	0.0835(140)	-0.0282(117)	-0.0009(72)	-0.0000(118)
C(3)	0.0500(72)	0.0514(77)	0.0415(96)	-0.0013(68)	-0.0009(72)	-0.0118(61)
C(4)	0.0446(62)	0.0310(66)	0.0425(80)	0.0085(58)	0.0162(60)	0.0018(50)
C(5)	0.0565(72)	0.0476(77)	0.0439(80)	-0.0063(65)	-0.0092(64)	0.0114(64)
C(6)	0.0386(58)	0.0251(62)	0.0526(82)	0.0009(55)	0.0031(61)	0.0068(49)
C(7)	0.0554(67)	0.0528(76)	0.0503(90)	0.0066(66)	-0.0076(68)	0.0081(59)
C(8)	0.0477(63)	0.0248(65)	0.0378(85)	0.0021(57)	-0.0057(61)	-0.0028(51)
C(9)	0.0520(69)	0.0366(69)	0.0533(106)	0.0058(64)	-0.0034(69)	-0.0105(55)
C(10)	0.0423(65)	0.0307(66)	0.0615(94)	-0.0160(60)	-0.0138(63)	-0.0036(54)
C(11)	0.0482(72)	0.0318(69)	0.0687(101)	0.0055(60)	-0.0071(66)	-0.0043(54)
C(12)	0.0541(73)	0.0308(70)	0.0609(102)	-0.0035(63)	-0.0126(73)	0.0032(58)
C(13)	0.0453(68)	0.0246(66)	0.0488(88)	-0.0042(59)	-0.0107(62)	-0.0046(49)
C(14)	0.0507(66)	0.0240(63)	0.0534(103)	-0.0009(61)	-0.0114(65)	0.0026(53)
C(15)	0.0526(66)	0.0444(80)	0.0665(108)	-0.0051(69)	0.0040(73)	0.0147(60)
C(16)	0.0424(65)	0.0351(73)	0.0625(102)	-0.0107(67)	-0.0221(67)	-0.0096(55)
C(17)	0.0524(69)	0.0342(70)	0.0794(101)	-0.0040(67)	-0.0171(71)	-0.0018(57)

Table 6.10 continued

C(18)	0.0482(70)	0.0368(70)	0.0588(89)	0.0049(63)	-0.0046(72)	-0.0074(55)
C(19)	0.0804(96)	0.0734(94)	0.0576(92)	0.0203(80)	0.0100(84)	-0.0011(78)
C(20)	0.0909(107)	0.1047(120)	0.0845(127)	-0.0051(97)	0.0184(98)	-0.0064(91)
C(21)	0.0567(78)	0.0452(77)	0.0704(101)	0.0122(70)	-0.0052(82)	-0.0056(66)
C(22)	0.0670(74)	0.0491(80)	0.0562(107)	-0.0066(70)	-0.0052(71)	0.0078(61)
C(23)	0.0496(0)	0.0438(0)	0.1196(0)	0.0092(0)	-0.0010(0)	-0.0240(0)
C(24)	0.0464(63)	0.0551(83)	0.0502(66)	-0.0059(66)	-0.0003(65)	-0.0019(61)
C(25)	0.0405(67)	0.0638(87)	0.0874(109)	-0.0139(75)	0.0018(69)	-0.0031(57)
C(26)	0.0553(76)	0.0477(77)	0.0838(114)	-0.0121(73)	0.0122(77)	-0.0085(59)
C(27)	0.0403(0)	0.1191(0)	0.0980(0)	-0.0191(0)	-0.0017(0)	0.0020(0)
C(28)	0.1017(0)	0.1146(0)	0.0804(0)	0.00142(0)	0.0266(0)	-0.0598(0)
C(29)	0.0827(0)	0.1026(0)	0.2066(0)	0.0414(0)	0.0045(0)	0.0341(0)
N(1)	0.0479(61)	0.0719(75)	0.0445(82)	0.0009(58)	0.0092(68)	0.0075(51)
N(2)	0.0698(68)	0.0654(74)	0.0710(82)	0.0132(66)	-0.0140(63)	0.0029(56)
N(3)	0.0526(62)	0.0689(73)	0.1292(123)	0.0022(72)	-0.0045(72)	-0.0005(56)
N(4)	0.0607(64)	0.0459(64)	0.0641(80)	0.0114(56)	-0.0062(63)	-0.0123(49)
N(5)	0.0515(55)	0.0414(59)	0.0545(77)	-0.0020(51)	-0.0123(55)	0.0113(45)
O(1)	0.0399(43)	0.0591(53)	0.0836(71)	-0.0045(48)	-0.0147(49)	0.0085(38)
O(2)	0.0614(57)	0.0994(70)	0.0508(69)	0.0257(54)	-0.0052(57)	-0.0087(50)
O(3)	0.0397(47)	0.1159(73)	0.0903(83)	0.0375(63)	-0.0062(54)	-0.0030(48)
O(4)	0.0660(50)	0.0605(73)	0.0769(73)	0.0101(48)	-0.0440(52)	0.0088(41)
O(5)	0.0521(48)	0.0526(55)	0.1033(83)	0.0002(51)	0.0184(52)	0.0018(40)
O(6)	0.0834(0)	0.0684(0)	0.1798(0)	0.0251(0)	0.0363(0)	0.0037(0)

Table 6.11

Bond lengths (A), with estimated standard deviations
in parentheses, for 1(d)

C(1) - C(2)	1.387(17)
C(2) - N(1)	1.532(14)
C(3) - N(1)	1.389(12)
C(3) - O(1)	1.268(11)
C(3) - C(4)	1.403(13)
C(4) - C(5)	1.443(13)
C(4) - C(6)	1.378(12)
C(5) - N(2)	1.148(13)
C(6) - C(7)	1.505(12)
C(6) - C(8)	1.420(12)
C(8) - C(9)	1.427(13)
C(8) - C(10)	1.426(12)
C(9) - O(2)	1.235(12)
C(9) - N(1)	1.421(11)
C(10) - C(11)	1.387(13)
C(11) - C(12)	1.435(13)
C(12) - C(13)	1.401(12)
C(13) - C(14)	1.438(13)
C(13) - C(21)	1.436(13)
C(14) - C(15)	1.484(12)
C(14) - C(16)	1.393(12)
C(16) - C(17)	1.452(13)
C(16) - C(18)	1.428(13)
C(17) - N(3)	1.147(12)
C(18) - O(4)	1.256(11)
C(18) - N(4)	1.377(12)
C(19) - N(4)	1.465(12)
C(19) - C(20)	1.510(15)
C(21) - N(4)	1.418(12)
C(21) - O(3)	1.222(12)
C(22) - N(5)	1.495(11)
C(23) - N(5)	1.478(11)

Table 6.11 continued

C(23) – N(5)	1.478(11)
C(24) – N(5)	1.510(12)
C(24) – C(25)	1.509(13)
C(25) – O(5)	1.451(10)
C(26) – O(5)	1.357(12)
C(26) – O(6)	1.227(12)
C(26) – C(27)	1.484(14)
C(27) – C(28)	1.287(16)
C(27) – C(29)	1.489(16)

Table 6.12

Bond Angles ($^{\circ}$) for 1(d), with estimated

standard deviations in parentheses

C(1) - C(2) - N(1)	
C(2) - N(1) - C(3)	118.6(9)
C(2) - N(1) - C(9)	118.0(1.0)
C(3) - N(1) - C(9)	123.1(9)
N(1) - C(3) - C(4)	117.2(9)
N(1) - C(3) - O(1)	117.8(1.0)
C(4) - C(3) - O(1)	125.0(1.1)
C(3) - C(4) - C(6)	122.7(1.0)
C(3) - C(4) - C(5)	114.9(9)
C(5) - C(4) - C(6)	122.5(1.0)
C(4) - C(5) - N(2)	177.9(1.3)
C(4) - C(6) - C(8)	120.0(9)
C(4) - C(6) - C(7)	118.1(1.0)
C(7) - C(6) - C(8)	122.0(8)
C(6) - C(8) - C(9)	119.3(9)
C(6) - C(8) - C(10)	119.8(1.0)
C(9) - C(8) - C(10)	120.9(1.0)
C(8) - C(9) - N(1)	117.7(1.0)
N(1) - C(9) - O(2)	116.2(1.0)
C(8) - C(9) - O(2)	126.0(1.0)
C(8) - C(10) - C(11)	128.1(1.1)
C(10) - C(11) - C(12)	114.2(1.1)
C(11) - C(12) - C(13)	126.3(1.1)
C(12) - C(13) - C(14)	117.8(1.1)
C(12) - C(13) - C(21)	122.1(1.0)
C(14) - C(13) - C(21)	120.1(1.1)
C(13) - C(14) - C(15)	122.6(1.1)
C(13) - C(14) - C(16)	117.3(1.1)
C(15) - C(14) - C(16)	120.0(9)
C(14) - C(16) - C(17)	122.1(1.1)
C(14) - C(16) - C(18)	124.0(9)

Table 6.12 continued

C(17) - C(16) - C(18)	113.8(1.1)
C(16) - C(17) - N(3)	179.0(1.2)
C(16) - C(18) - O(4)	122.5(1.0)
C(16) - C(18) - N(4)	117.3(1.0)
N(4) - C(18) - O(4)	120.3(1.1)
C(18) - N(4) - C(21)	122.6(1.0)
C(18) - N(4) - C(19)	119.8(1.1)
C(19) - N(4) - C(21)	117.6(1.0)
N(4) - C(19) - C(20)	111.8(9)
C(13) - C(21) - N(4)	118.8(1.0)
C(13) - C(21) - O(3)	125.4(1.2)
N(4) - C(21) - O(3)	115.8(1.1)
C(22) - N(5) - C(23)	110.1(9)
C(22) - N(5) - C(24)	108.8(8)
C(23) - N(5) - C(24)	113.6(8)
N(5) - C(24) - C(25)	111.1(9)
C(24) - C(25) - O(5)	114.1(9)
C(25) - O(5) - C(26)	116.3(8)
O(5) - C(26) - O(6)	121.4(1.0)
O(5) - C(26) - C(27)	115.0(1.1)
O(6) - C(26) - C(27)	123.6(1.2)
C(26) - C(27) - C(28)	120.3(1.3)
C(26) - C(27) - C(29)	114.6 (1.3)
C(28) - C(27) - C(29)	125.1(1.2)

6.1.5 Other Investigations

Attempts were made to investigate the structures of two other dyes. Crystals of HPT297 (I(e), M = Ph_3MeP^+) proved to be too small for satisfactory data collection, and our efforts to obtain better specimens of this key material were unsuccessful (10.4.1.6). The N-methyl morpholinium salt (HPT308) produced two crystal habits (dark blue needles and metallic green cubes). Preliminary photographs of the cuboid form revealed that the structure was disordered at room temperature. Time did not permit a low temperature data collection to be carried out. The needles were of much poorer quality, many being twinned and have not yet been further investigated.

6.1.6 The three solid-state structures fully determined provided an example of each of the cyanine dye structural classes and a second example of the herringbone structure first observed for MI1579 (Ia).

6.2   Solid State NMR Spectroscopic Studies [75,76,77]

6.2.1 Our aim was to investigate how structural features observed from the X-ray crystal structure might influence the materials solid state ^{13}C n.m.r. spectrum. In the longer term, we hoped to use solid state n.m.r. as a routine analytical tool to predict potentially interesting structures. These investigations were primarily concerned with how the ^{13}C solid state n.m.r. spectrum of the anion was influenced by the changing structural features induced by variation of the cation.

6.2.2 The Spectra

Figure 6.14 shows the ^{13}C solid state spectra of 1(a), (b), (c) and (d) compared to the solution (d^6-DMSO) ^{13}C spectrum of 1(a). The assignment of the solution spectrum is listed in Table 6.13, the carbon atom numbering being consistent with Figure 6.4.

Table 6.13

δ(d^6-DMSO, ppm)	Assignment
8.52	C(23), C(25), C(27)
13.01	C(1), C(20)
18.47	C(7), C(15)
33.82	C(2), C(19)
45.91	C(22), C(24), C(26)
92.15	C(6), C(14)
110.42	C(8), C(13)
117.64	C(5), C(17)
120.89	C(11)
157.05	C(10), C(12)
158.03	C(4), C(16)
161.41	C(3), C(9)
161.86	C(18), C(21)

Common to all of the solid state spectra is the broadening/ splitting of any peak when the corresponding carbon atom bears a nitrogen atom. Nitrogen being a quadrupolar nucleus, one would expect to observe doublets for these carbon atom peaks, presumably as a result of the poorer resolution of the 200 MHz machine we only see a broadening.

The spectrum of most interest in figure 6.14 is clearly that of 1(a) where splitting of the peaks corresponding to C(1), C(20); C(6), C(14) and C(8), C(13) is seen. A number of possible explanations might enable us to account for this apparent disymmetry about the two halves of the anion molecule.
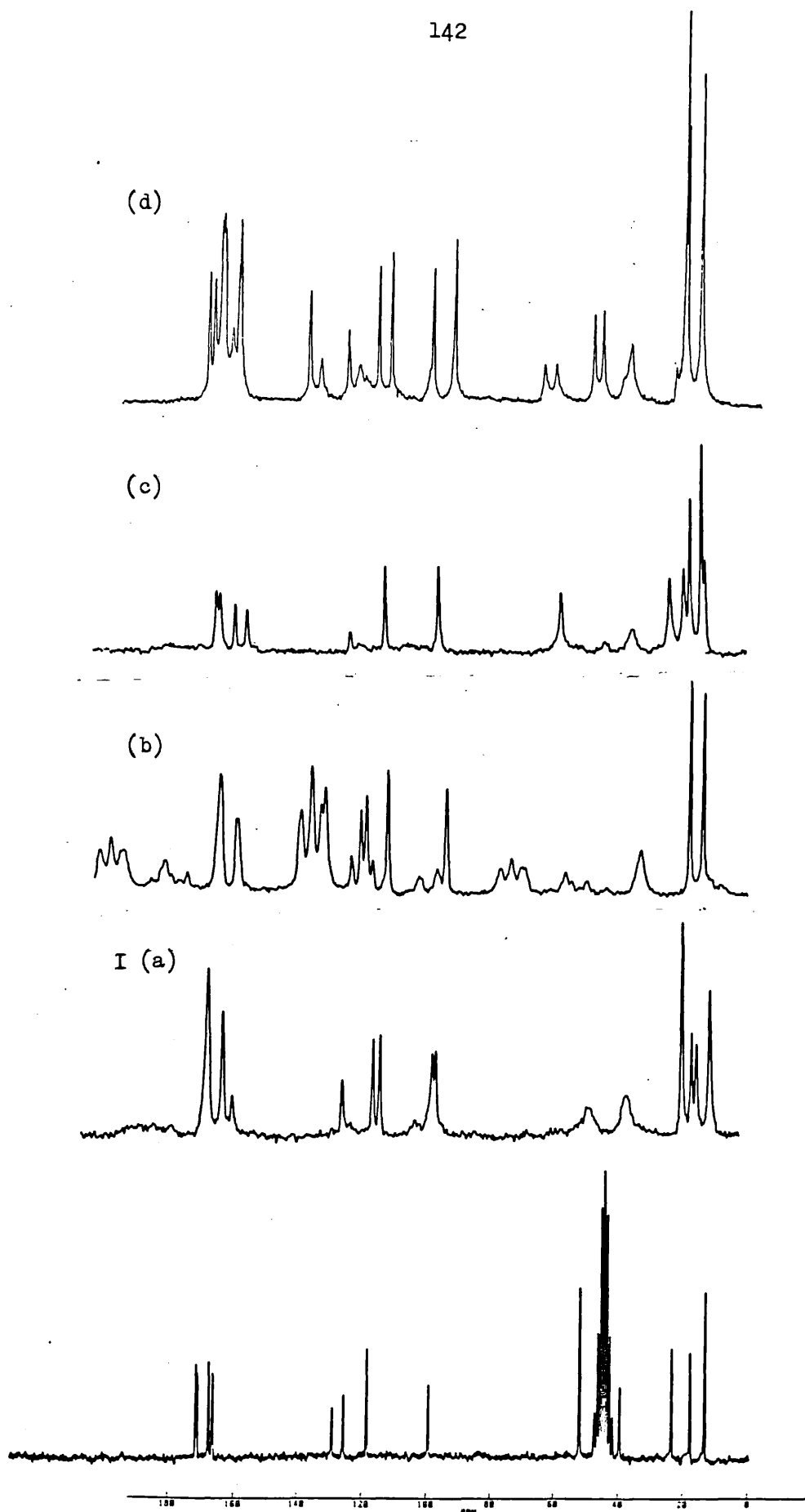
Figure 6.14

For example, it might be:

(i)   the distortion about the methine bridge,

(ii)   the hydrogen bonded cation on one side, or even

(iii) an intermolecular interaction between adjacent molecules
       within the stack.

But however:

(1) The material with the largest angle of twist about the methine
bridge, 1(b), shows no splitting,

(2) Similar splitting is observed for (HPT 297, I(e)), figure 6.15,
where a hydrogen bond between anion and cation is not a possibility.
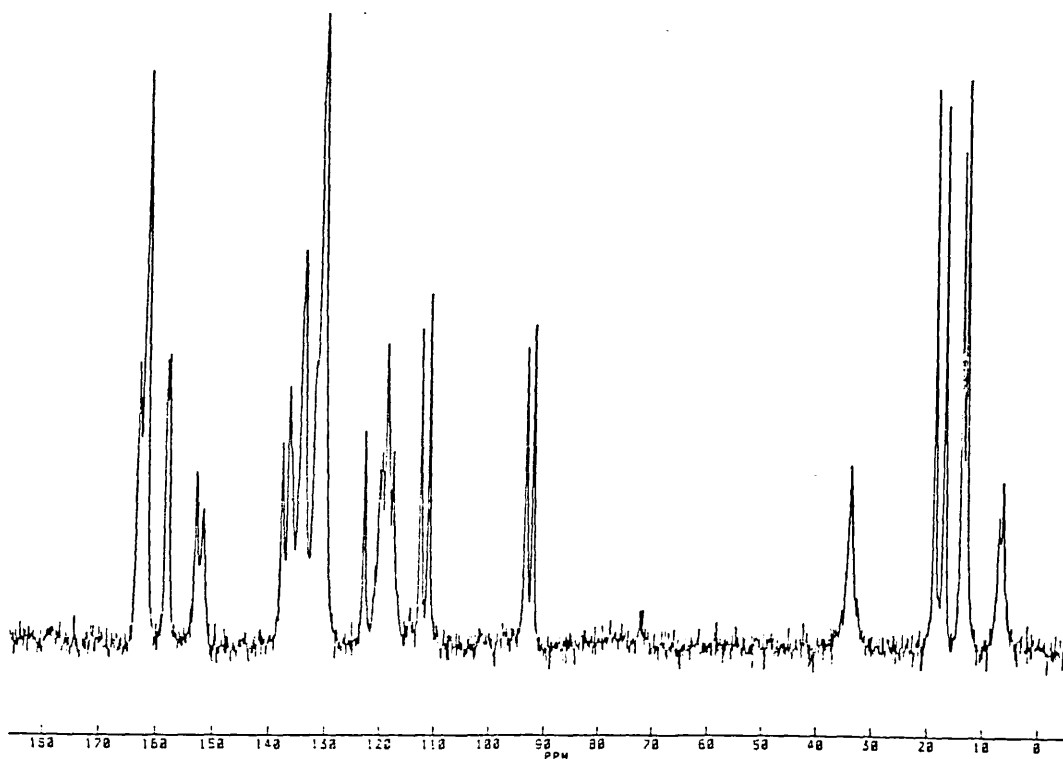
Figure 6.15

HPT 297 is of particular interest as not only does the replacement of a phenyl ring (Ib) for a methyl group in this phosphonium cation introduce this characteristic splitting but also a 3-4 order of magnitude increase in d.c. conductivity.

(3) Materials I(a) - I(d) have the interplanar distances significantly larger than van der Waals spacing (3.4 $\overset{\circ}{A}$). Were the interplanar distance < 3.4 $\overset{\circ}{A}$ one might realistically expect the possibility of shielding/deshielding effects between adjacent molecules within a stack.

Why the ^{13}C solid state n.m.r. spectra of I(a) and I(e) show this characteristic splitting is not clear. Obviously a more extensive range of materials has to be investigated. The crystal structure of I(e) alone would be highly enlightening.

CHAPTER 7

Electrochemical Investigations : The Design of a

Radical Cation-Dye Complex

7.1[78] It is well known that radical-ion salts may be prepared

electrochemically by inducing either the reduction or oxidation of the

parent species. The method involves the electrolysis of a solution of the

donor or acceptor in the presence of a source of the adductant, resulting

in the electrocrystallisation of the desired adduct on one of the

electrodes. Usually either the current or the potential is kept constant

during electrolysis; these are termed galvanostatic and potentiostatic

electrolyses, respectively. The electrocrystallisation may be anodic

(donors) or cathodic (acceptors). For the anodic method, the donor may be

an organic compound, such as a thio donor, for example, tetra-

thiafulvalene, TTF, or its selenium analogue. The donor may be a metal

from a sacrificial metal anode, on which the adduct grows, as in the case

of TTF $(AgNO_3)_{0.67}$. Examples of the adductant in the anodic method

are anions of tetracyanoquinodimethane, (TCNQ), thiocyanate, (SCN^-),

azide (N_3^-), acetate (AcO^-), and halides $(Cl^-, Br^-$ or $I^-)$;

their sources being the corresponding salts or acids. For the cathodic

method, the acceptor may be, for example, TCNQ. Adductant cations,

include copper (Cu^{2+}), silver (Ag^+), or chromium (Cr^{3+}), their

sources again being salts.

This method is known to yield products reported to be unobtainable

by chemical means such as $TTF(N_3)_{0.74}$ and is preferably performed

under an oxygen-free atmosphere. The electrocrystallisation potential can

initially be determined voltammetrically. That giving the highest current

is selected for the start of the galvanostatic preparation and the current

is maintained at its highest value by an adjacent galvanostat.

Our intention, was then, to carry out an anodic electro-crystallisation using TTF as a donor with an oxonol dye salt adductant. Before this could be achieved the electrochemistry of both TTF and a range of oxonol dye salts had to be investigated by cyclic voltammetry[79,80,81].

7.2. The Electrochemistry of Tetrathiafulvalene, TTF.

Figure 7.1(b) shows the cyclic voltammagram of TTF in acetonitrile as solvent in the presence of a tetrabutylammonium perchlorate supporting electrolyte using Pt electrodes. Figure 7.1(a) is the voltammagram of the supporting electrolyte in acetonitrile demonstrating that neither solvent nor supporting electrolyte have any electrochemistry of their own in this region. As can be seen, TTF undergoes two oxidation reactions, the first
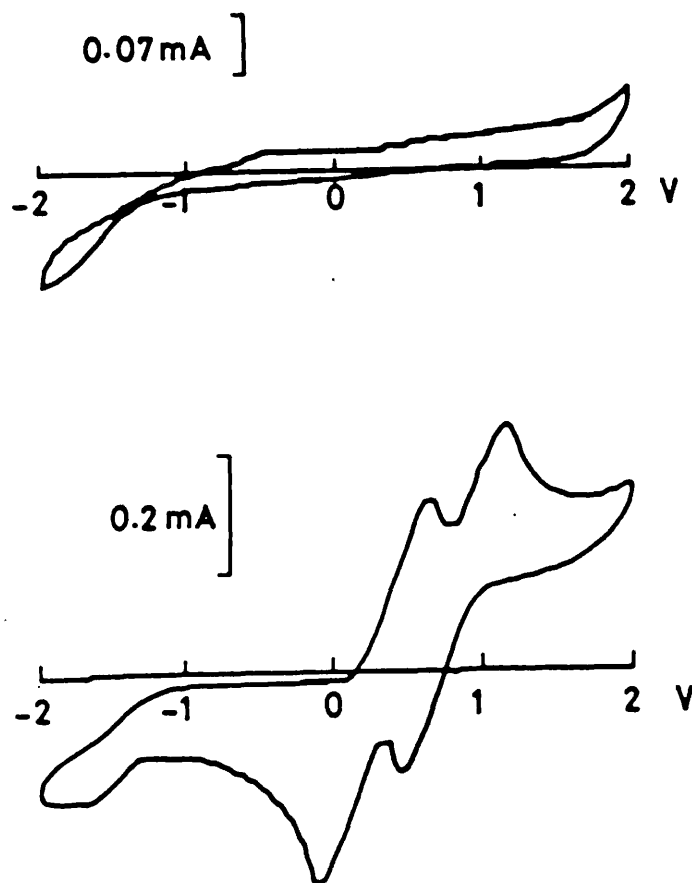
Figure 7.1

leads to the formation of the TTF radical monovalent cation the second to the divalent cation, both being reversible processes, Scheme 7.1.
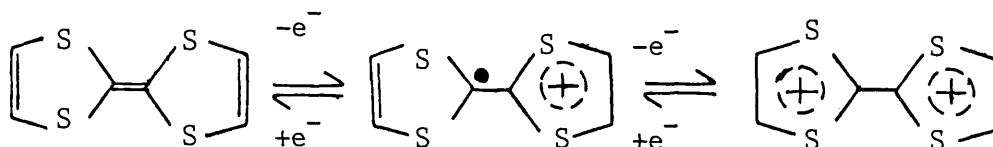
Scheme 7.1.

It is the unpaired electron of the radical cation which is the potential charge carrier and which makes the most significant contribution to electronic conduction in TTF complexes. Hence we need to stop the reaction at the first oxidation stage, and thus an electrocrystallisation potential of about 0.7 V v's S.C.E. is required.

7.3. The Electrochemistry of a Selection of Oxonol Dye Salts

Figures 7.2. and 7.3. show the voltammagrams of a range of oxonol dyes in acetonitrile in the presence of a tetrabutylammonium supporting electrolyte with Pt electrodes, Figure 7.2. demonstrates the effect on the electrochemistry of varying the N-alkyl substituent on the pyridone rings and Figure 7.3. the effect of increasing the methine chain length. It can be seen that the electrochemistry remains largely unaffected by variation of cation, N-alkyl substituent or methine chain length. The
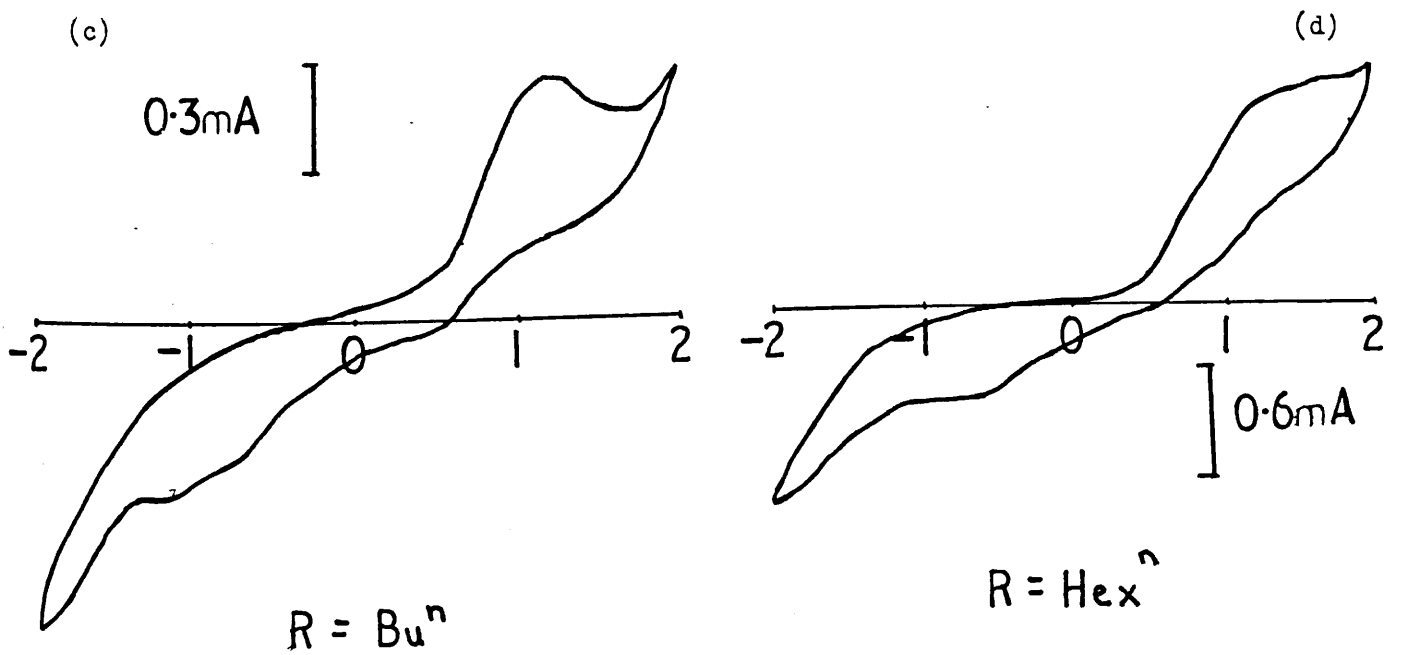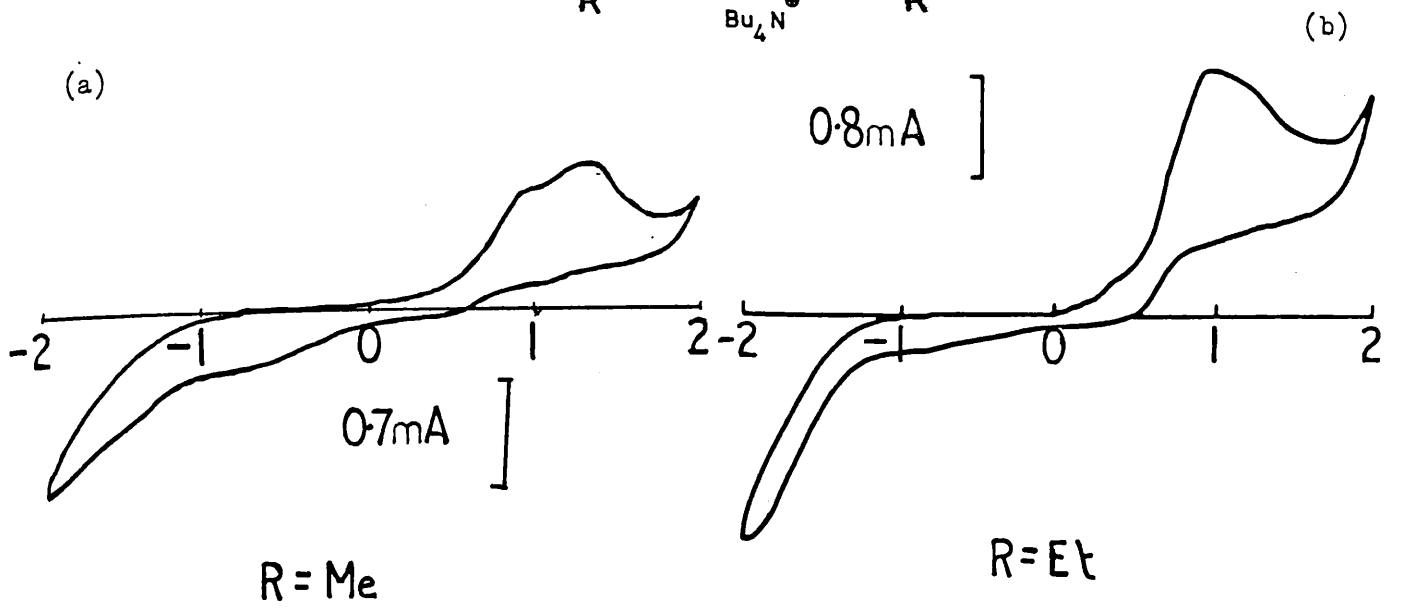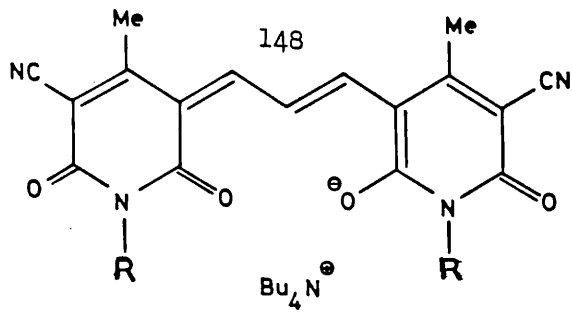
Figure 7.2
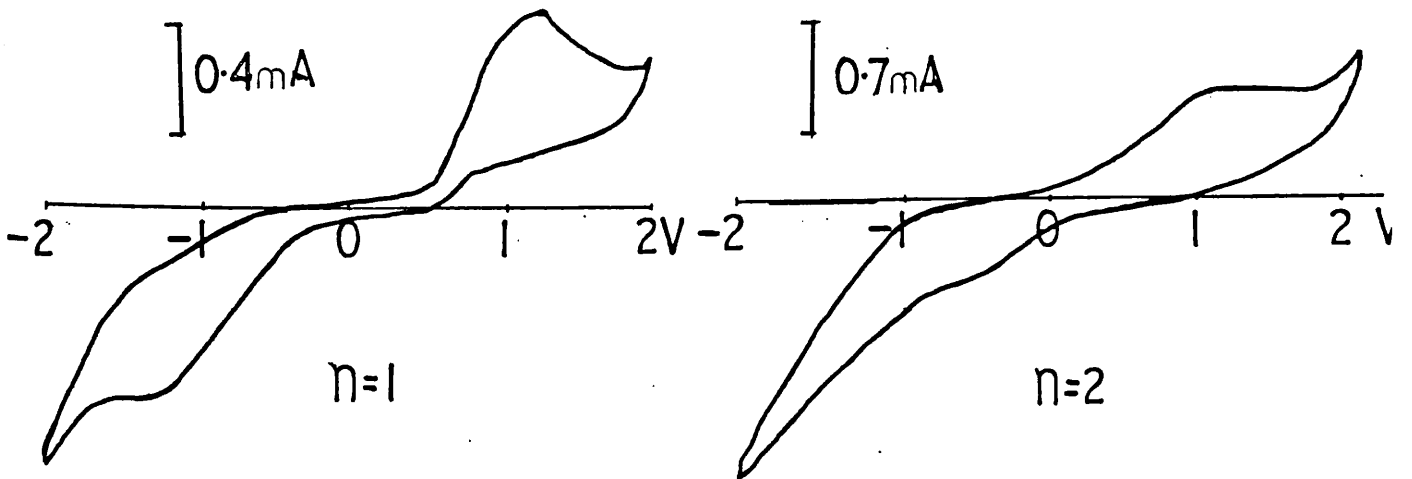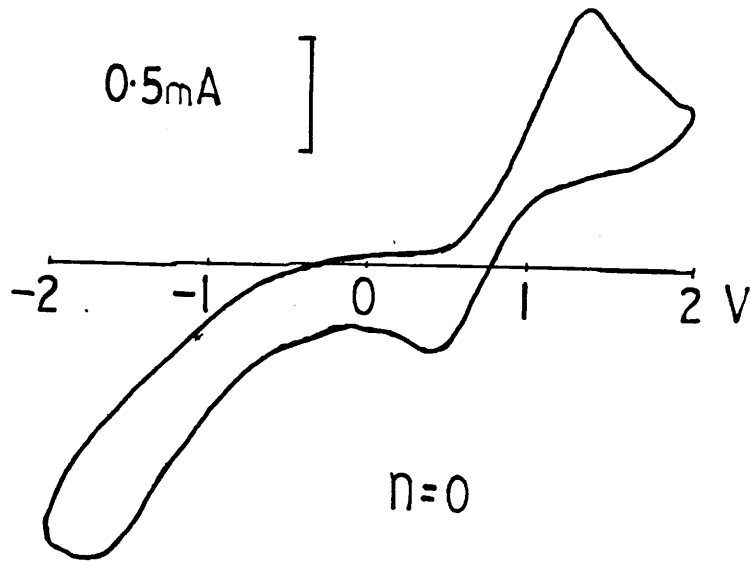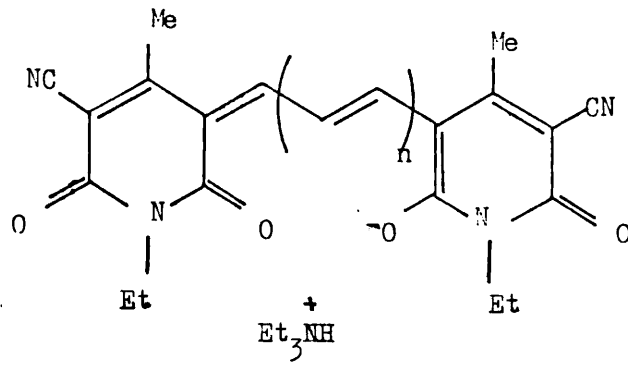
Figure 7.3

dyes undergo oxidation, in some cases, irreversibly. The "bleaching" of

the solutions during the cycle suggests this oxidation to be of the

methine bridge.

7.4. The Preparation of a TTF-Oxonol Dye Complex

We chose dye I, Scheme 7.2. mainly as a result of its high

solubility in acetonitrile; Figure 7.2.(b) shows its cyclic voltammagram.

It shows one irreversible oxidation at 1.0 V v's S.C.E. With an
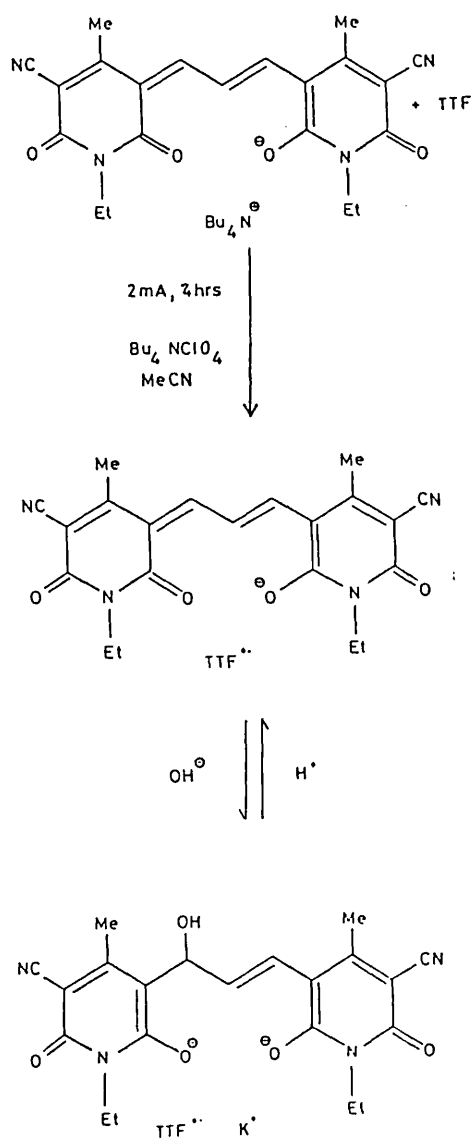
Scheme 7.2

electrocrystallisation potential of 0.7 V v's S.C.E. (generating TTF

radical cations at the anodes surface) the adductant dye should undergo no

electrochemistry of its own. The dye anion simply co-crystallises with

the TTF radical cations forming the complex on the anode. Scheme 7.2

shows the eventual reaction conditions (2mA, 4 hrs, Pt electrodes).

II forms as a black crystalline solid on the anode. Its solution

(50:50, H_2O: MeCN) and solid state e.s.r. spectra are shown in

Figure 7.4.

As well as having a room temperature d.c. conductivity of

$\simeq 10^{-3} \Omega^{-1} cm^{-1}$, II maintains a number of its photographic dye

properties. Notably it can be "bleached" (the α,β-unsaturated carbonyl

centre provides a soft electrophilic centre susceptible to nucleophilic

attack by a range of nucleophiles thereby destroying the chromopore and

bleaching the semiconductor, Scheme 7.2). In the case of hydroxide ion

this process is reversible.

Solution

Solid
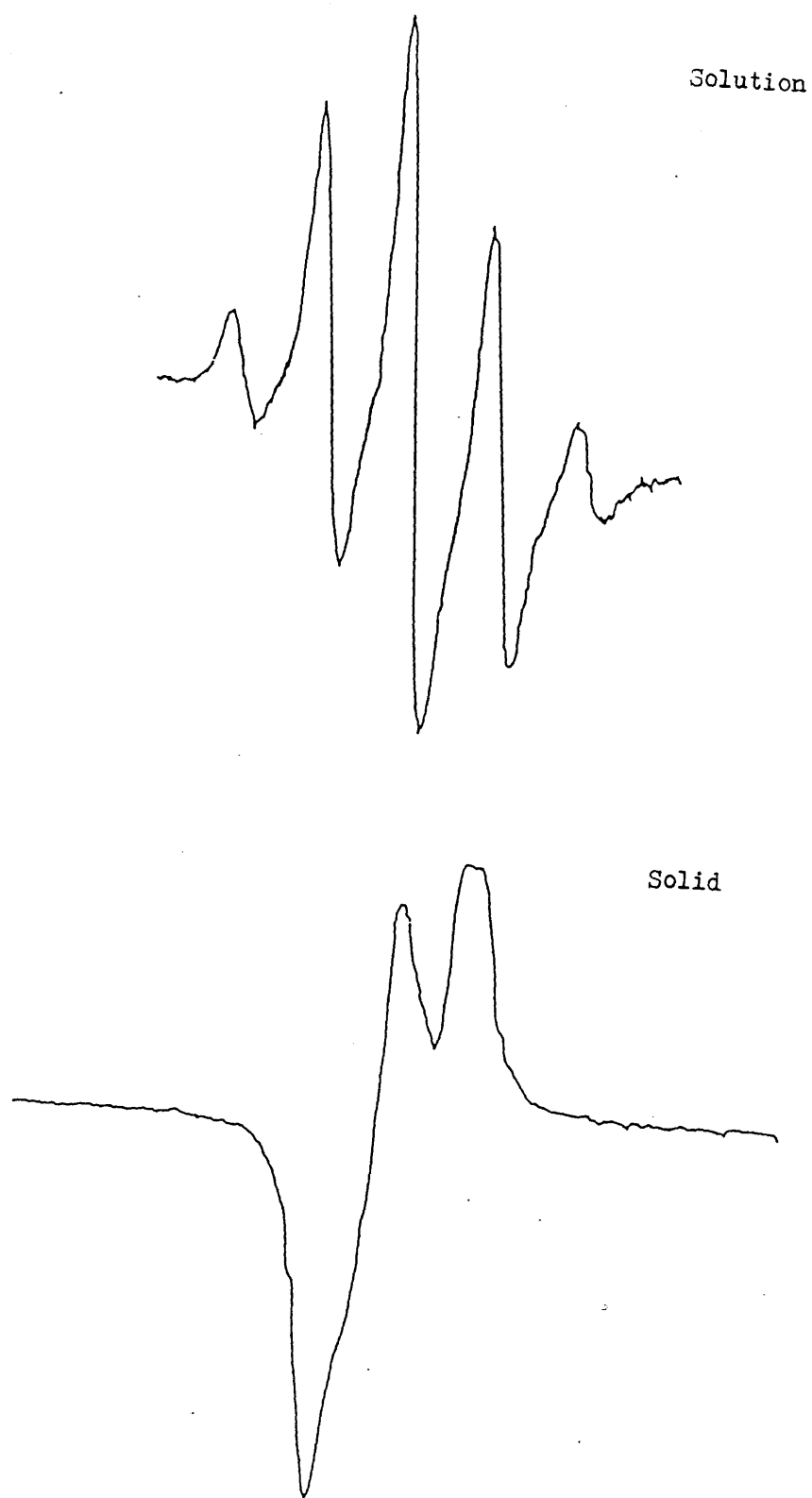
Figure 7.4

7.5.   The preparation of these TTF-dye complexes by direct chemical

means, that is the co-crystallisation of either neutral TTF or of a TTF

salt with oxonol dye salts proved unsuccessful.   Therefore electro-

crystallisation appears to be the synthetic method of choice, although the

possibility of co-sublimation has not yet been explored.

The electrochemistry of the oxonol dyes, as illustrated by Figures

7.2. and 7.3. appears to be remarkably non-versatile, that is structural

changes induce little variation in oxidation potentials.   In the case of

the formation of complex II, above, we were fortunate that the dye's

inherent electrochemistry could not interfere.   However, when attempting

to prepare the dibenzotetrathiafulvalene complex we obtained highly impure

material.   The cyclic voltammogram of dibenzo TTF, (Figure 7.5) suggests
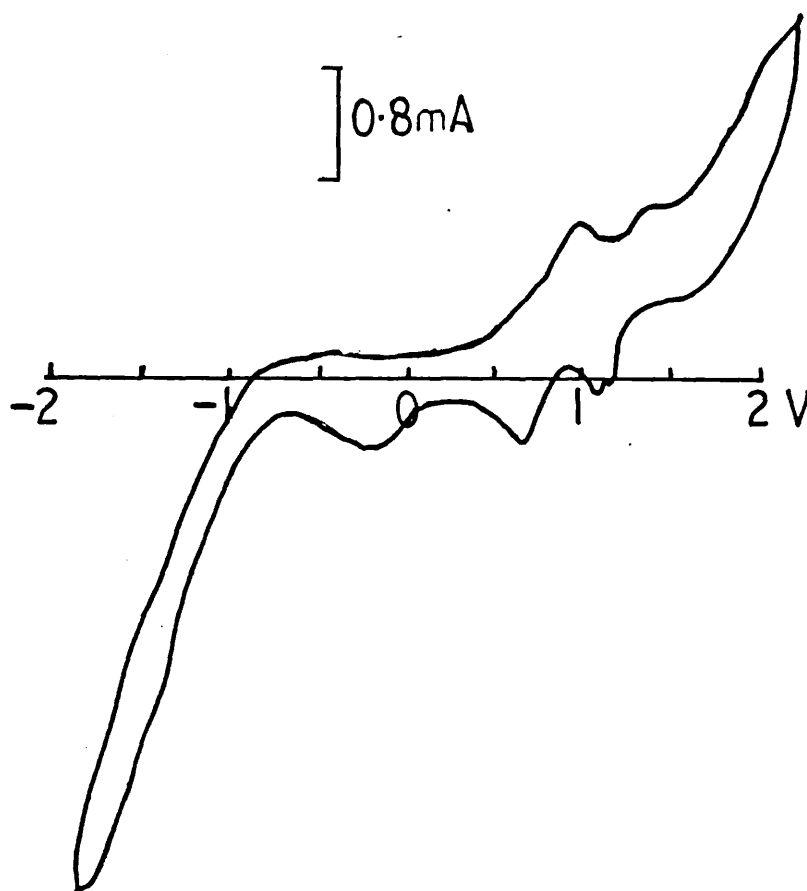
Figure 7.5

why. Its first oxidation potential, Scheme 7.3., coincides with that of

the initial dye I. We therefore have to be careful in our selection of

Scheme 7.3.
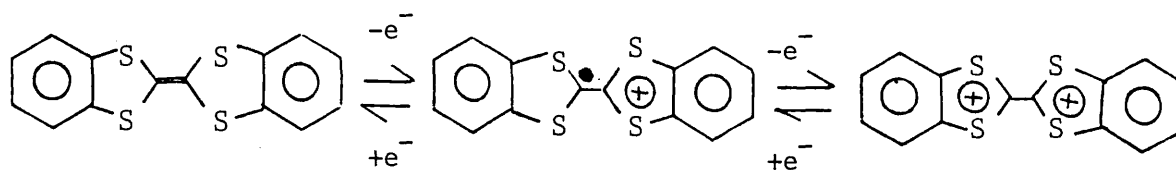
donors. Their electrocrystallisation potentials have to lie within a

limited range of potentials (< 0.9 V v's S.C.E., Pt electrodes, MeCN).

These radical cation-dye complexes have a wide range of potential

applications commercially, e.g., as antistatic agents in film assemblies,

gas detectors, infrared radiation detectors, and indeed complex II is

undergoing evaluation at present.

CHAPTER 8
D.C. Conductivity and Dielectric Spectroscopic Measurements

8.1   D.C. Conductivity

The current (I) vs. voltage (V) characteristics at varying

temperatures revealed Ohmic behaviour for all of our samples where silver

dag contacts were employed. Thus from Ohms Law (8.1)

$$\frac{V}{I} = R \qquad\qquad 8.1$$

the resistance (R) and hence from (8.2)

$$\sigma_O = \frac{L}{A}\frac{1}{R} \qquad\qquad 8.2$$

(where L is the thickness and A the cross-sectional area of the sample),

the d.c. conductivity (σ_O), at varying temperatures could be obtained.

If the material is assumed to be intrinsic (refer to Chapter 5) then

$$\sigma_O = A\exp\ -\Delta\epsilon/2kT \qquad\qquad 8.3$$

and from ln σ vs. $\frac{1}{T}$ plots, thermal activation energies or band gap

energies, can be obtained, for each of the samples.

8.2   Dielectric Spectroscopy

Refer to Appendix 2

It was our intention not only to investigate the bulk properties of

our materials but also to look more deeply into the contact effects;

dielectric spectroscopy enabled us to do both. In general four different

types of dielectric response were seen for our samples, each of which is

shown theoretically mimiced by conventional R.C. (Resistance-Capacitance)

82

circuits in Figure 8.1.
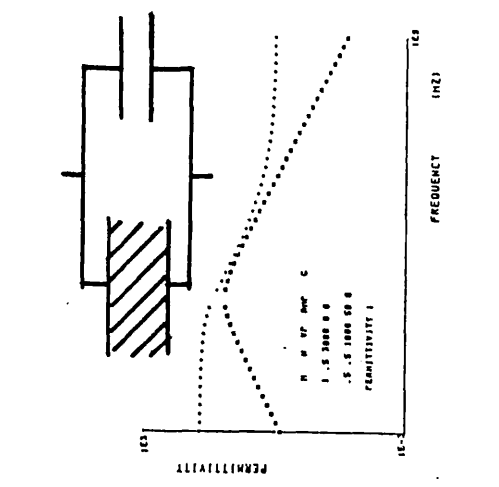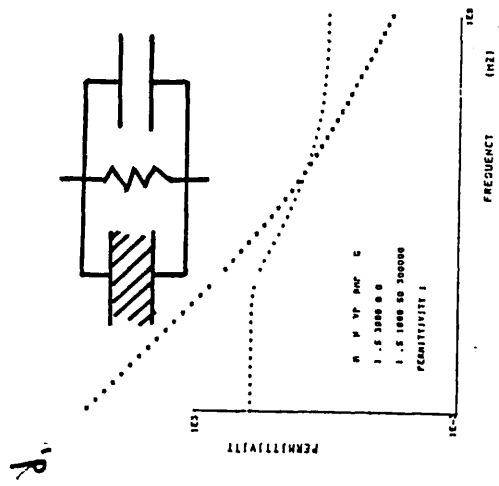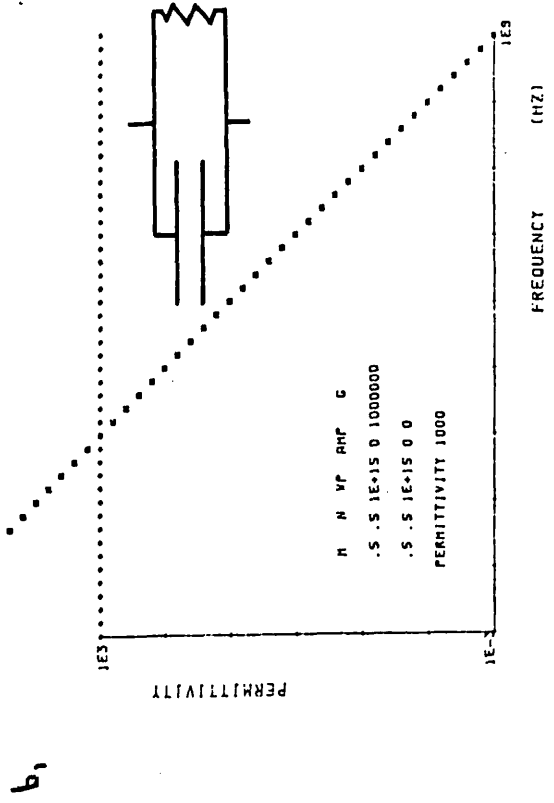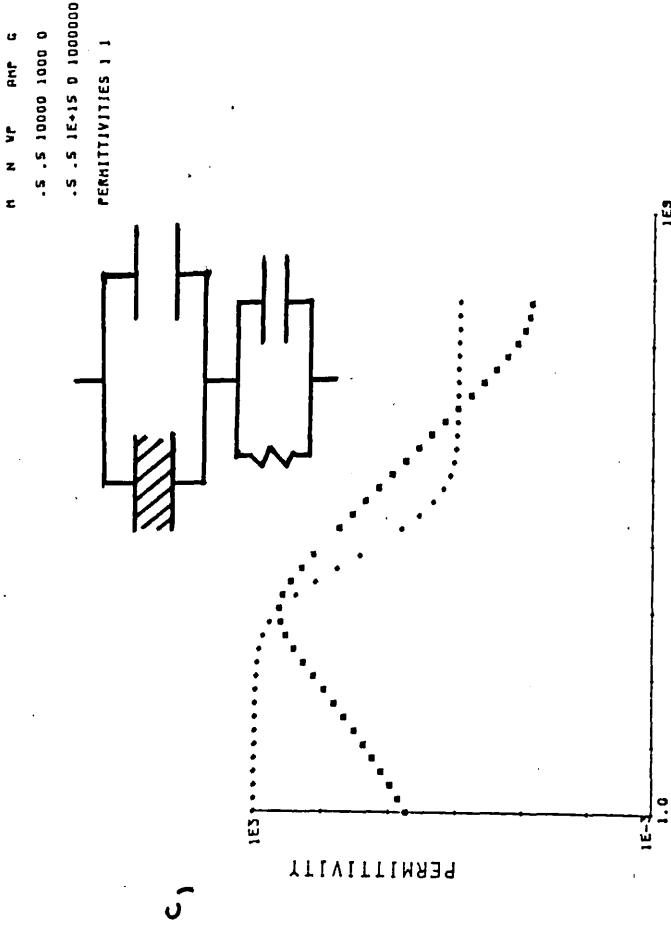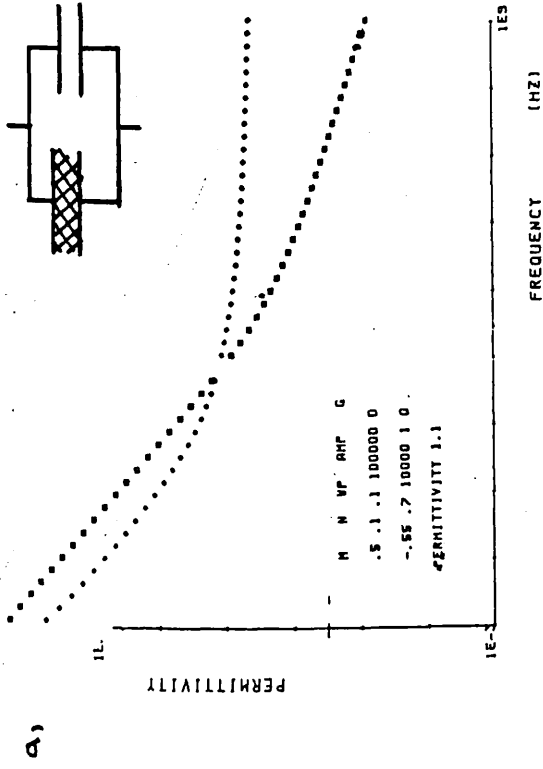
Figure 8.1

(a), which is discussed in detail in Appendix 2, shows the so-called low frequency dispersion (L.F.D.) or quasi d.c. conductivity and is shown represented by a parallel combination of two capacitances, one dispersive the other non-dispersive in nature;

(b) like (a) is a carrier dominated response, however, in con trast, here we are seeing charges moving from one electrode to the other, the real susceptibility χ' (ω) remains constant and the imaginary susceptibility χ'' (ω) has the frequency dependence of ω^{-1} . This is a d.c. conductivity dominated response, which is represented by a parallel combination of a non-dispersive capacitance and a resistance (conductance);

(c) illustrates the Maxwell-Wagner effect. It is an interfacial phenomenon caused, in general, by blocking contacts. It is simply represented as a series combination of a bulk resistance and a capacitance arising from the interfacial contact barrier. The responses seen in (d) (i) and (ii) are the result of diffusion. Whether it be on a microscopic scale as in the diffusion of ions or, as in our case, on a macroscopic scale in the diffusion of the silver paint of our electrodes into the bulk material.

(d)(i) and (ii) shows this diffusion with and without additional d.c. conductivity present, respectively and their corresponding circuit representations.

8.3   The measurements

The dielectric response curves to follow are shown with LOG(C)/LOG(G/ω) vs. LOG(F) axes as a consequence of equations (2.31(A)) and (2.32(A)), Appendix 2; where χ' (ω) α C'(ω) and χ''(ω) α G(ω)/ω; also refer to the experimental section, 10.6.5.
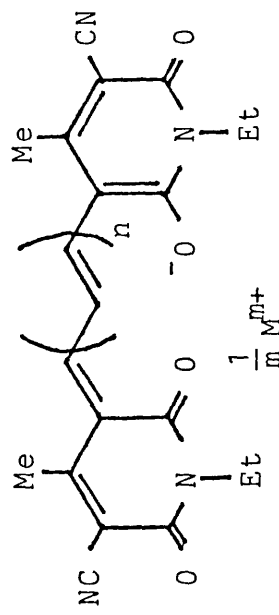
Structure (top center):

M^{m+}
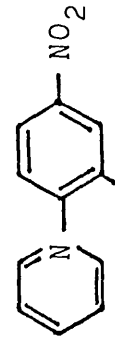
- Bu_4N
- $(Ph_3PCH_2)_2$
- Ca
- pyridinium with 2,4-NO_2 substituents
- Ph_4P
- Et_3NH
- Et_3NH
- Ni
- Co
- $H_2C=C(Me)CO_2CH_2CH_2NH(Me)_2$
- Ph_3MeP
- Et_3NH
- TTF
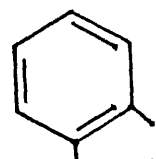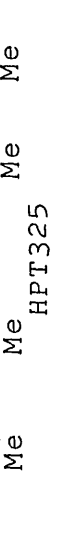
$2I^-_3$

HPT325 structure

HPT N°	n	M	$\frac{1}{m}M^{m+}$ m
288	1	Bu_4N	1
299	1	$(Ph_3PCH_2)_2$	2
261	1	Ca	2
324	1	pyridinium(2,4-NO_2)	1
289	1	Ph_4P	1
338	0	Et_3NH	1
(MI1579)	1	Et_3NH	1
335	1	Ni	2
336	1	Co	2
314	1	$H_2C=C(Me)CO_2CH_2CH_2NH(Me)_2$	1
297	1	Ph_3MeP	1
(HPP337)	2	Et_3NH	1
332	1	TTF	1

HPT320 structure

All of the theoretical curve fits for the dielectric responses below are either one or a combination of two or more of those shown in Figure 8.1 with slightly modified parameters (m, n, ωp, amp, and G). Where m and n are exponents of the power laws, equation (2.43(A)) and equation (2.44(A)), described in Appendix 2, ωp is the loss peak frequency, amp is the loss peak amplitude and G is the conductance of the sample.

8.4. Class I Type Material

These materials are semi-insulating. D.c. conductivity is only apparent at the higher temperature. All have d.c. conductivities lower than $1 \times 10^{-8} \, \Omega^{-1} \, m^{-1}$ at 373 K and have thermal activation energies (assuming materials to be intrinsic) greater than 1.45 eV. The dielectric response is therefore dominated by the polarisation of bound charges, essentially ionic polarisation.

8.4.1. HPT 288

The dielectric measurements suggest the existence of a small amount of d.c. conductivity at the highest temperature of 373 K, Figure 8.3. However, conformation of this by theoretical curve fitting is not possible as we have very little information at the low frequency end of the spectrum where the conductance dominates. We, however, have a measured d.c. conductivity of $6.92 \times 10^{-9} \, \Omega^{-1} \, m^{-1}$ at 373 K, Figure 8.2.

8.4.2. HPT 299

Essentially identical to HPT 288, Figure 8.5 differing however in its measured d.c. conductivity of $1.92 \times 10^{-9} \, \Omega^{-1} \, m^{-1}$ at 373 K, Figure 8.4.
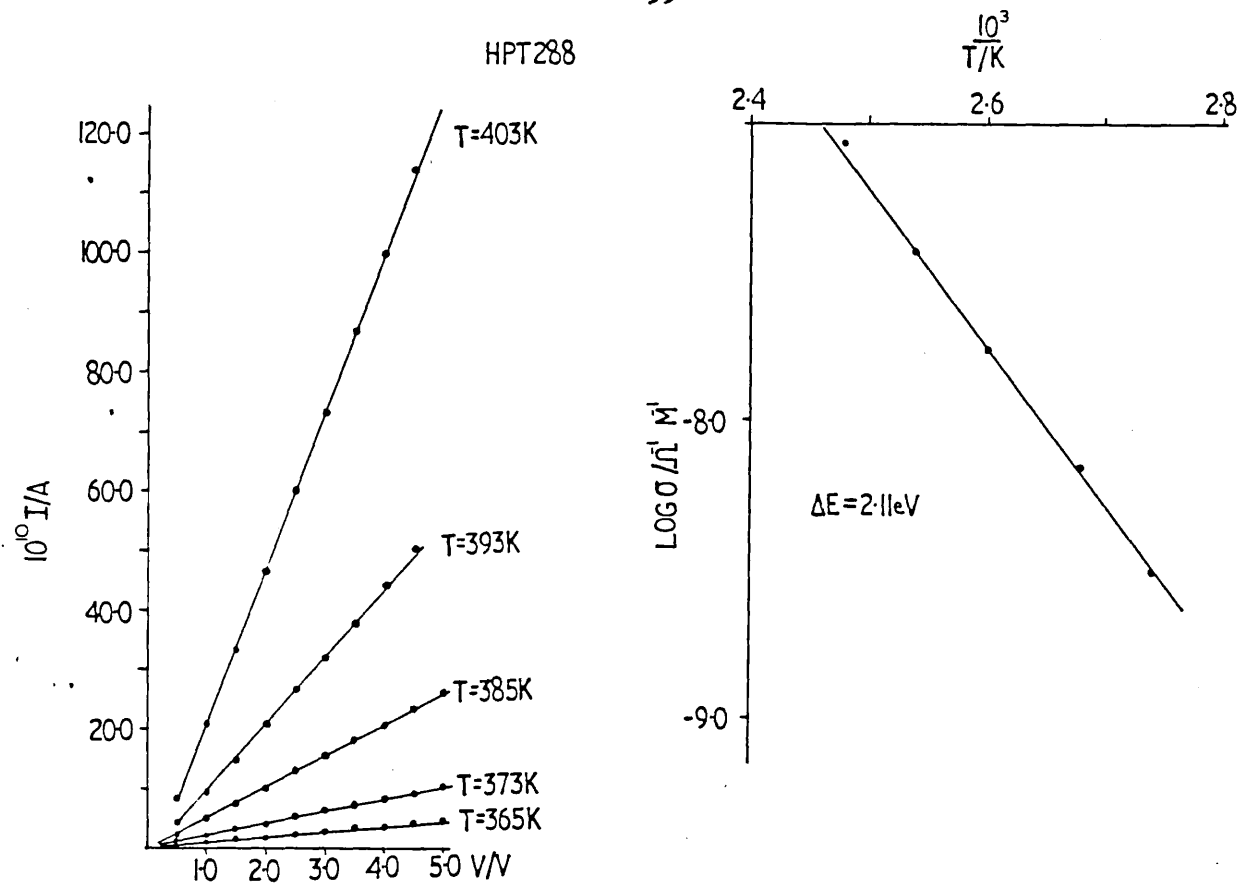
Figure 8.2
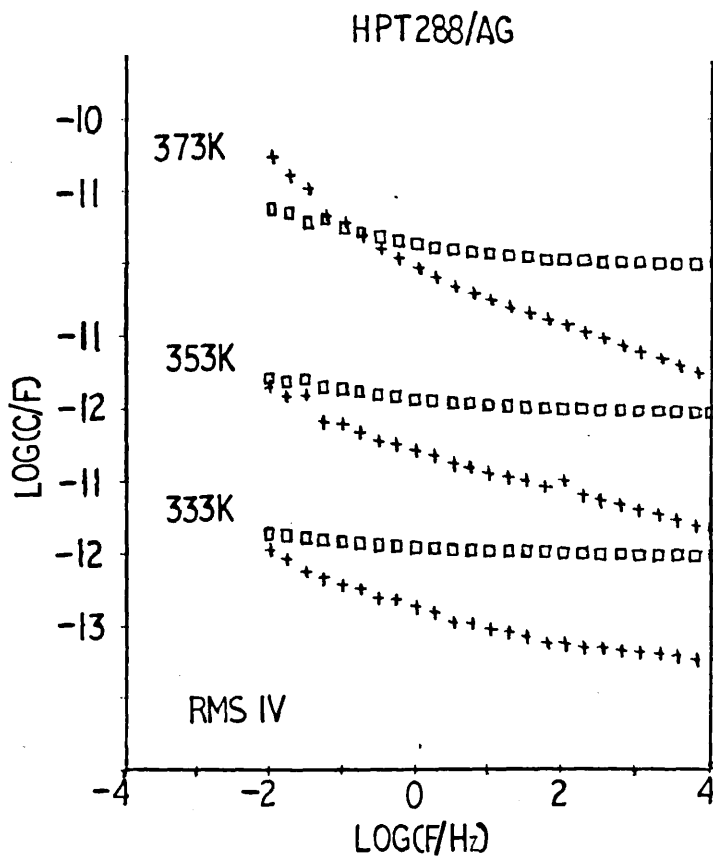
Figure 8.3
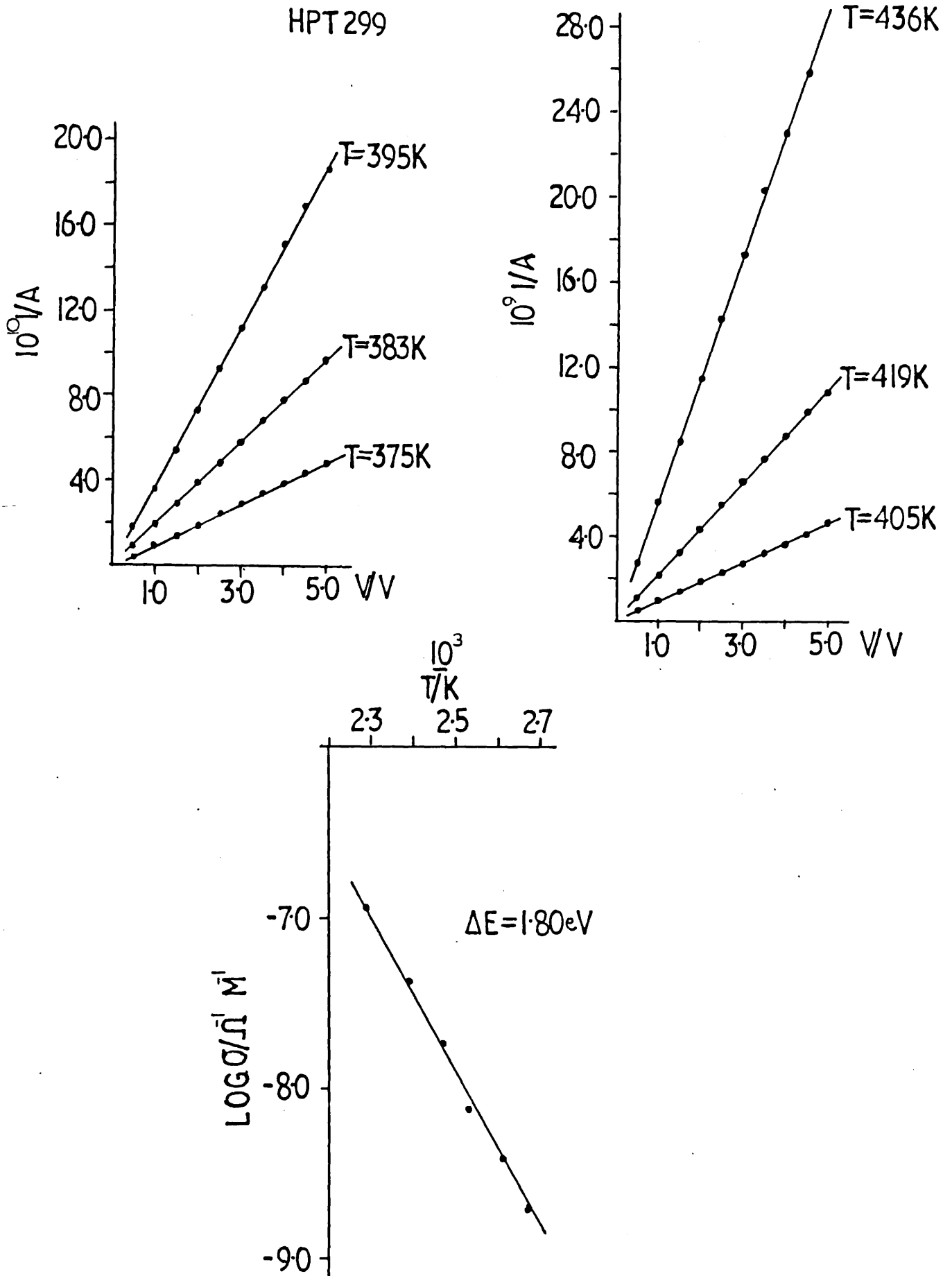
Figure 8.4
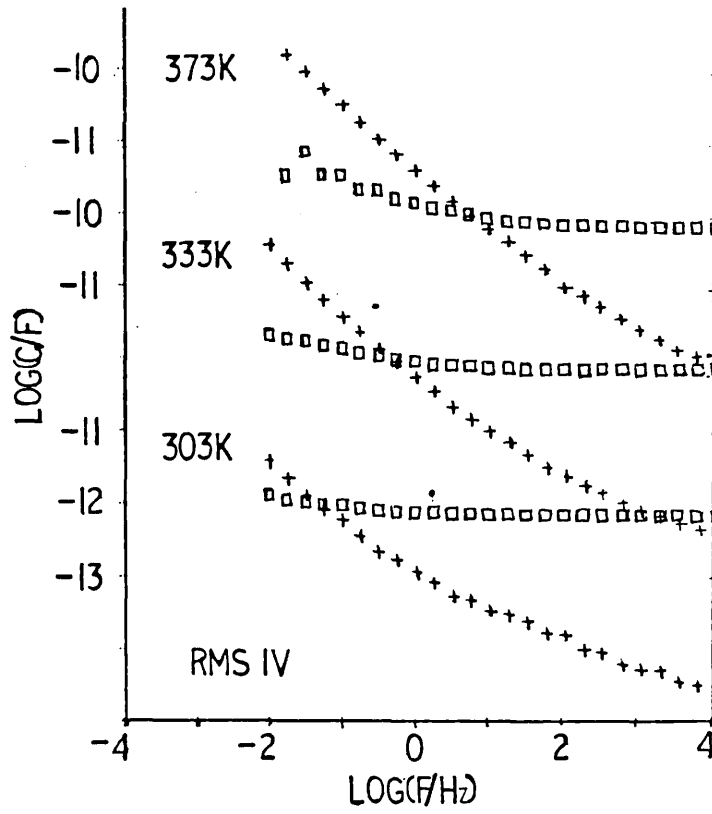
HPT 299/AG
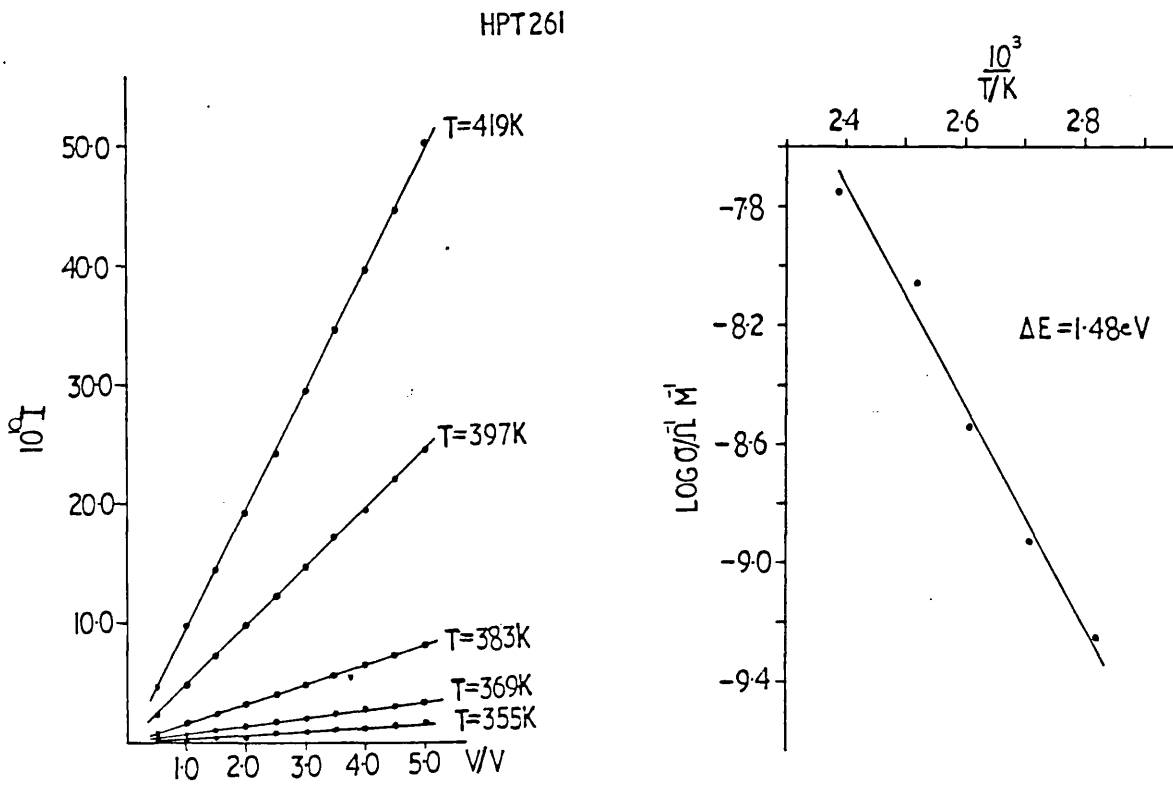
Figure 8.5

HPT 261

Figure 8.6

8.4.3. HPT 261 and HPT 324

Dielectric spectra were not measured for these two materials as from examination of their d.c. characteristics, Figures 8.6 and 8.7, similar responses to those seen for HPT 288 and HPT 299 were expected.

8.4.4. HPT 289

Two different contacts were tried for this sample (Ag, Al) each gave essentially the same dielectric response. The dominant spectral feature for both contacts is that of LFD or quasi d.c. conduction which is confirmed by curve fitting, Figures 8.9, 8.10. The slight dispersion in complex capacitance at the lower frequency end of the higher temperature spectra for the silver contacted sample suggests, also the existence of a diffusive process (Ag diffusion; see Class II type material). Figure 8.8. shows the d.c. characteristics.

8.4.5. HPT 338

The spectra show a number of interesting features. At the lower temperatures a loss peak is clearly visible, caused by the polarisation and subsequent relaxation of bound charges (in our case ions). At the higher temperatures there is evidence for an interfacial contact barrier limiting the d.c. transport in the system; this is reflected in the saturation of both χ' and χ'' at low frequency, Figure 8.12. Figure 8.11 shows the d.c. characteristics.

HPT 324
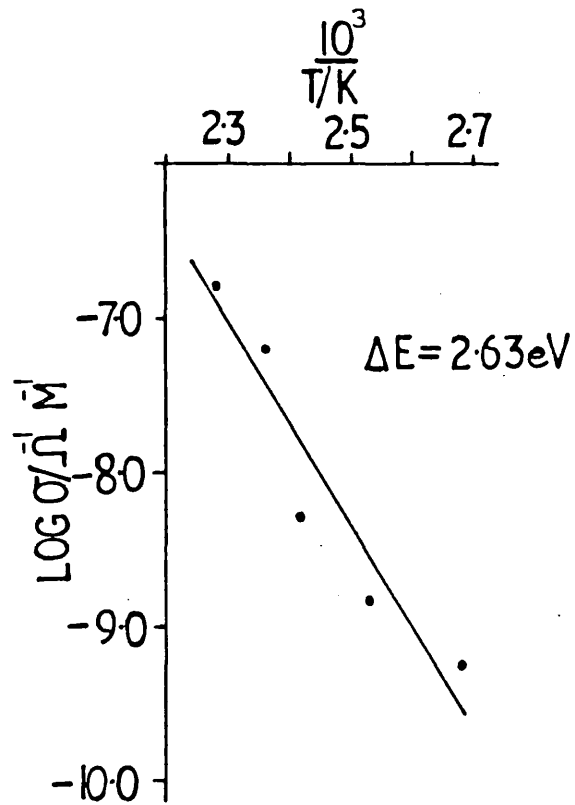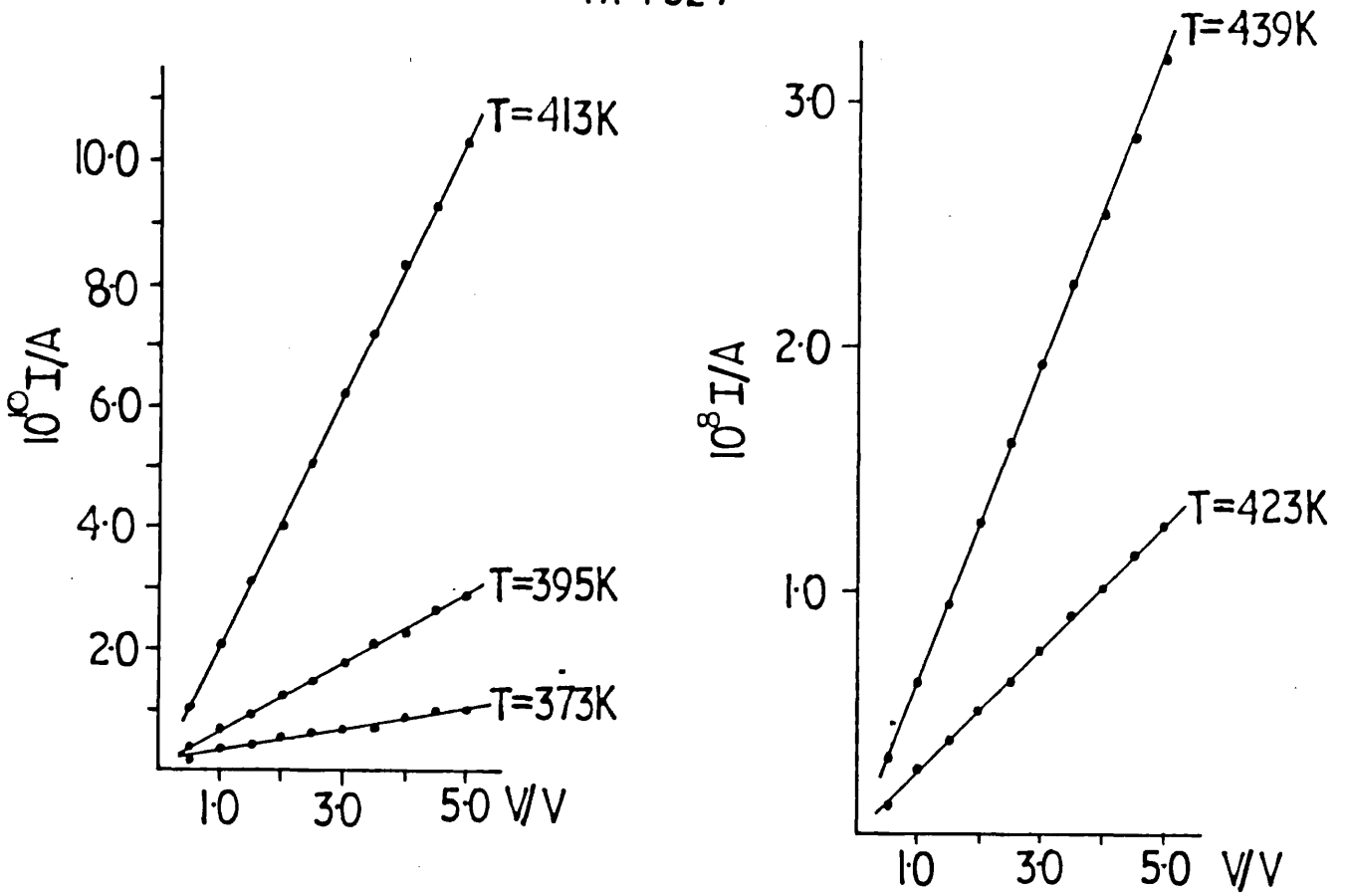
Figure 8.7

HPT 289
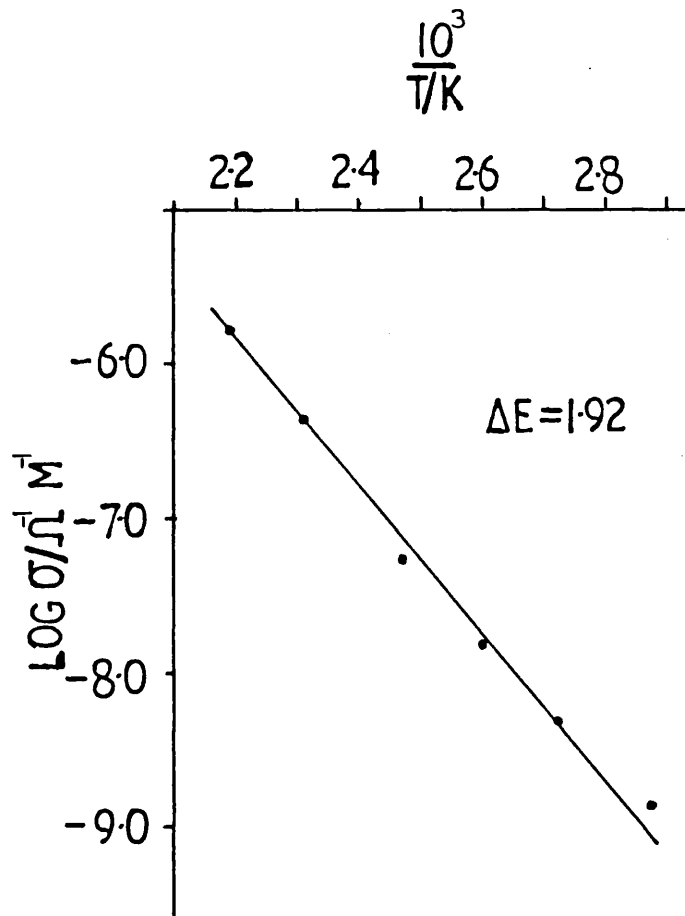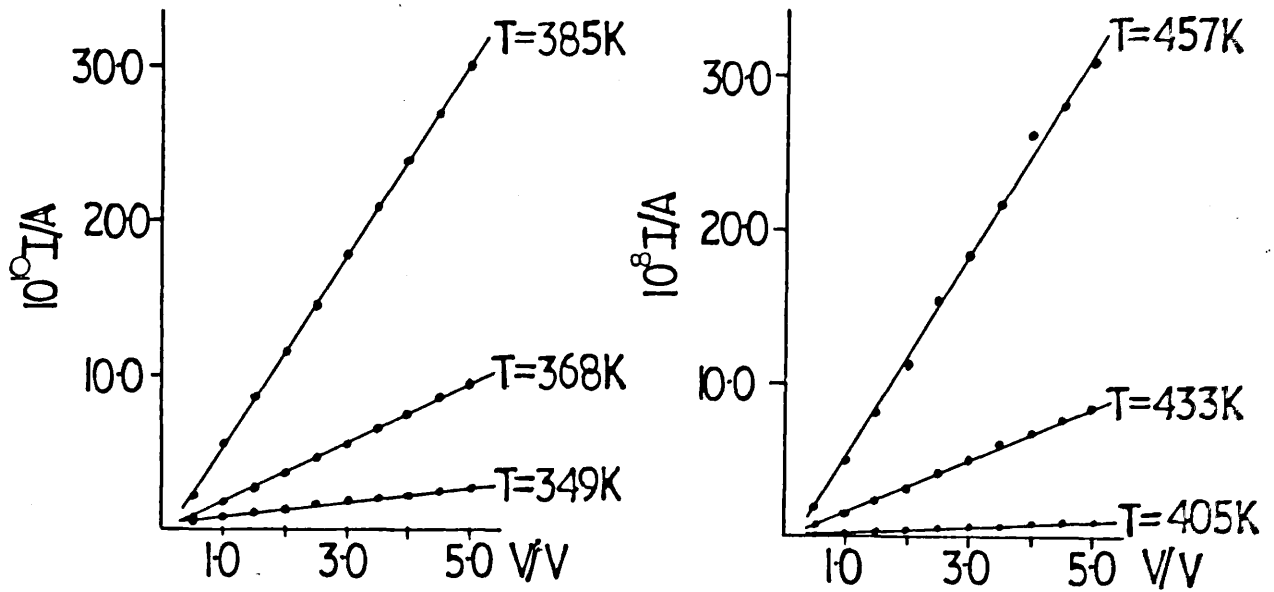
Figure 8.8
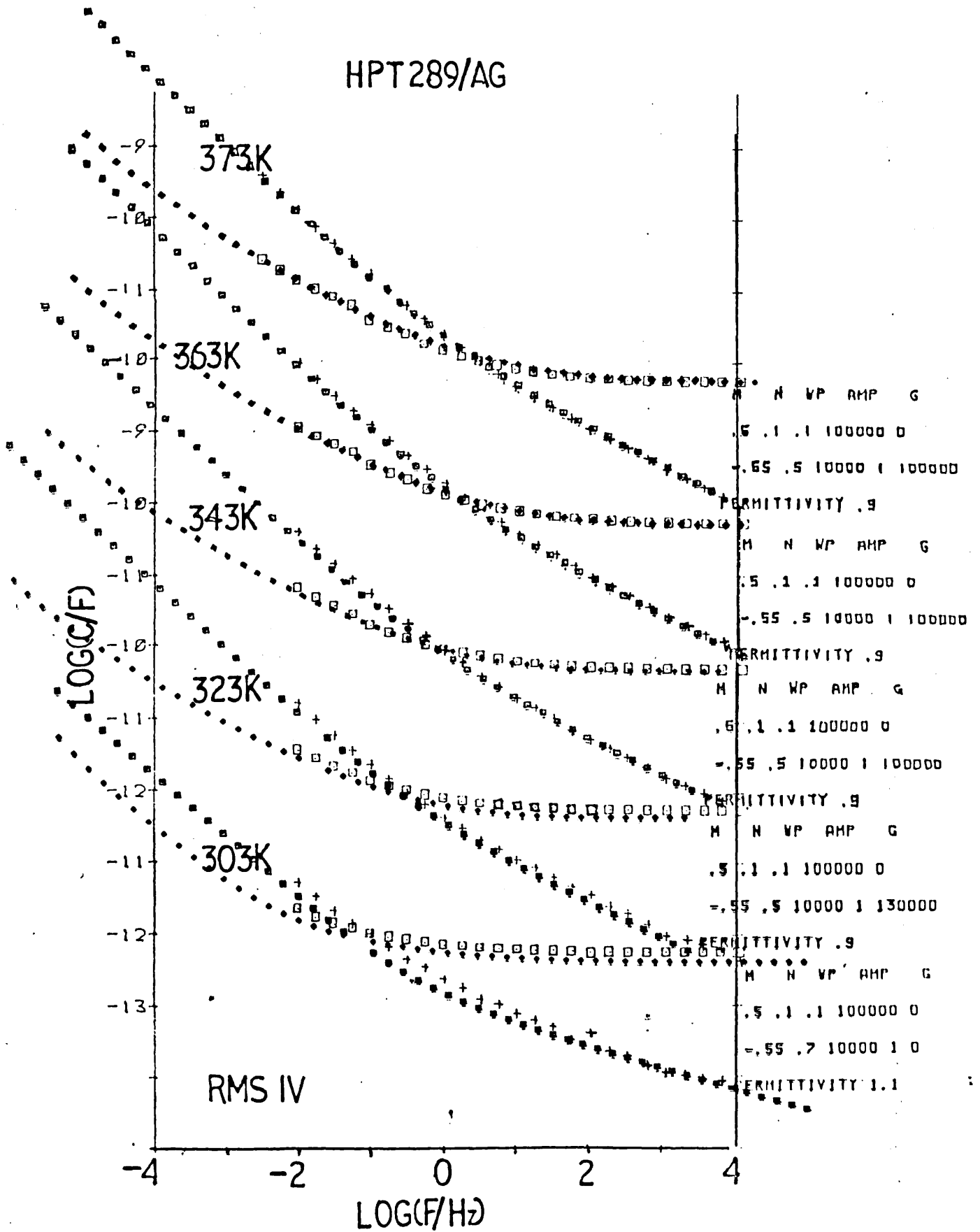
Figure 8.9
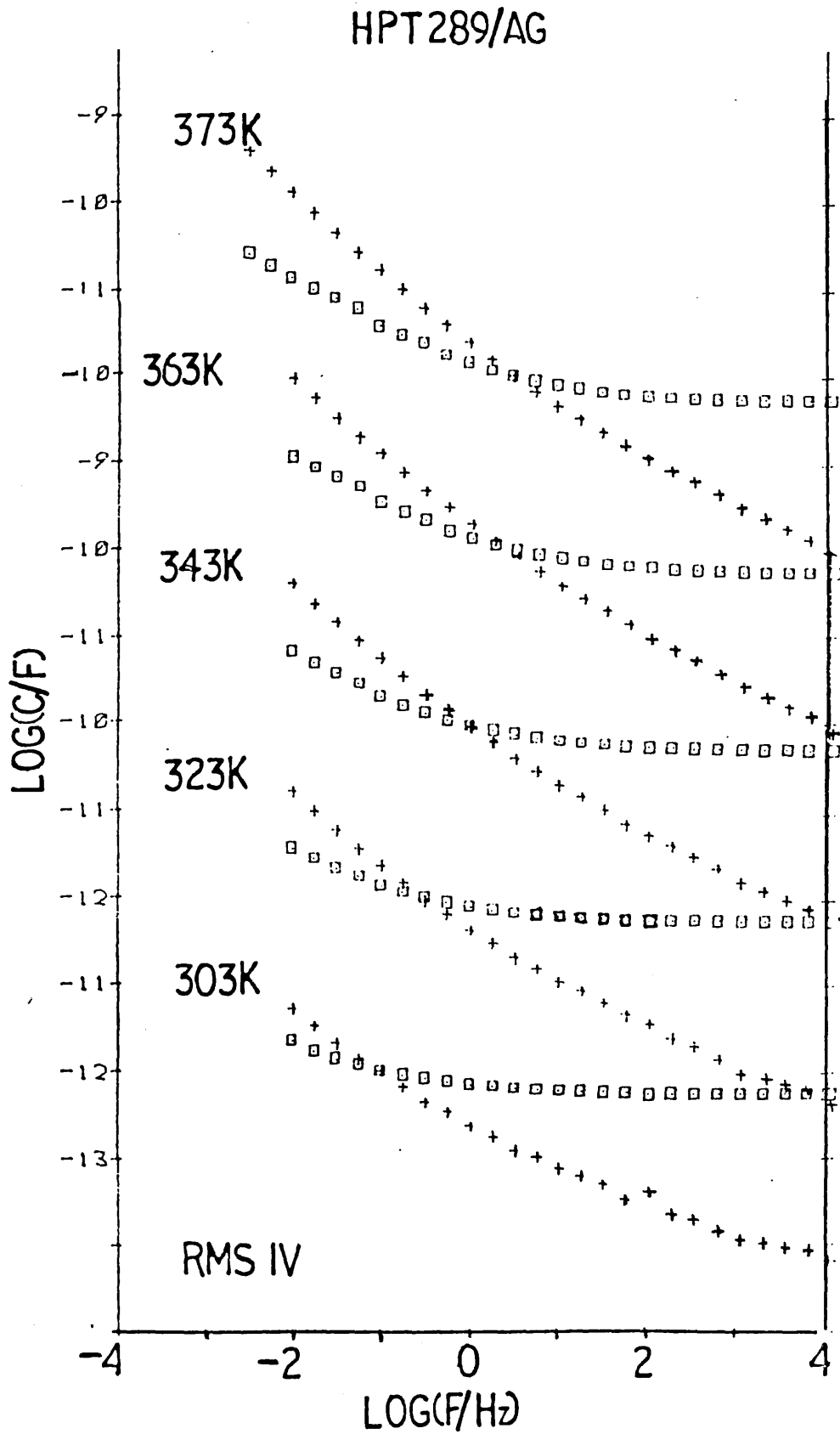
Figure 8.9
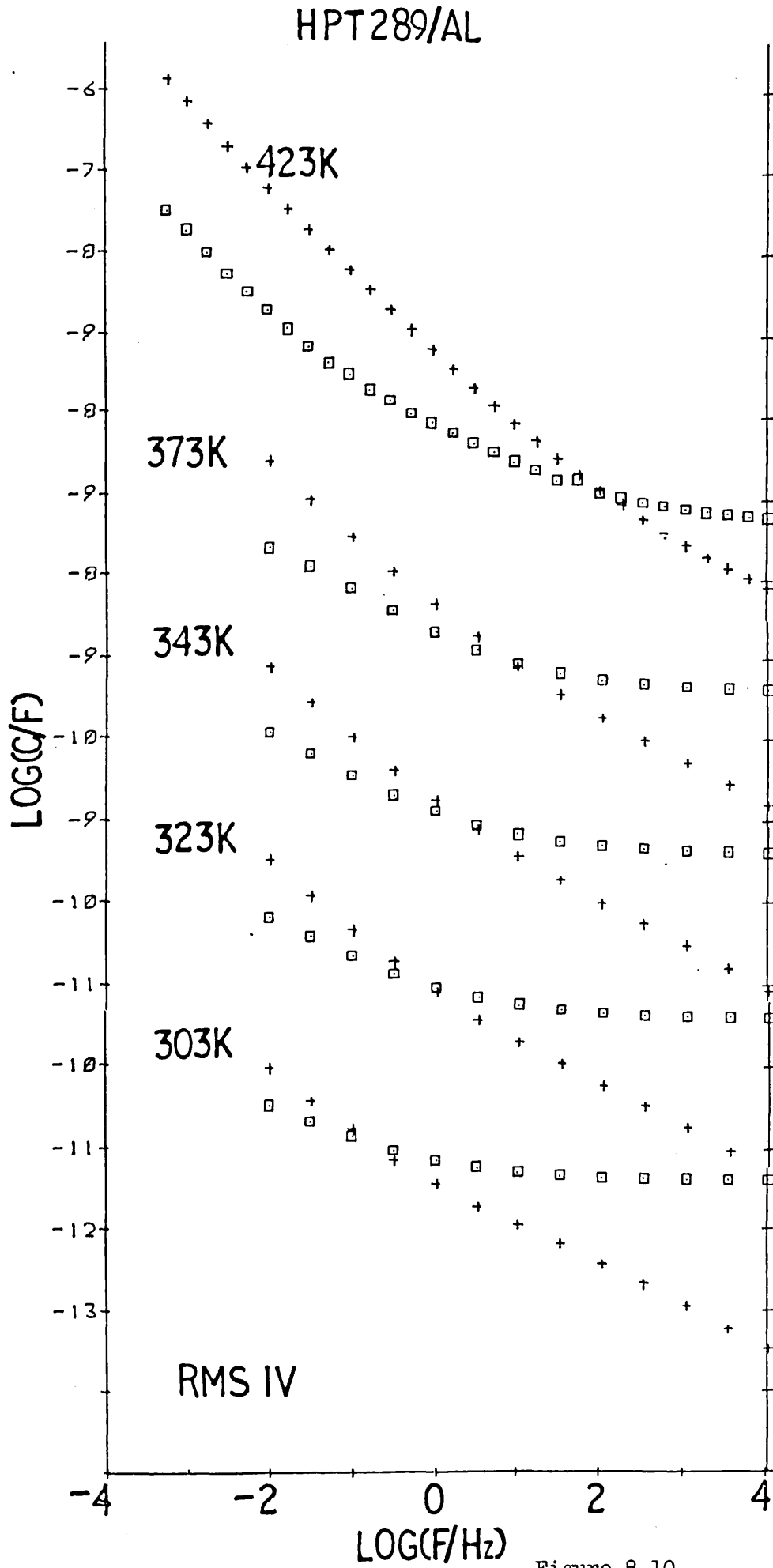
Figure 8.10

HPMI(HPT338)
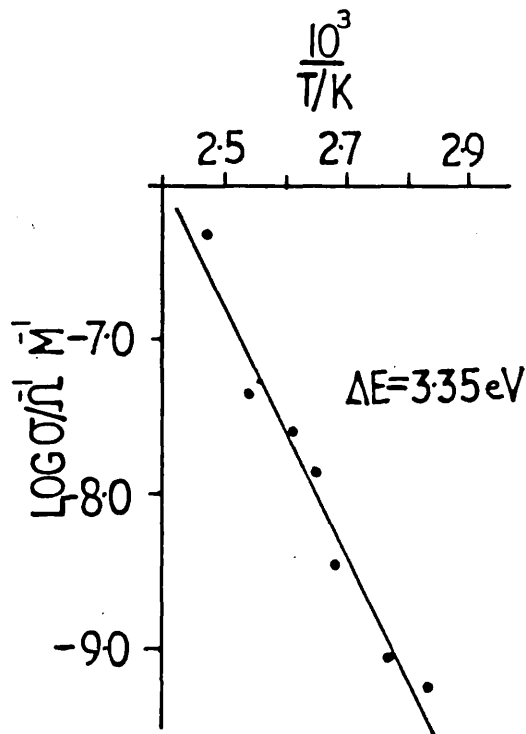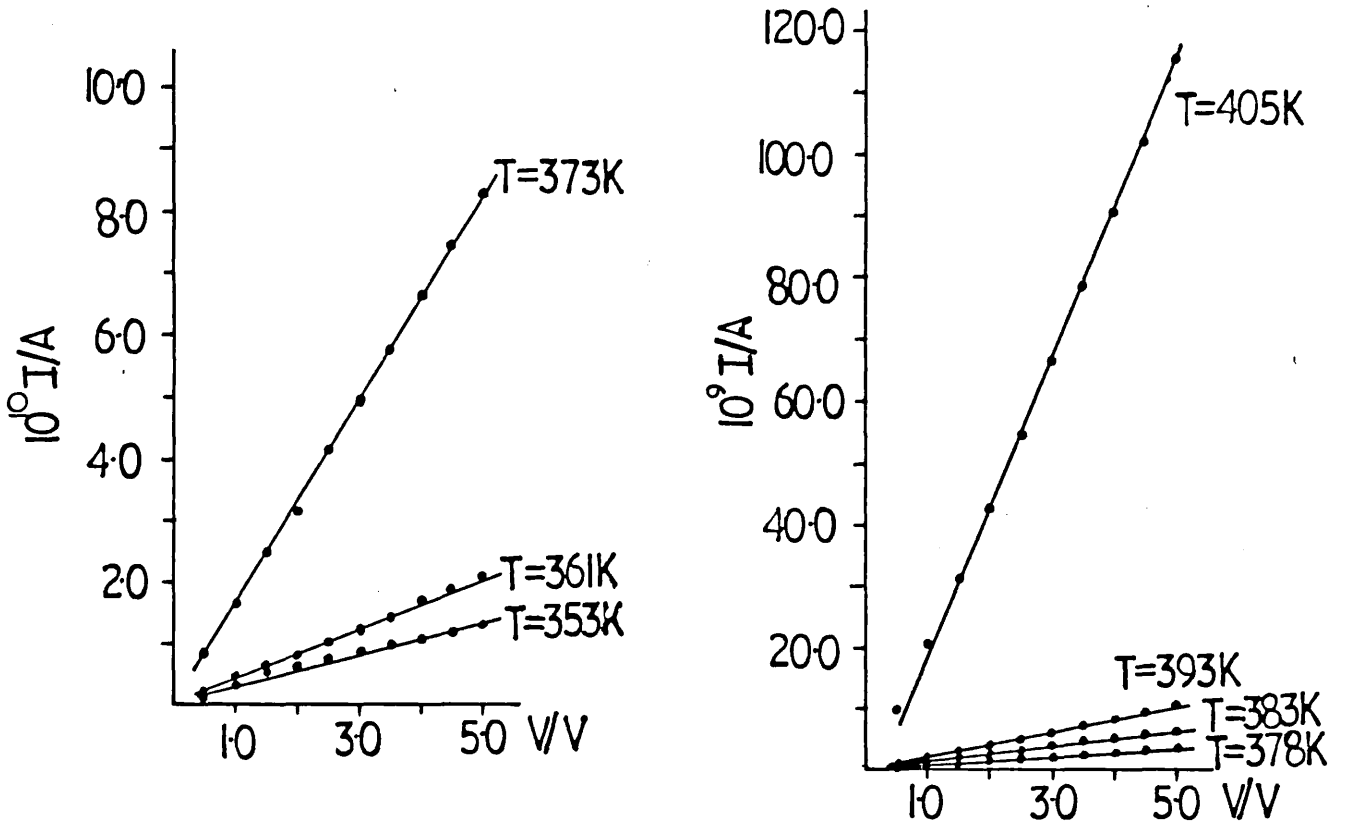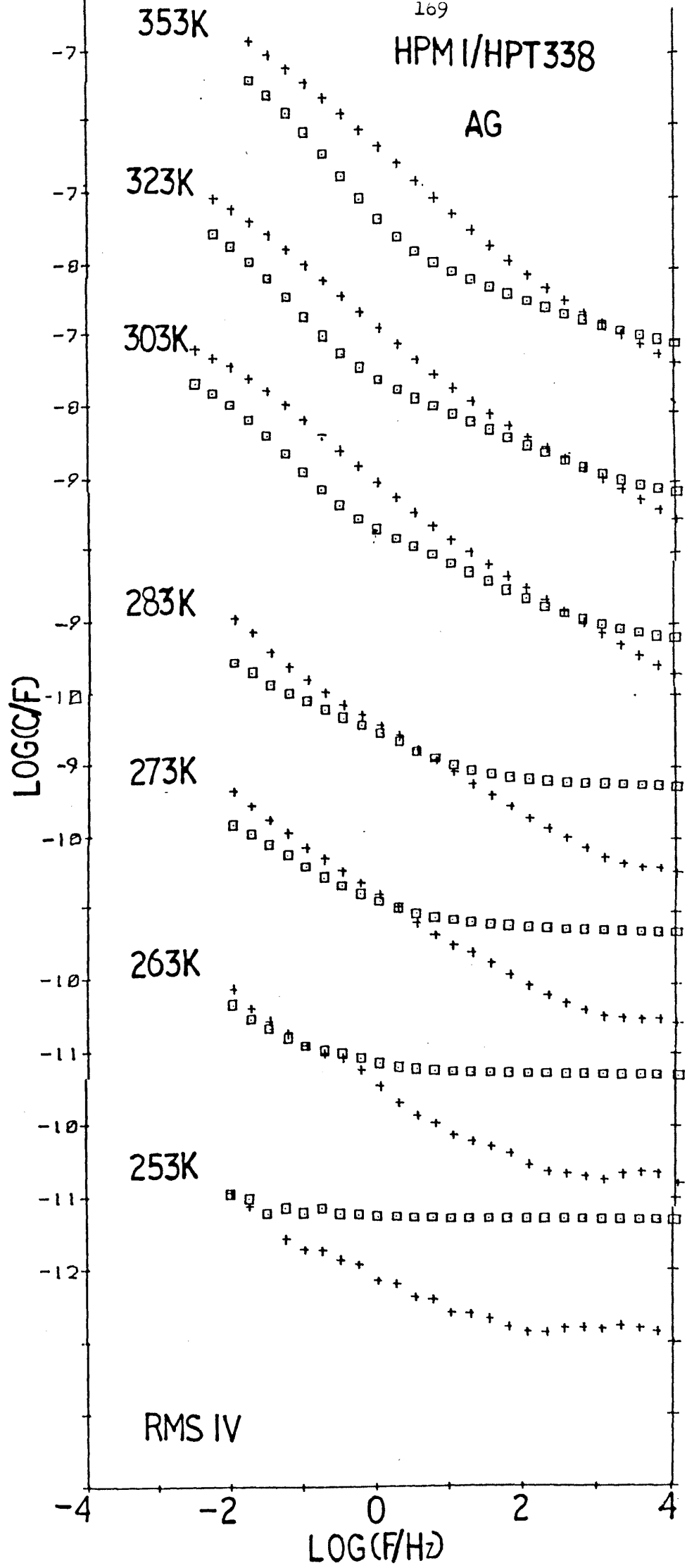
Figure 8.11

Figure 8.12

8.4.6. MI 1579

Again two contacts were investigated (Ag, Al). For the Ag contacted material the lower temperature spectral signatures are similar to those of HPT 338 in that a .loss peak is present, it is however in this case, far more clearly defined. The complex capacitance in the higher temperature responses appears to be saturating and resembles very closely Figure 8.1(d)(i) where we have a diffusive process with parallel d.c. conductivity, Figure 8.14. The Al contacted material at these elevated temperatures exhibits a classic example of LFD, Figure 8.15. All features being clearly confirmed by theoretical curve fitting. The samples d.c. characteristics are shown in Figure 8.13.

MII579
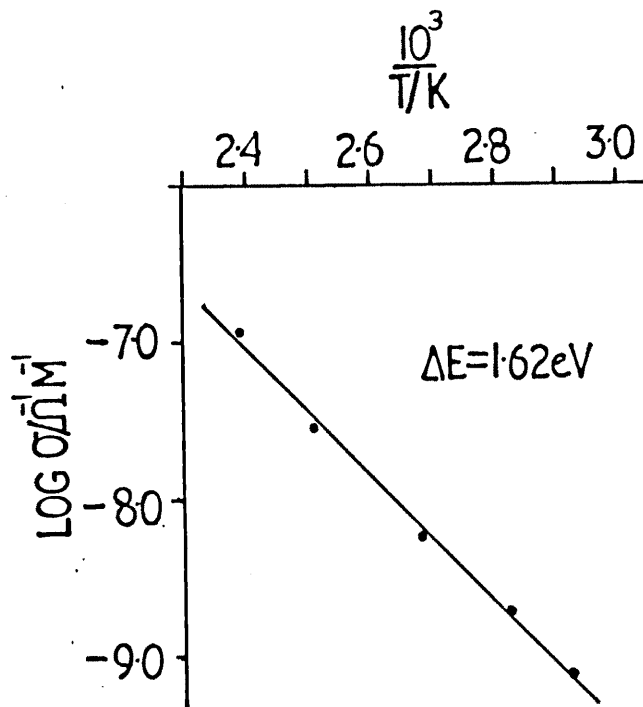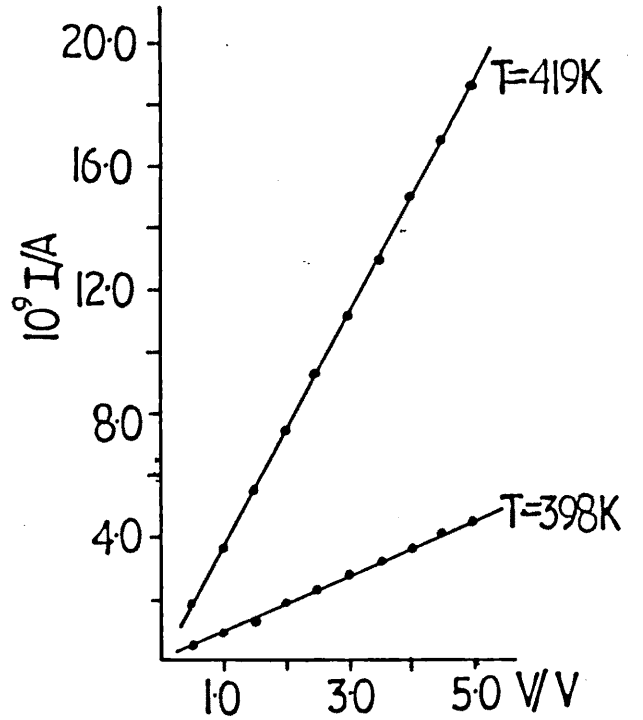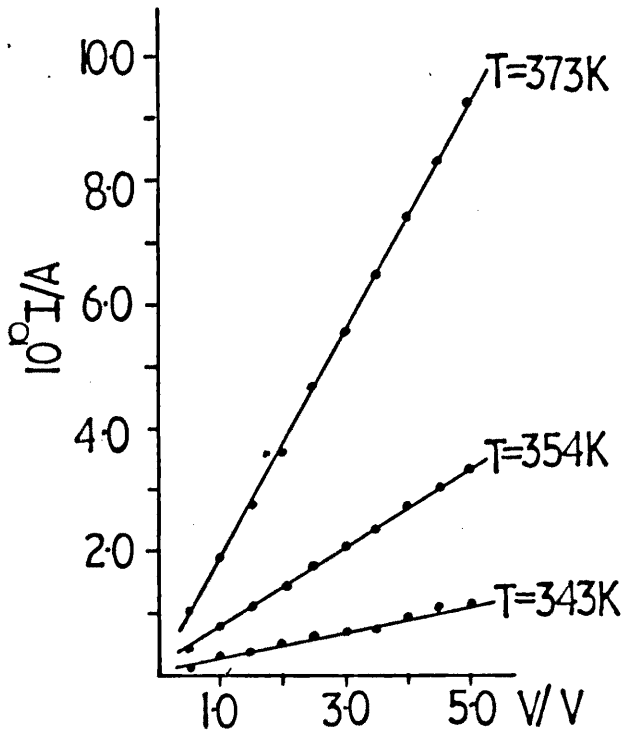
Figure 8.13
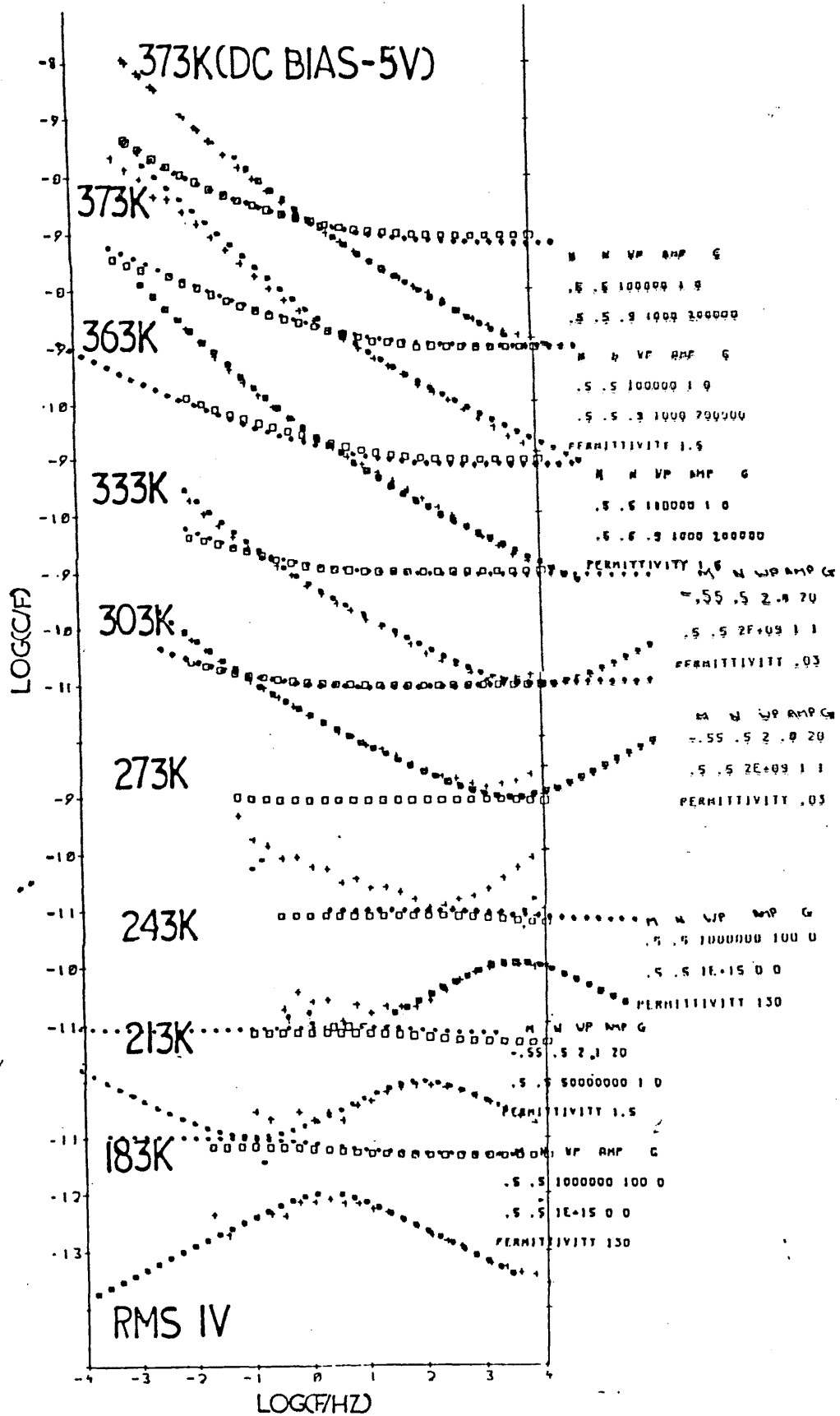
Figure 8.14

Figure 8.14
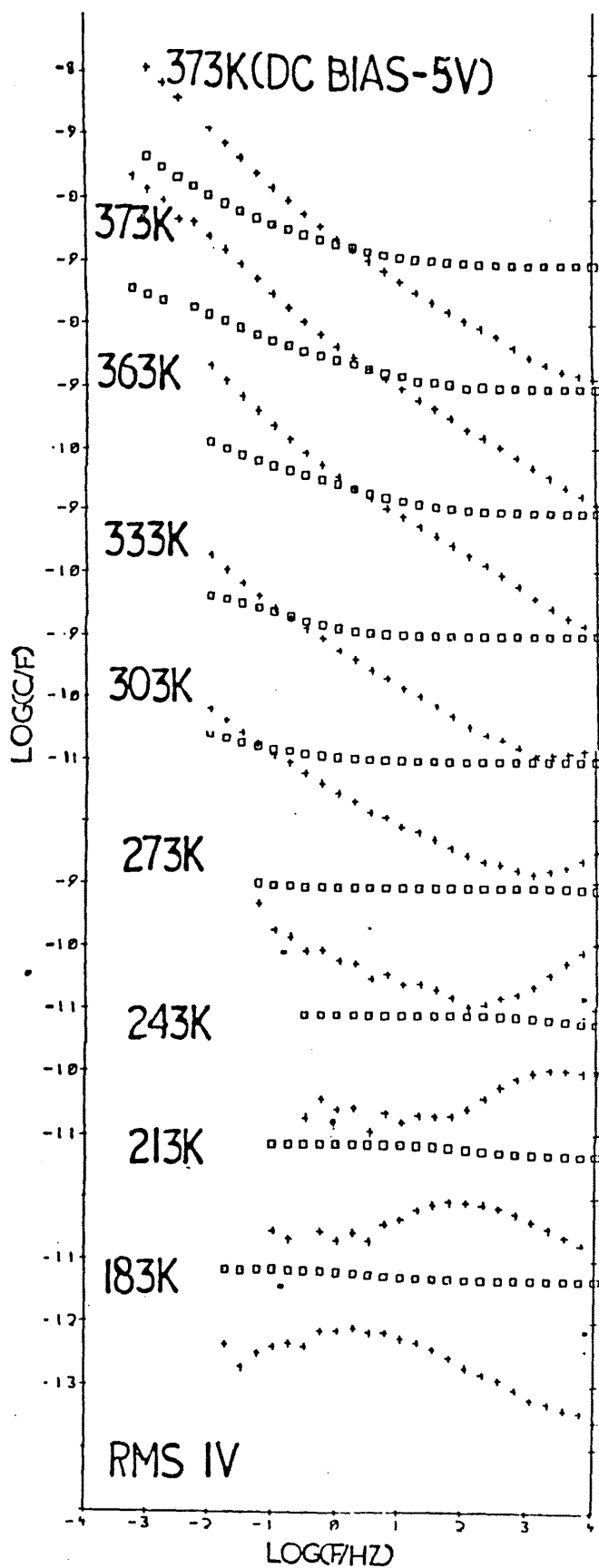
MI1579/AL
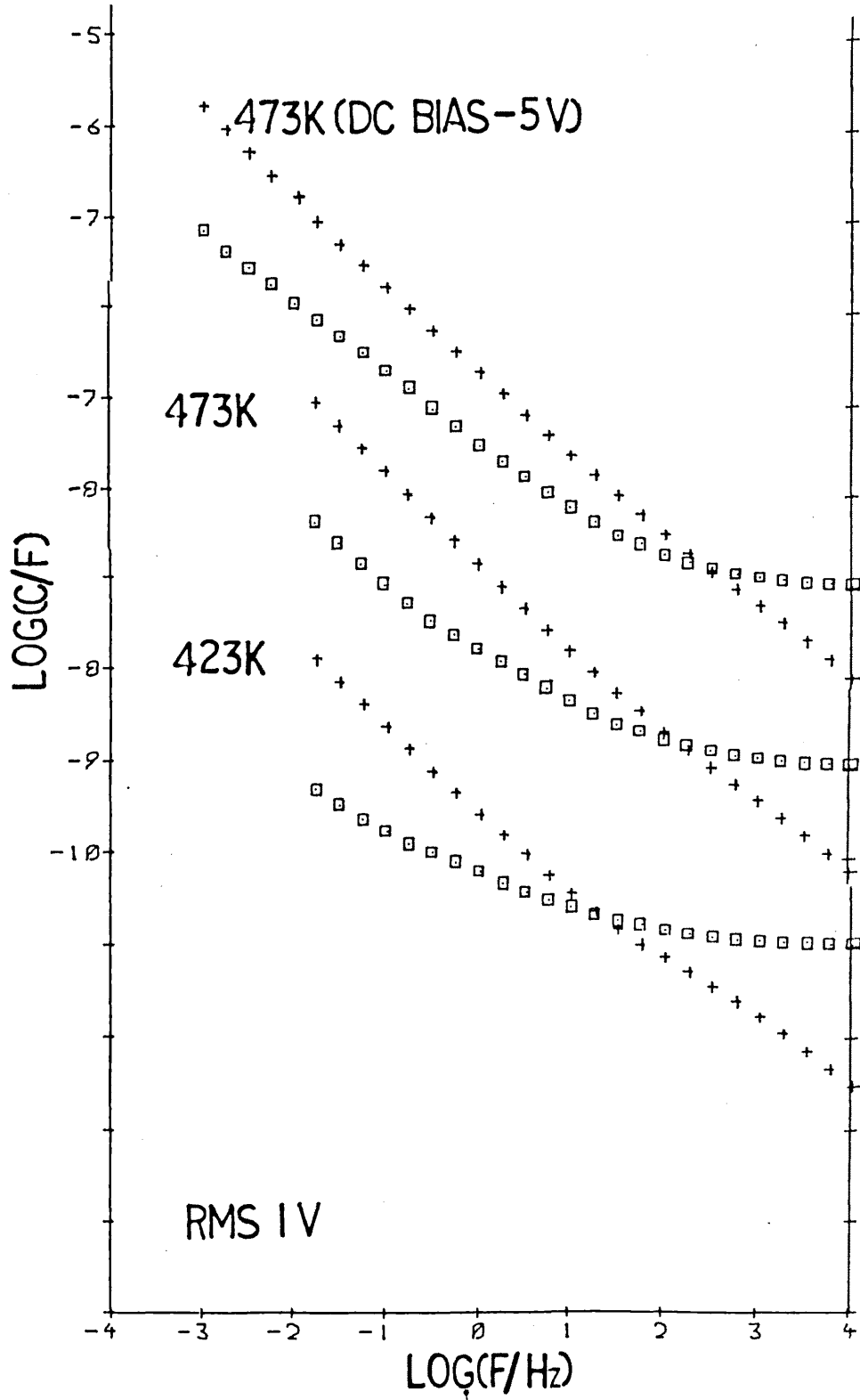
Figure 8.15

8.5. Class II Type Material

These materials HPT 335, HPT 336 and HPT 314, although still generally classed as semi-insulating, have d.c. conductivities of two orders of magnitude higher and significantly lower thermal activation energies than those materials of the Class I type.

The dielectric spectra of both HPT 336, Figure 8.17 and HPT 314, Figure 8.19, are dominated by a diffusive process with parallel d.c. conductivity very similar to that seen for Ag contacted MI 1579 at its higher temperatures. These responses are supported by theoretical curve fitting. It was expected that the dielectric response for HPT 335 would be similar. Figure 8.16, 8.18 and 8.20 show the d.c. characteristics of HPT 336, HPT 314 and HPT 335 respectively. Samples of HPT 335 and HPT 336 were left overnight and a repeat measurement of their d.c. characteristics was attempted. However, on doing so, both sample assemblies produced a shorting-out (R = 0) of the circuit.

Figure8.16

HPT 336/AG
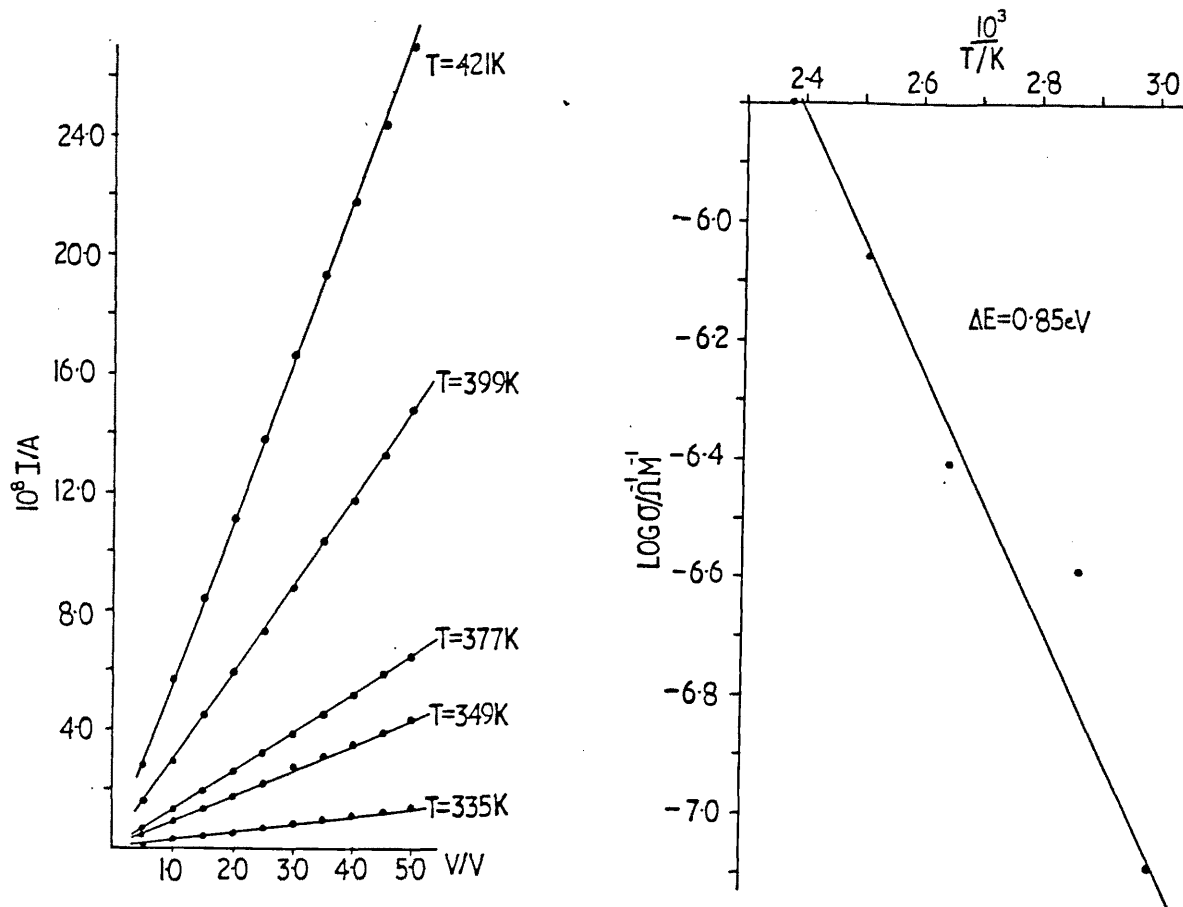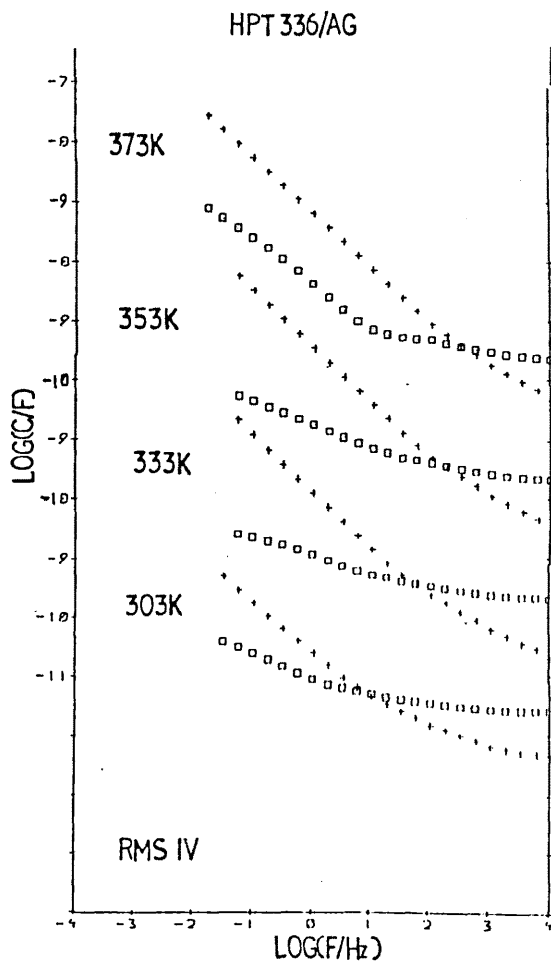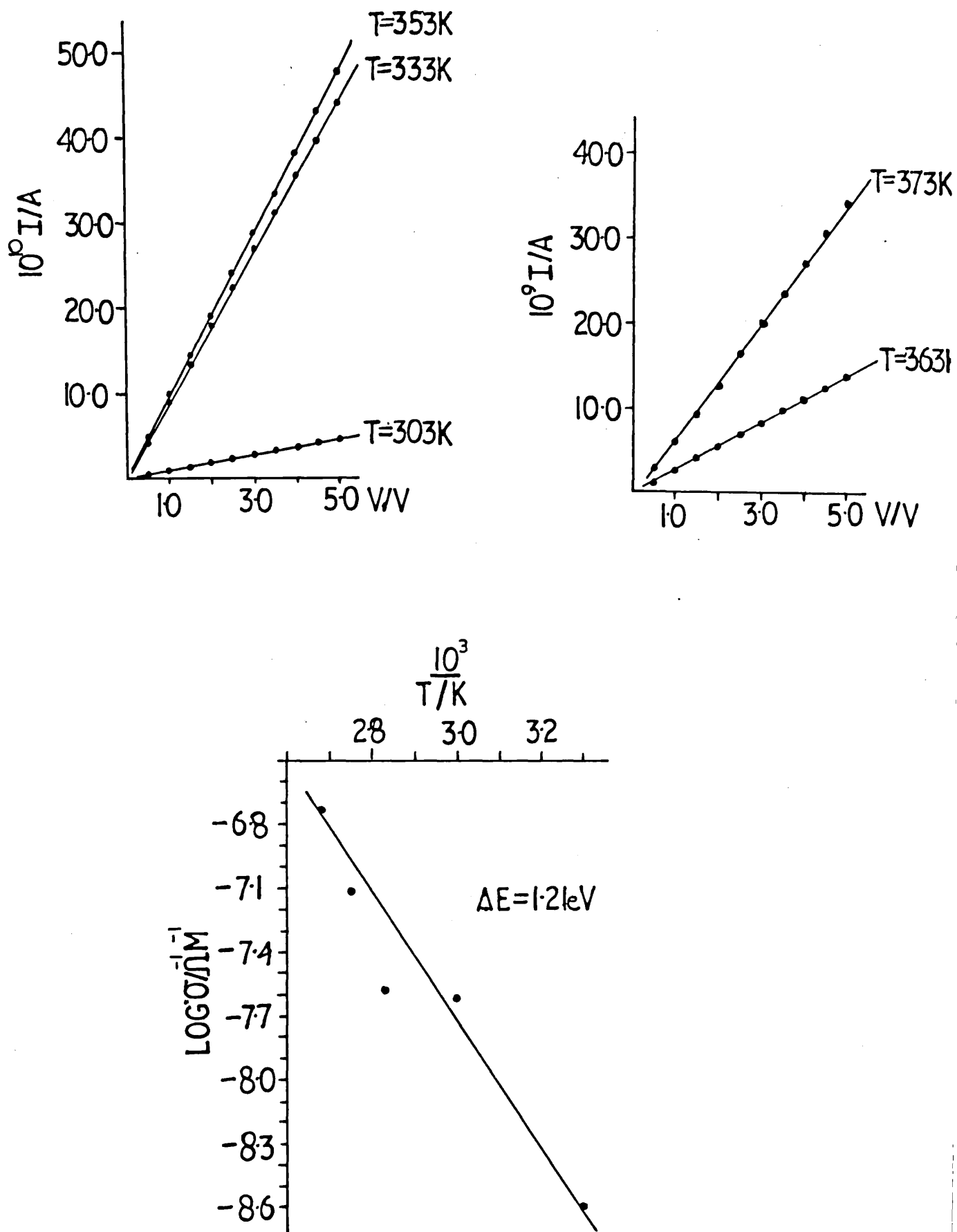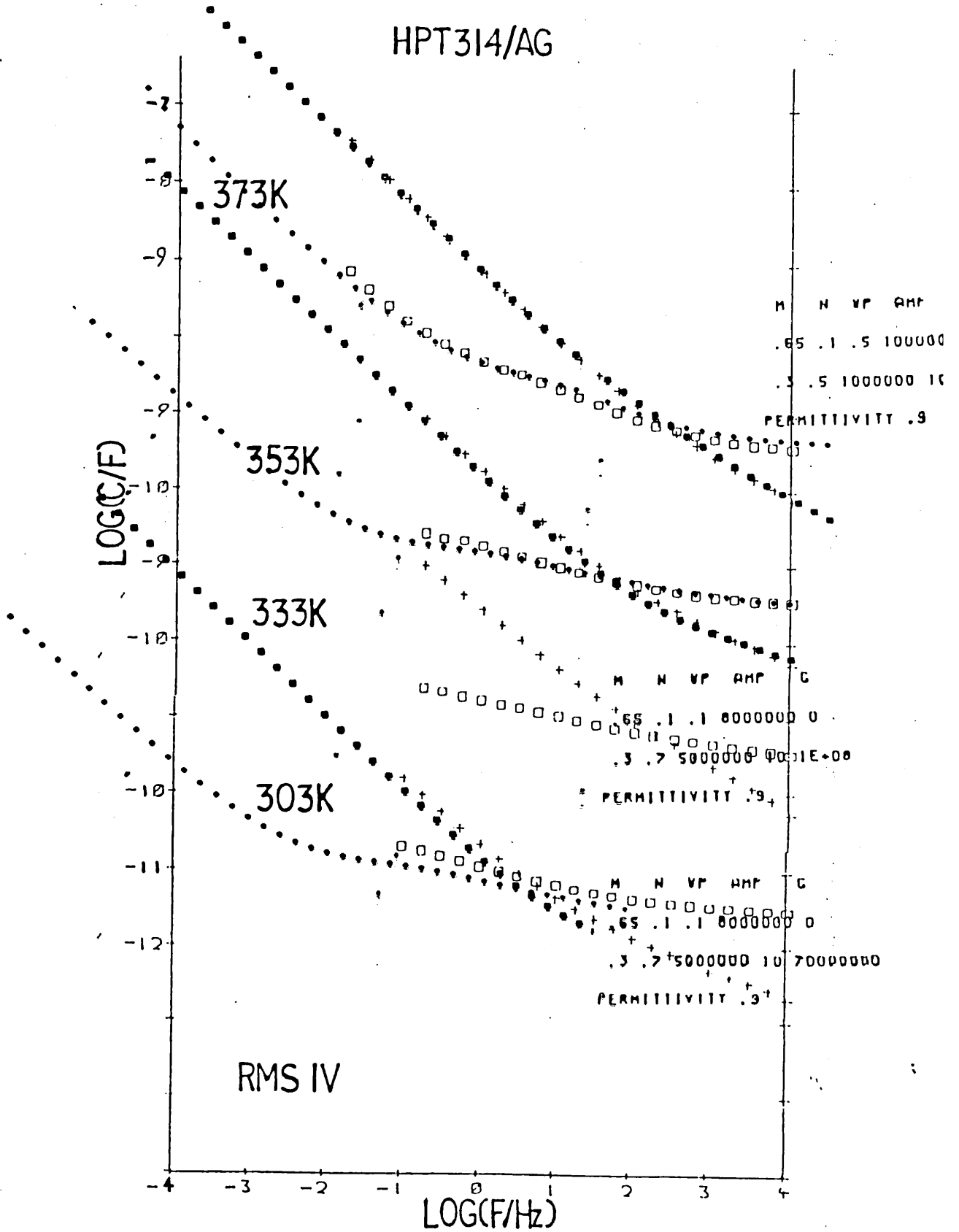
Figure 8.17

Figure 8.18

Figure 8.19
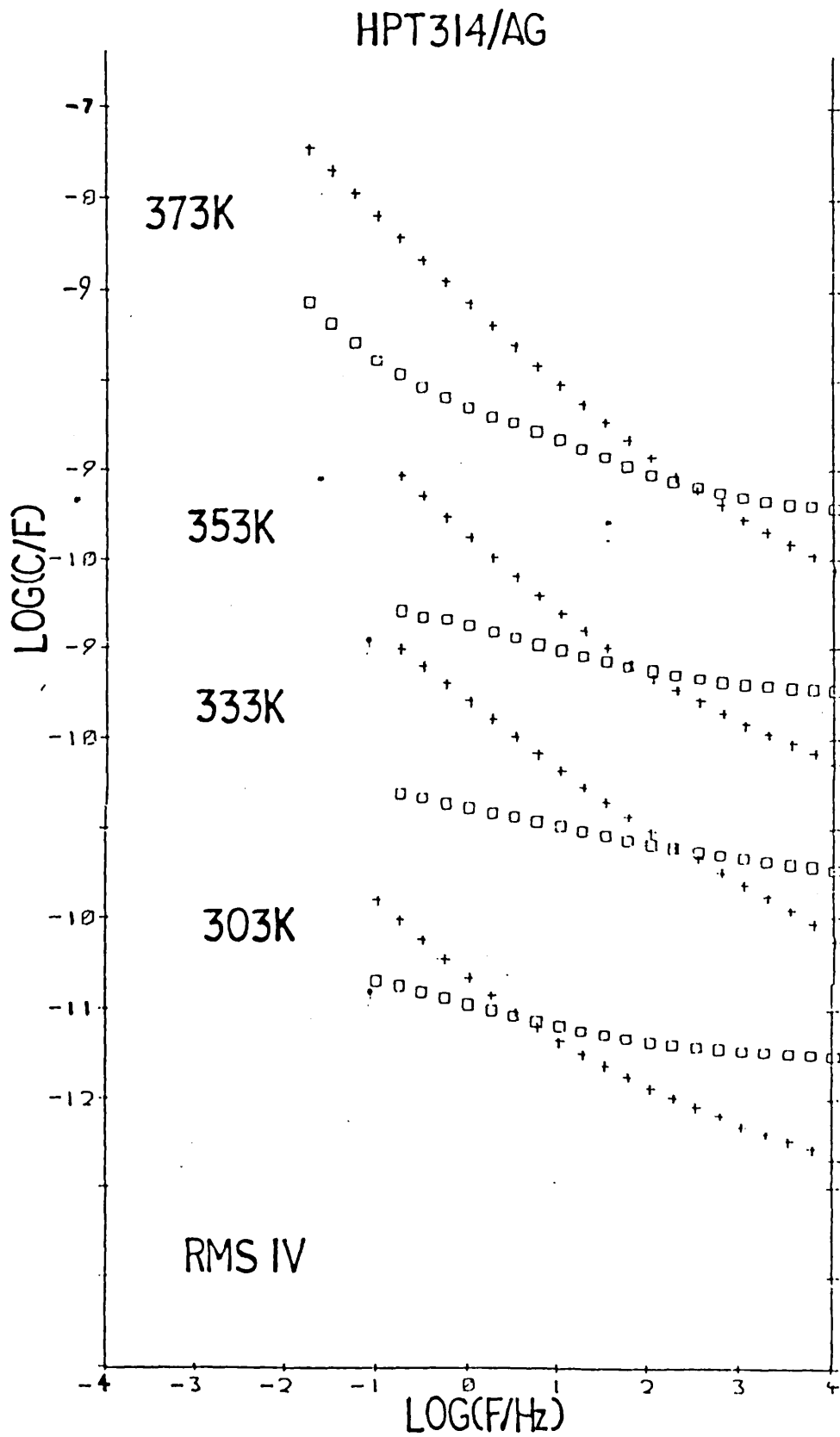
Figure 8.19
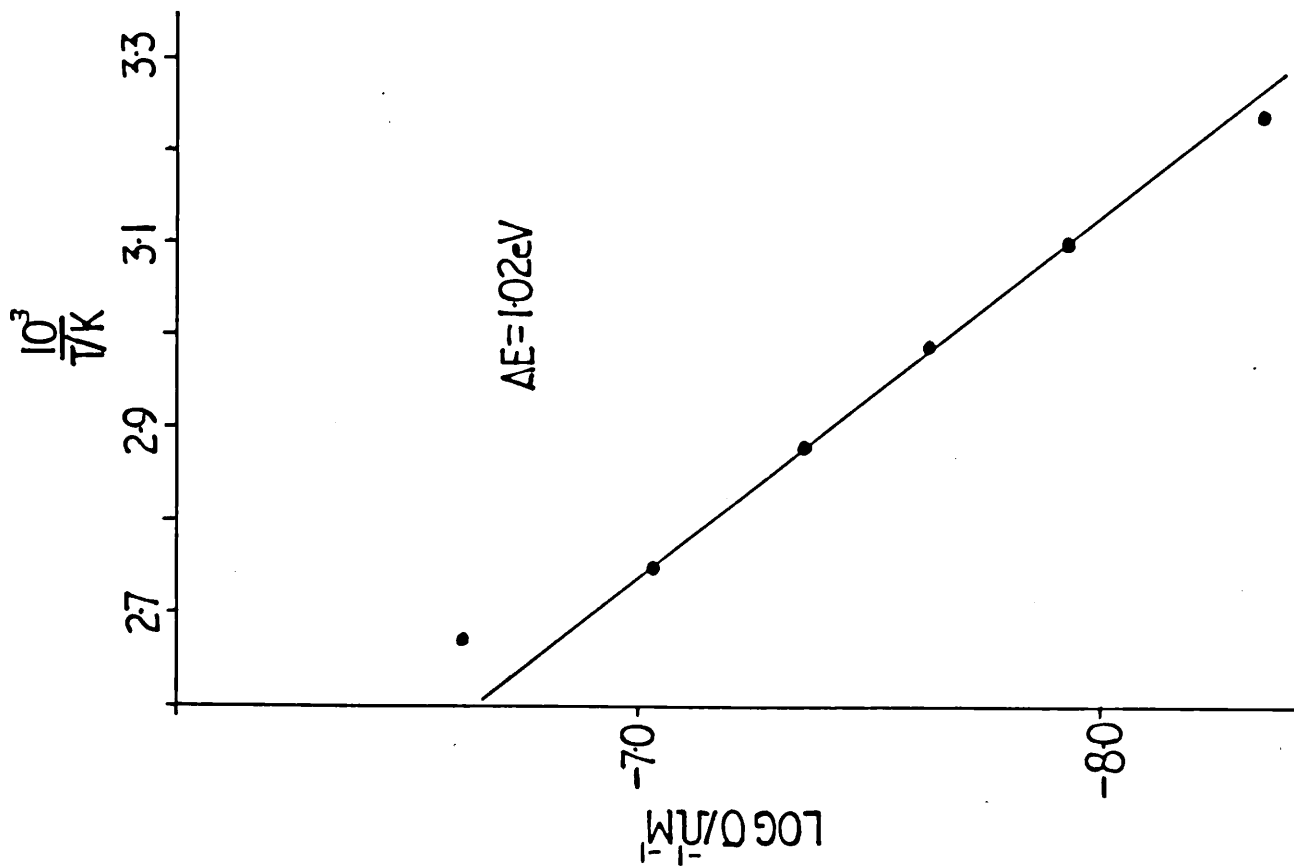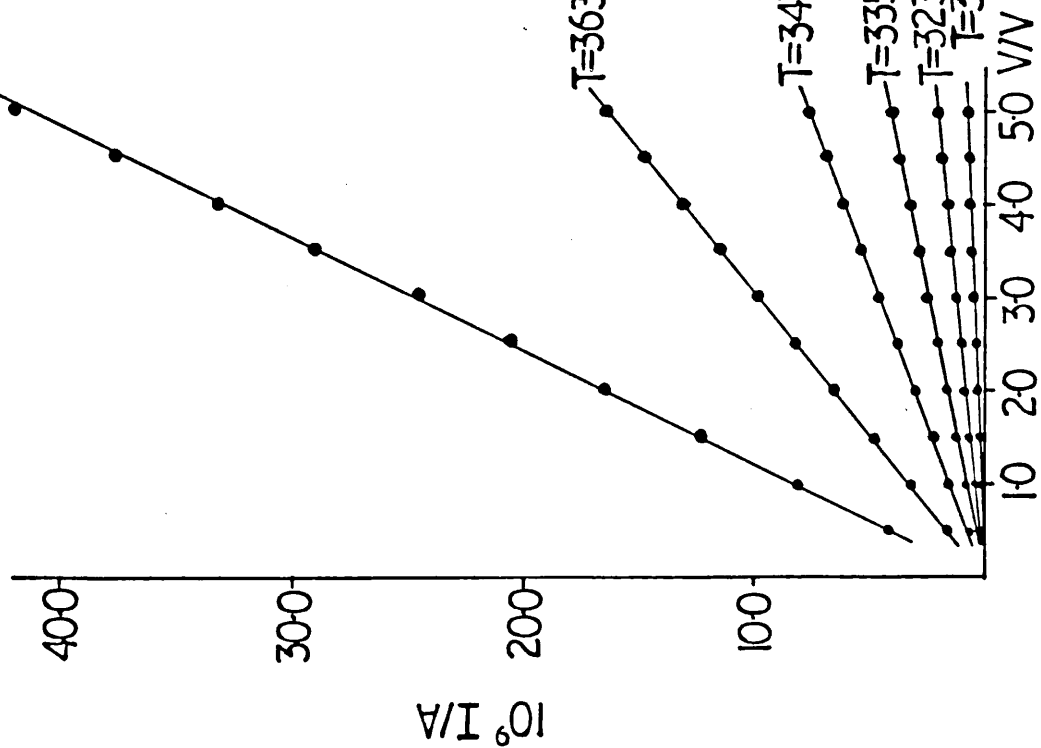
Figure 8.20

8.6   Class III Type Material

This material (HPT 297) is semi-conducting with a d.c. conductivity of $4.82 \times 10^{-6} \ \Omega^{-1} \ m^{-1}$ at 373 K and a thermal activation energy of 0.66 eV (assuming the material to be intrinsic), Figure 8.21. It has been placed in a class of its own for two reasons: (i) its three order of magnitude increases in d.c. conductivity over HPT 289 has been brought about simply by the replacement of one of the phenyl rings of the Ph_4P^+ cation by a methyl group, and (ii) its Ag contacted dielectric response classically illustrates a diffusive process.

Three different contacts were investigated. The silver paint contacted material shows two distinct dispersions in the complex capacitance, and the ω^{-1} frequency dependence of the loss component shows clear evidence for d.c. conductivity even at the lower temperatures, Figure 8.22. The In contacted material shows a distinctive saturation of the complex capacitance at low frequencies, however the diffusive process ·is still evident. The pressure contact, however, which involves sandwiching the sample between two copper disc electrodes, shows LFD, Figure 8.23(b).

Both the Ag paint and In contacted materials involve the application of Ag paint to the sample; the former directly and the latter to attach the vacuum deposited In layer via copper wire to the external measuring circuit. Thus it is possible in both cases for silver paint to diffuse into the bulk material itself. This appears to be borne out, in that, contact effects (silver paint diffusion), are seen in the dielectric spectra of both samples. Whereas, in the absence of Ag paint, as in the pressure contacted material, no contact effects are visible. It appears then, that the diffusive processes observed in many of our samples

HPT 2971AG
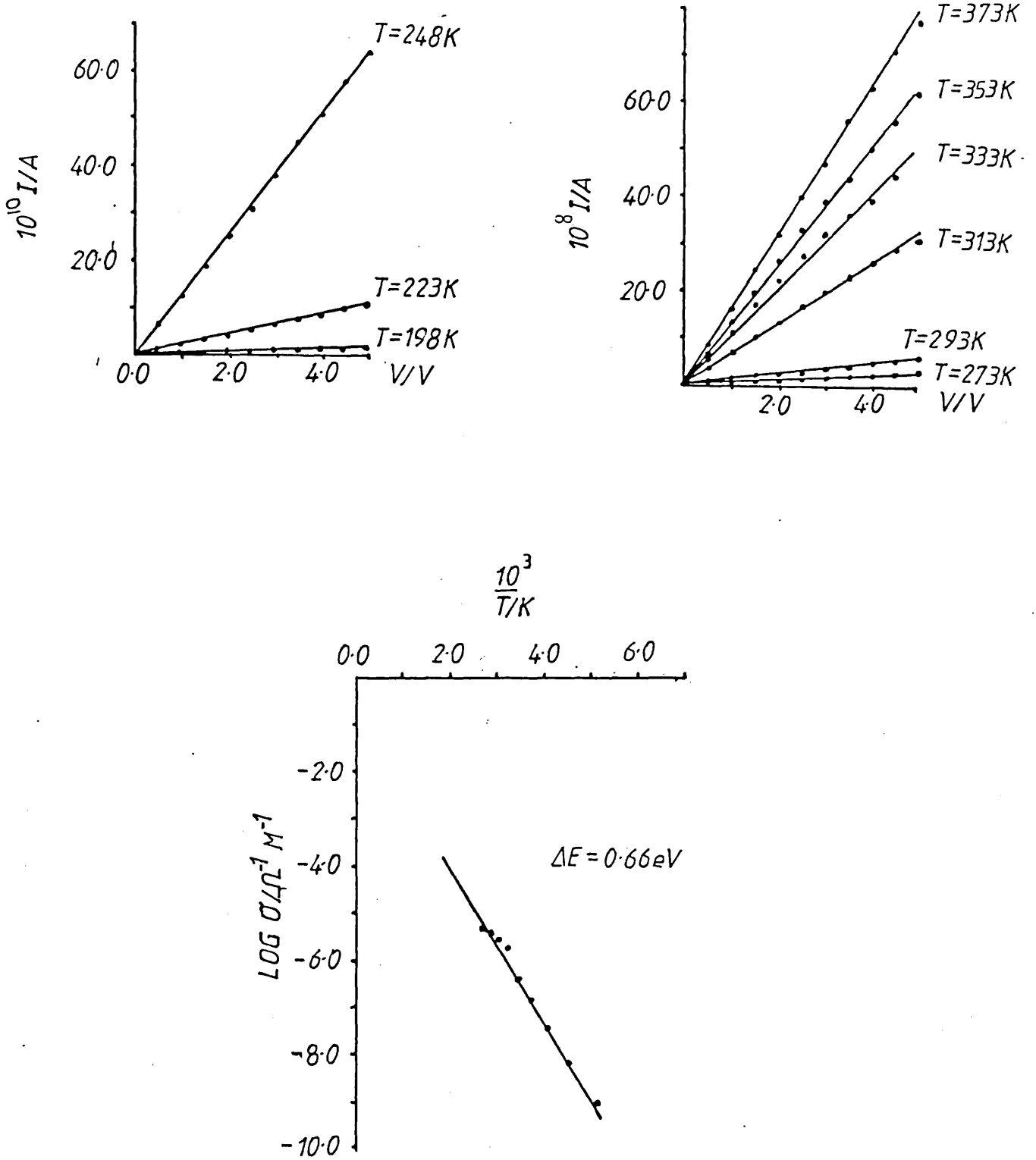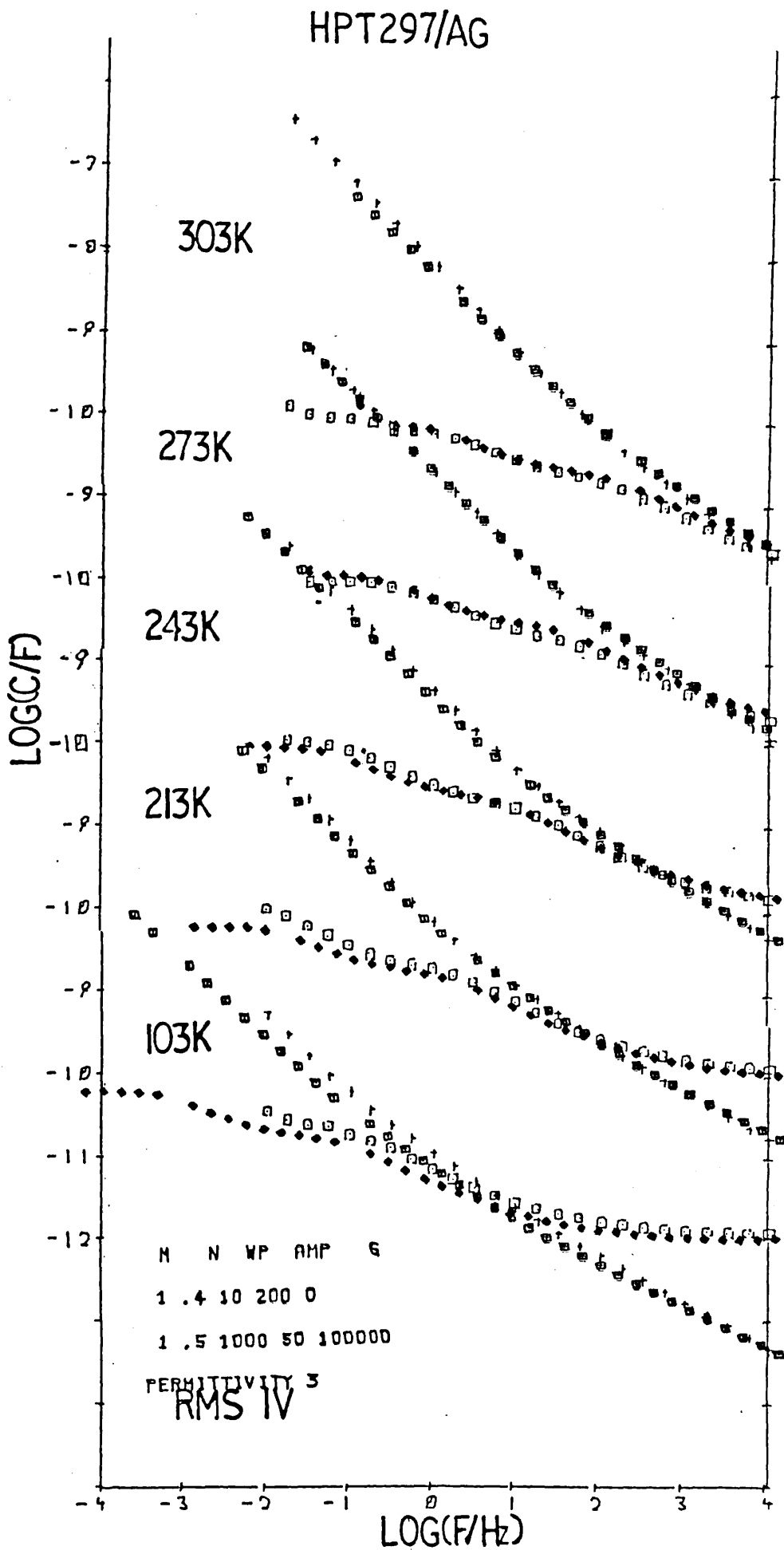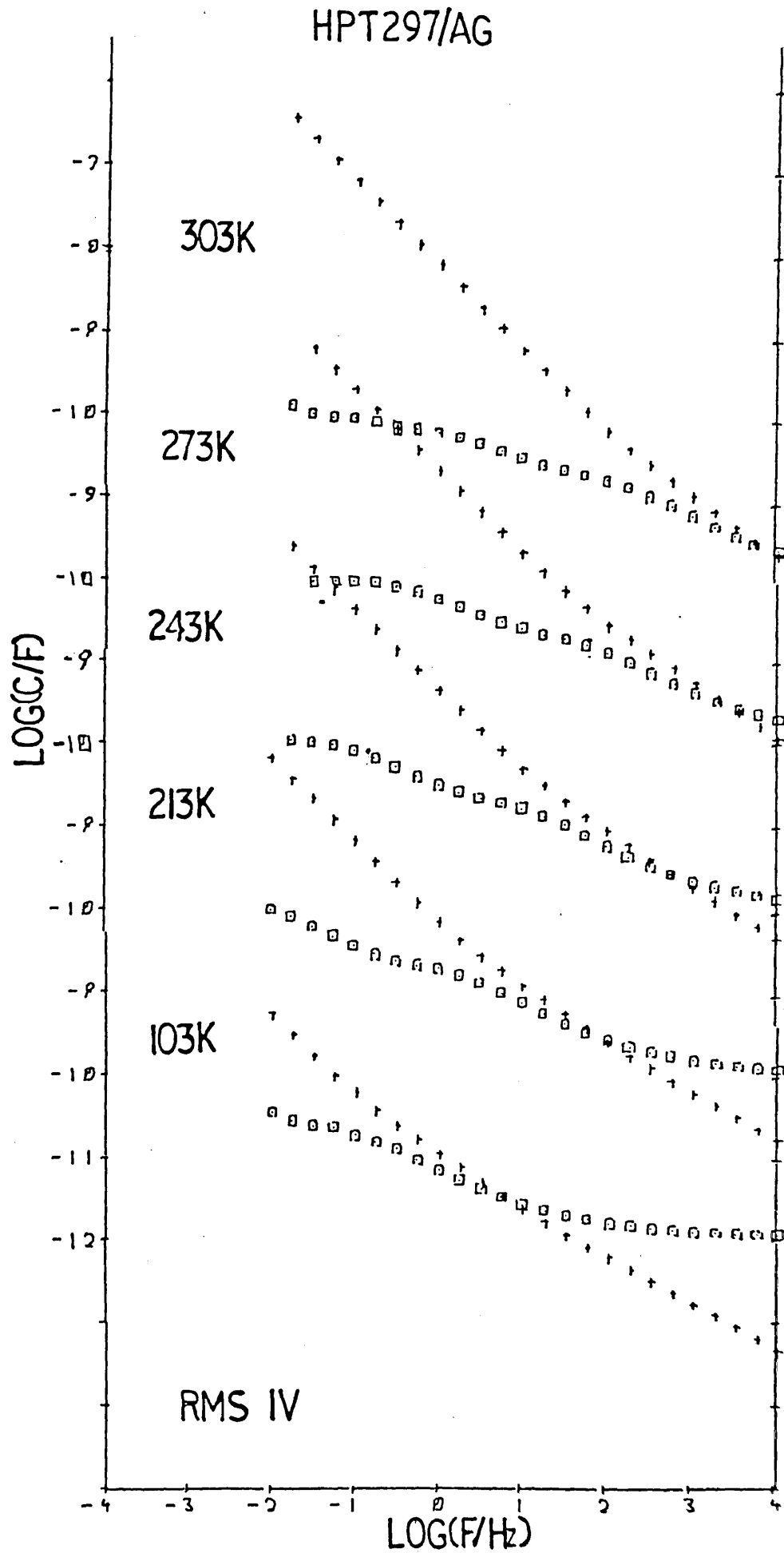
Figure 8.21

HPT297/AG

Figure 8.22

Figure 8.22
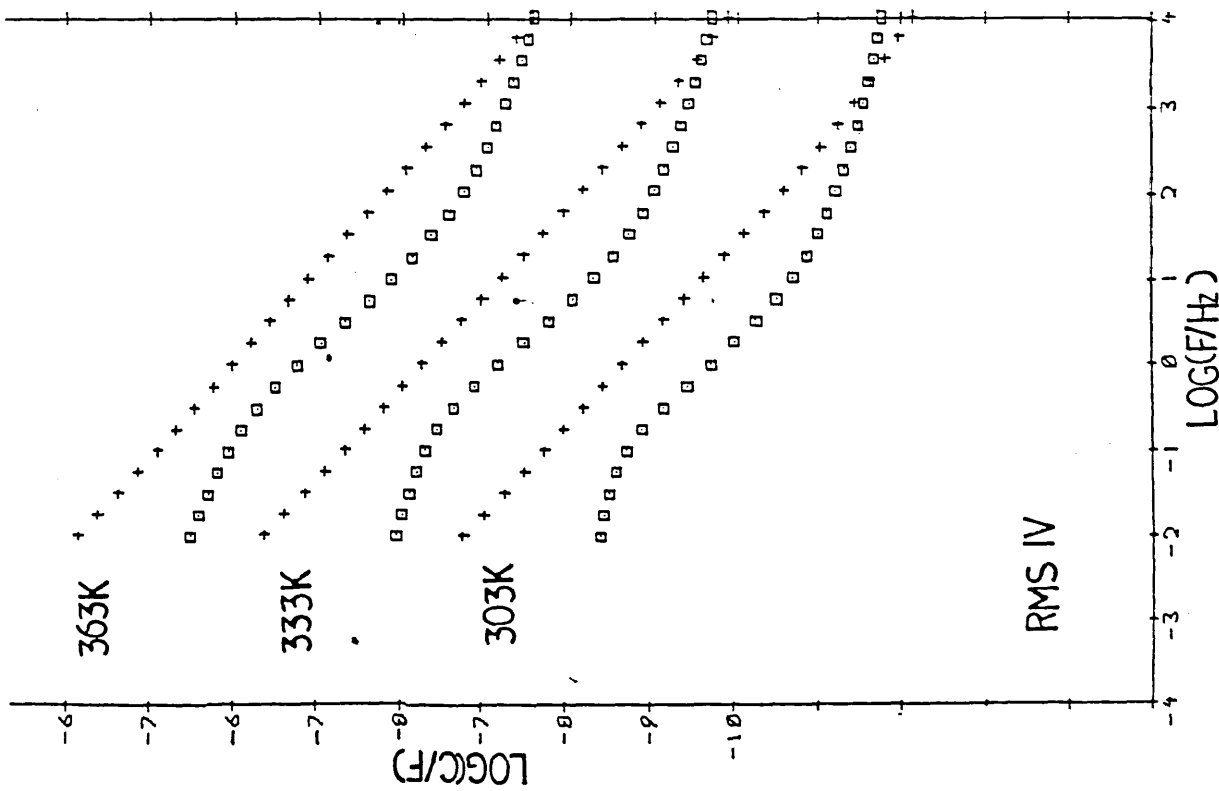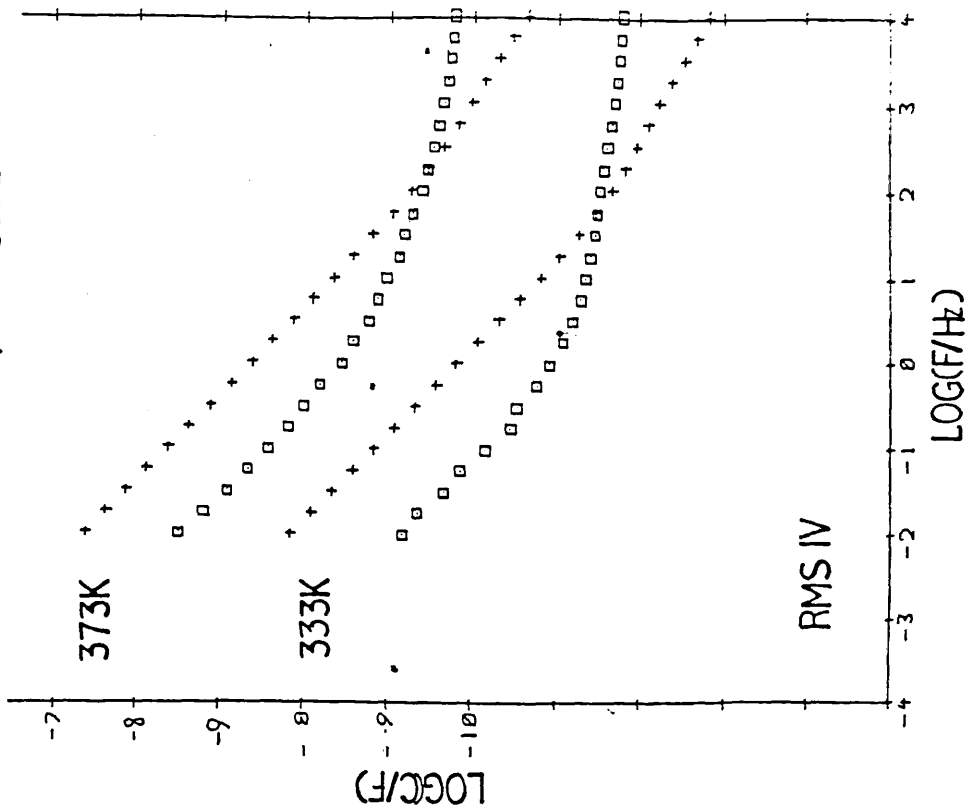
Figure 8.23

dielectric responses are most likely the result of Ag paint diffusion.

8.7. Class IV Type Material

These materials like HPT 297 are semi-conducting with d.c. conductivities of the order of $10^{-5}\Omega^{-1}m^{-1}$ at 373 K, Figures 8.24, 8.26 and 8.28. There is evidence to suggest the existence of two different types of charge carrier being present in these materials (electronic as well as ionic). This is supported by the theoretical curve fits.

The dielectric responses of HPP 337, HPT 320 and HPT 325, Figures 8.25, 8.27 and 8.29, respectively, are virtually identical showing at higher temperatures a small, followed by a very large, dispersion in complex capacitance.

HPP337/AG
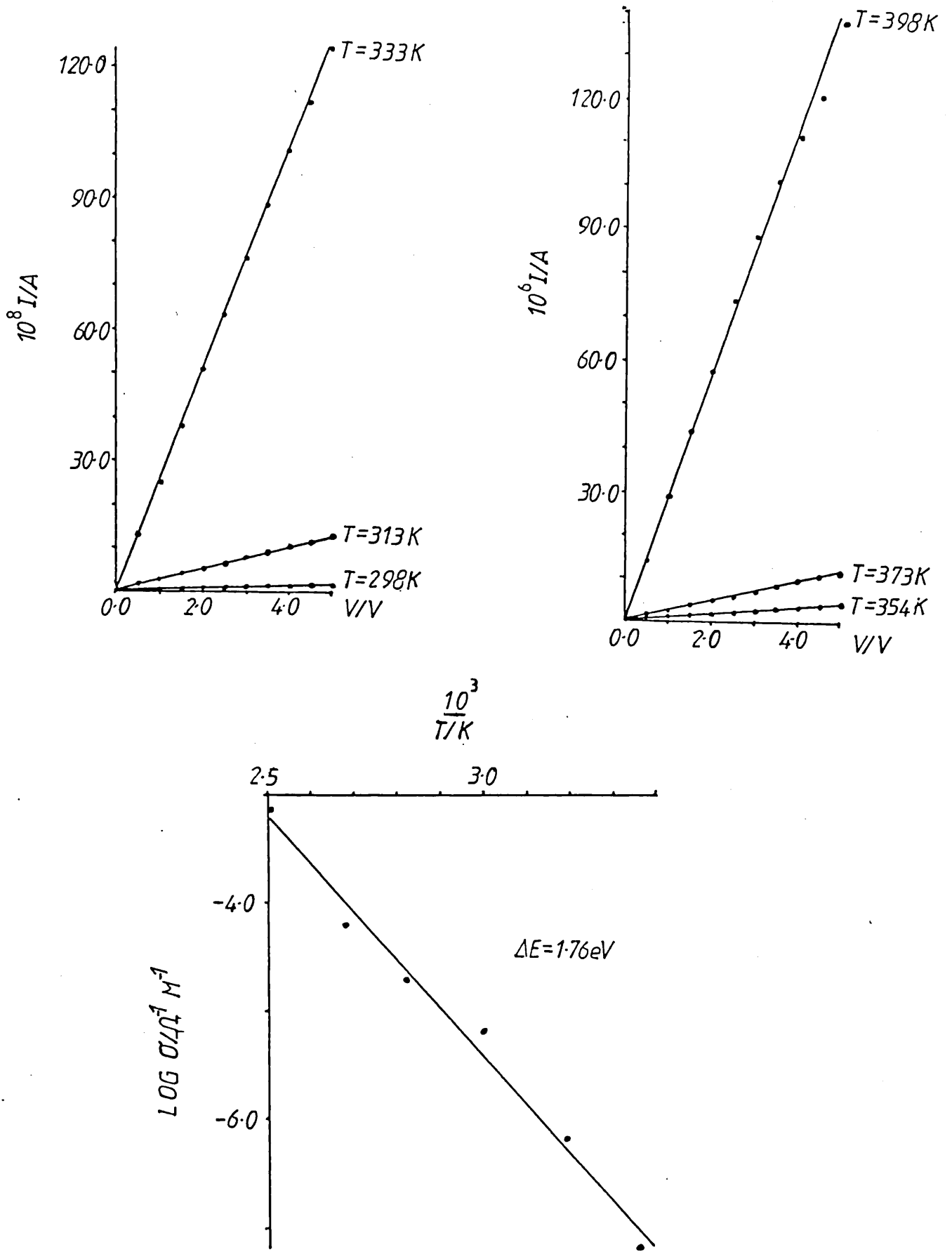
Figure 8.24

Figure 8.25

Figure 8.25

Figure 8.26

HPT 320/AG

373K

354K

334K

327K

315K

298K

RMS IV

LOG(C/F)

LOG(F/Hz)
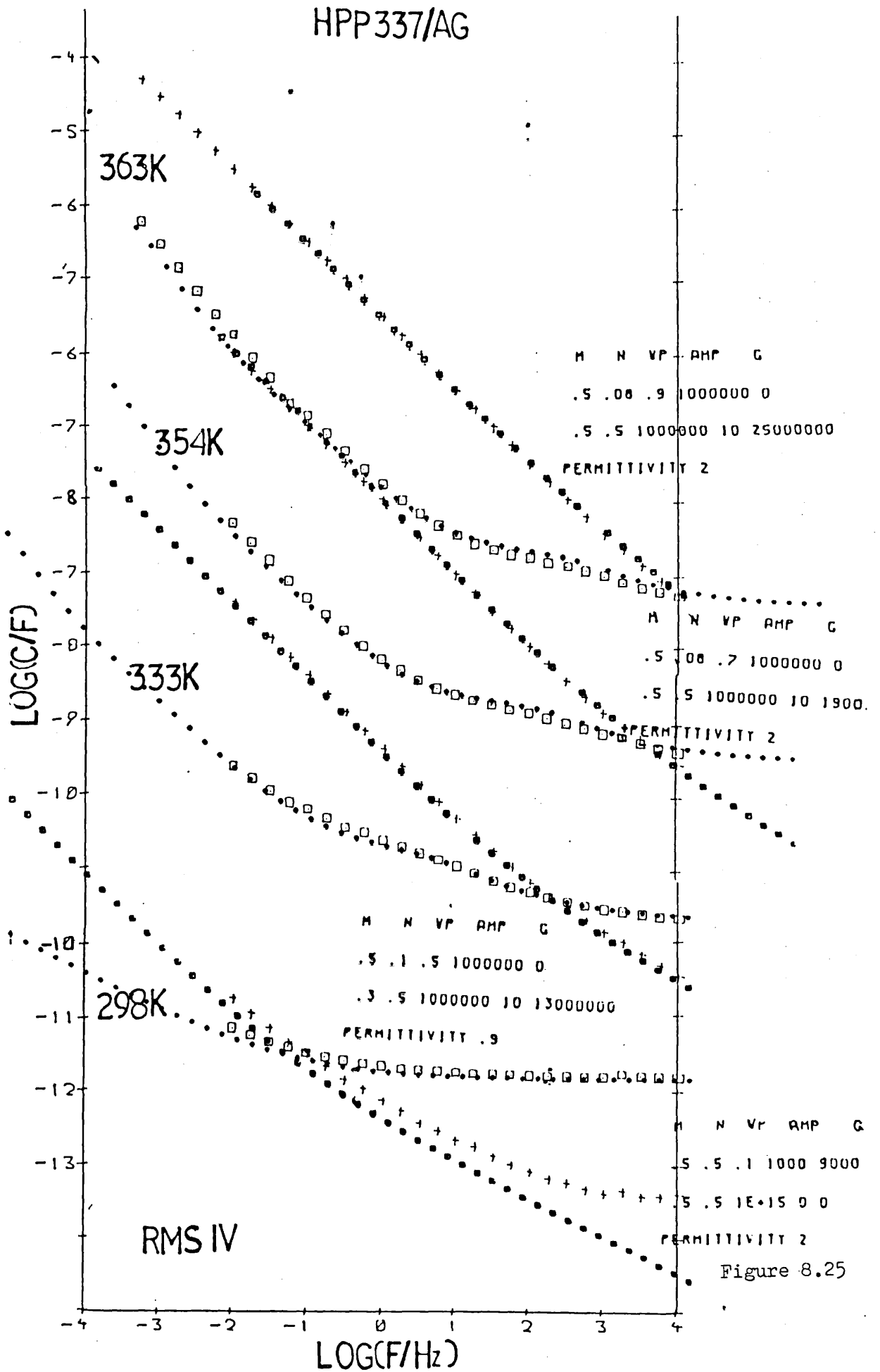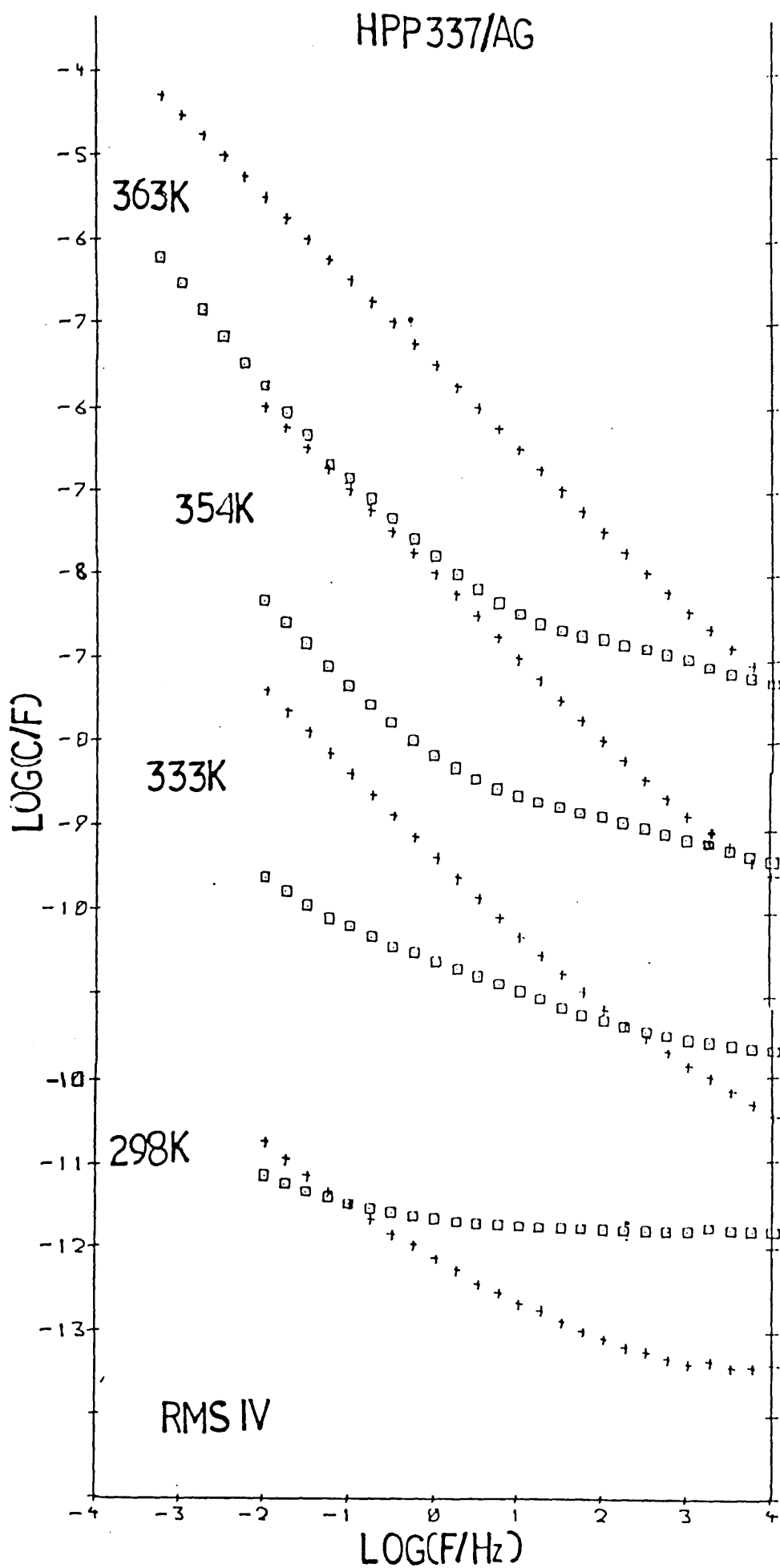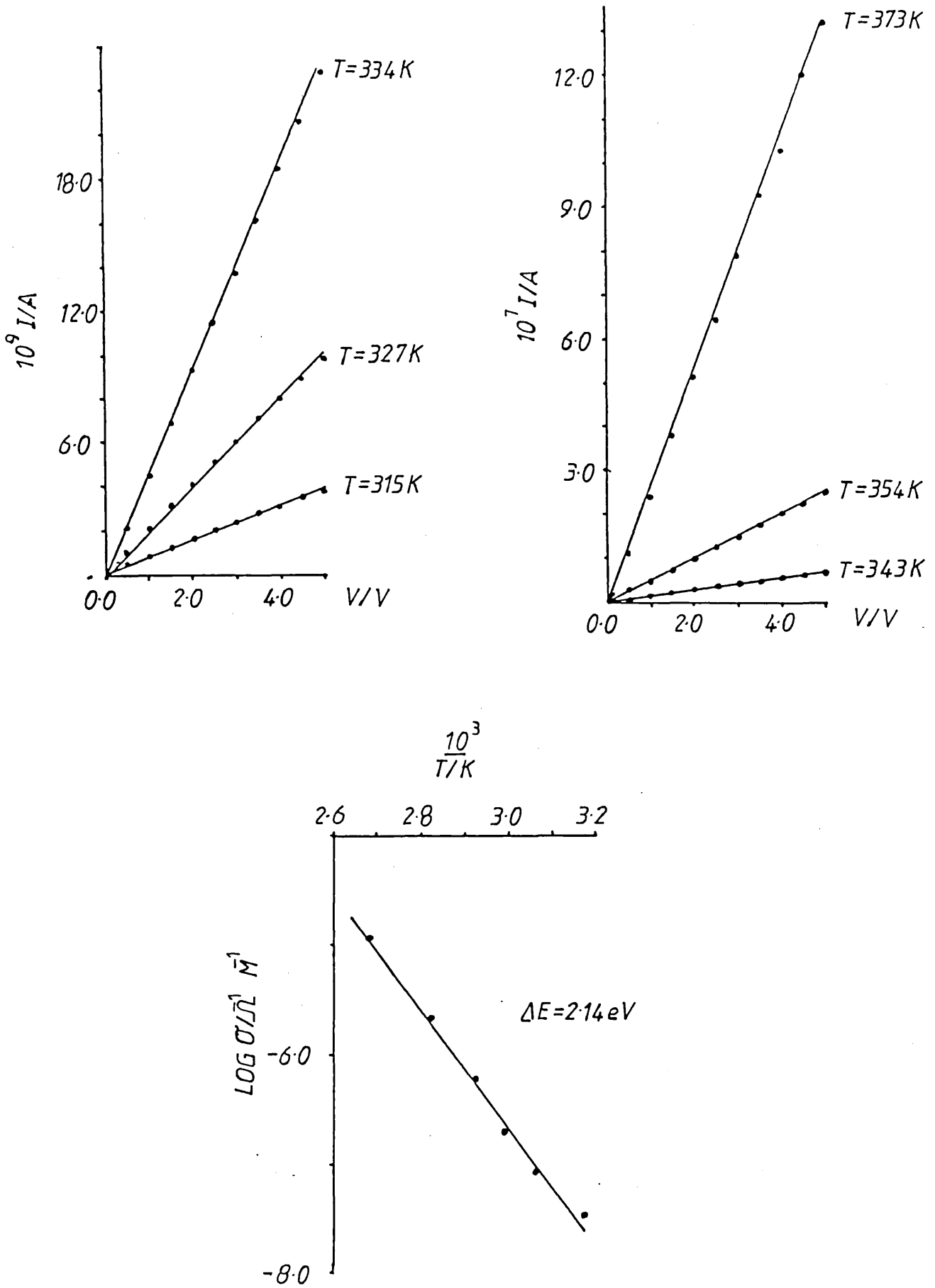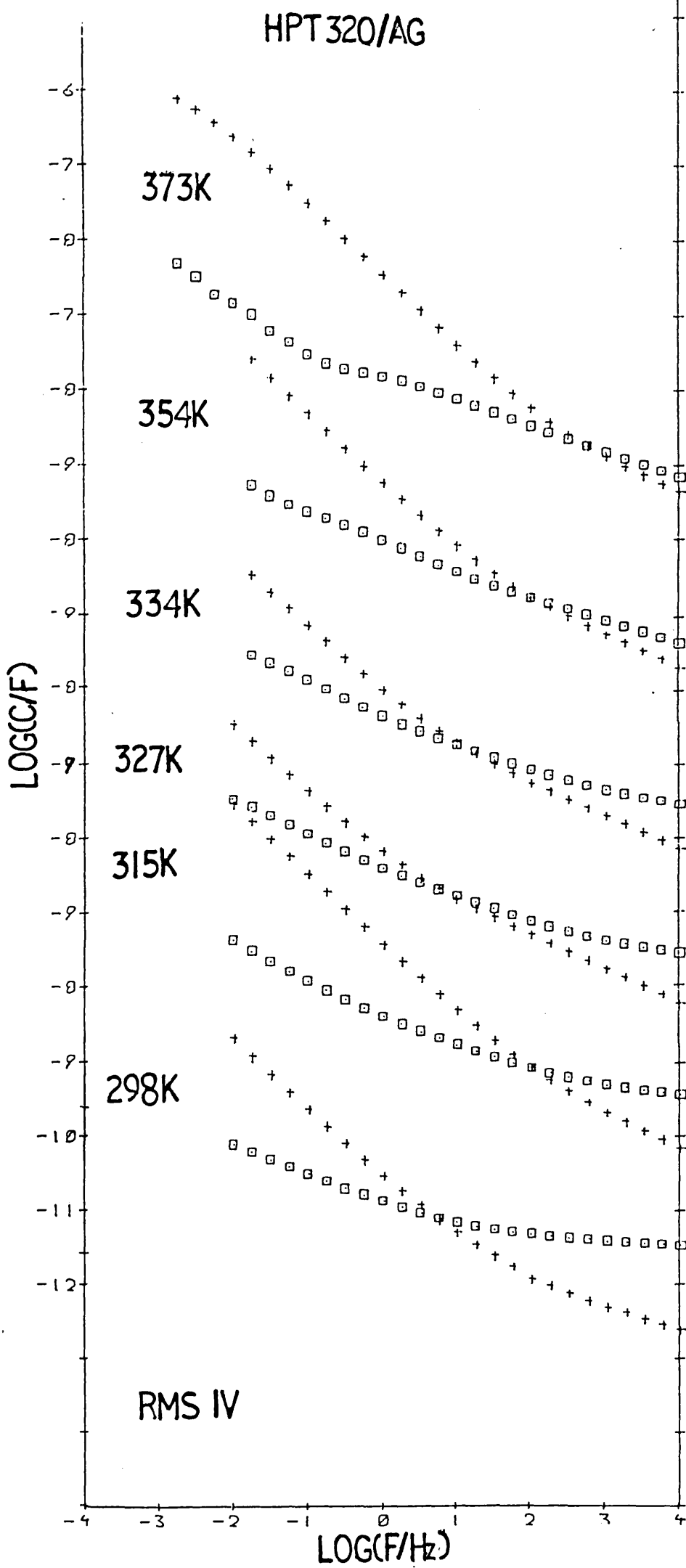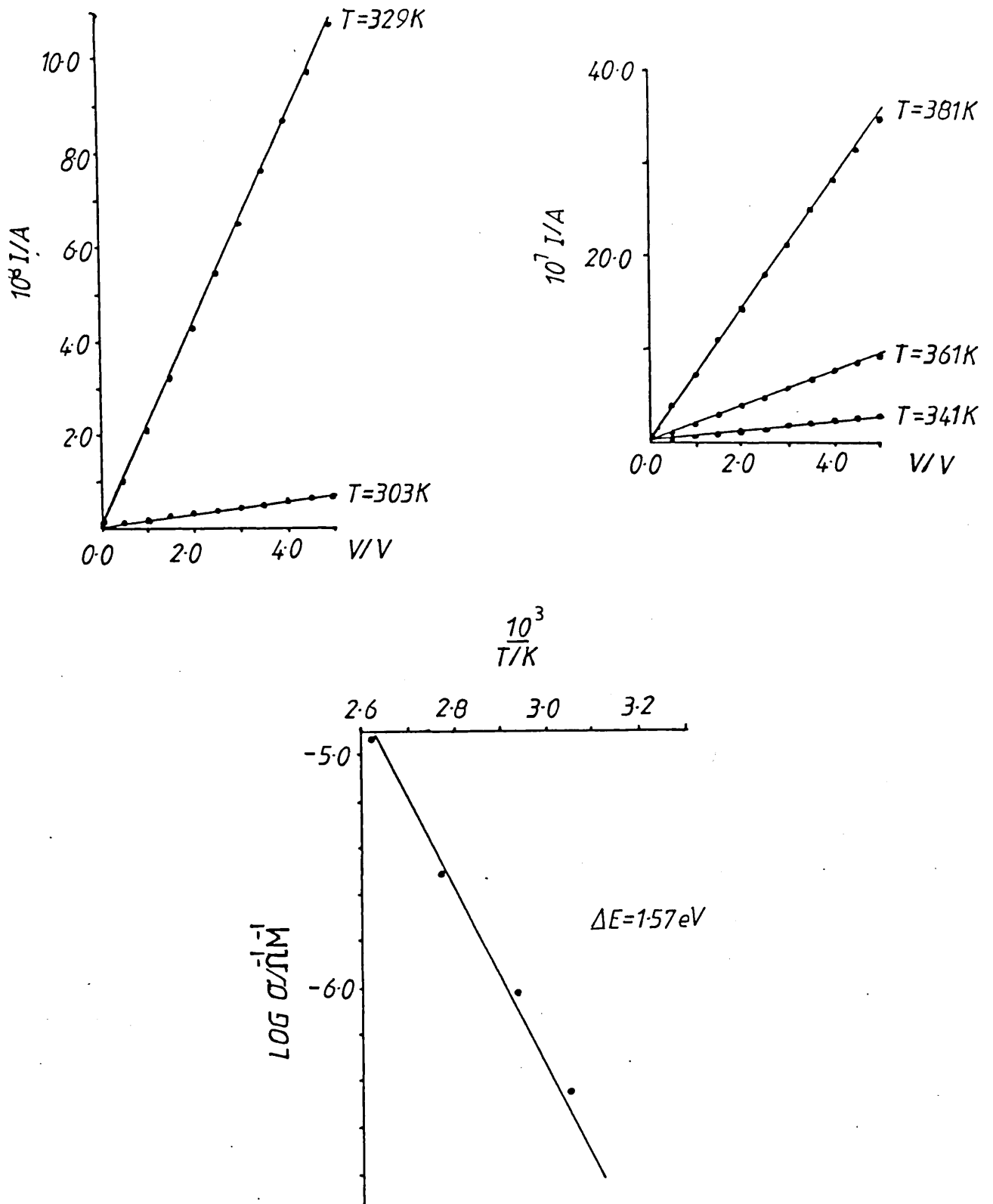
Figure 8.27

HPT 325/AG
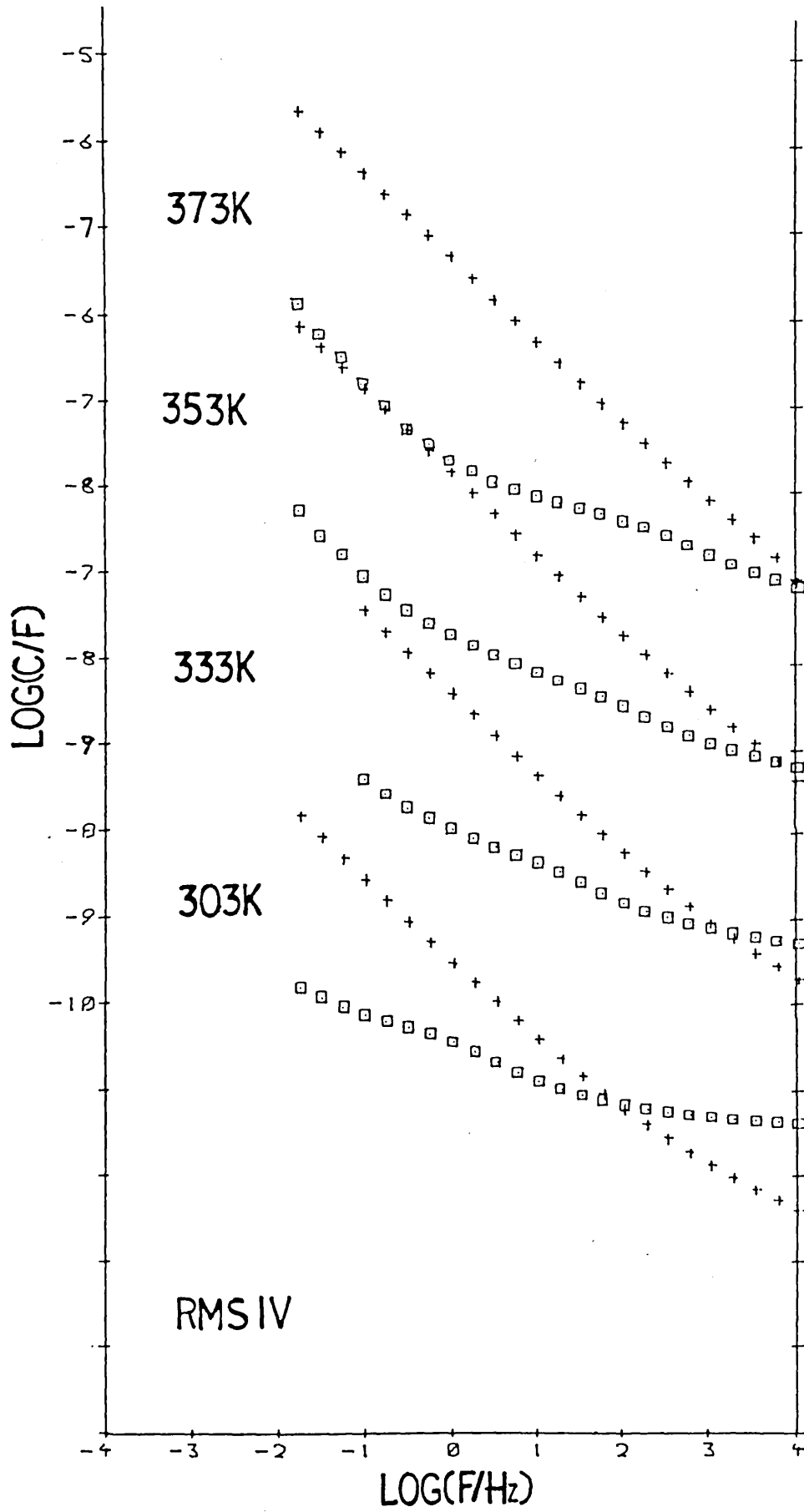
Figure 8.28

Figure 8.29

8.8.   Class V Type Material

Both the d.c. conductivity and dielectric response measurements were carried out on a sample of this tetrathiafulvalene dye complex HPT 332 sandwiched between two copper disc electrodes to overcome the considerable problems of silver paint diffusion encountered. Possibly as a result we observed non-linear current-voltage characteristics (non-Ohmic), Figure 8.30. The dielectric spectra reveal a d.c. conductivity, carrier dominated response, Figure 8.31. This infers that charges are moving from one electrode to the other and that contact barrier effects are absent, which seemingly contradicts the d.c. measurements. One has to bear in mind, however, that for the dielectric measurements we are dealing with voltages of the order 0.1 V. It is not clear from our d.c. measurements whether the non-Ohmic behaviour extends to these lower voltage values. Time did not permit further detailed investigation of this sample, however, we were able to obtain an estimate of the d.c. conductivity (at room temperature) by measuring the current passing through our sample at 0.1 V and hence from equations 8.1 and 8.2 deduce a value ($\sigma_o = 8.0 \times 10^{-4} \; \Omega^{-1} \; cm^{-1}$).

8.9.   This work has given us a great deal of information about contact (or electrode) effects and has stressed their importance in influencing electrical behaviour. This is an area that many of our co-workers in the field have totally neglected.

Consider for example, the question of the Ohmic nature of contacts. Equation (8.2) provides the route

$$\sigma_o = G \; \frac{L}{A} \quad \text{where} \quad G = \frac{1}{R} \qquad\qquad 8.2$$
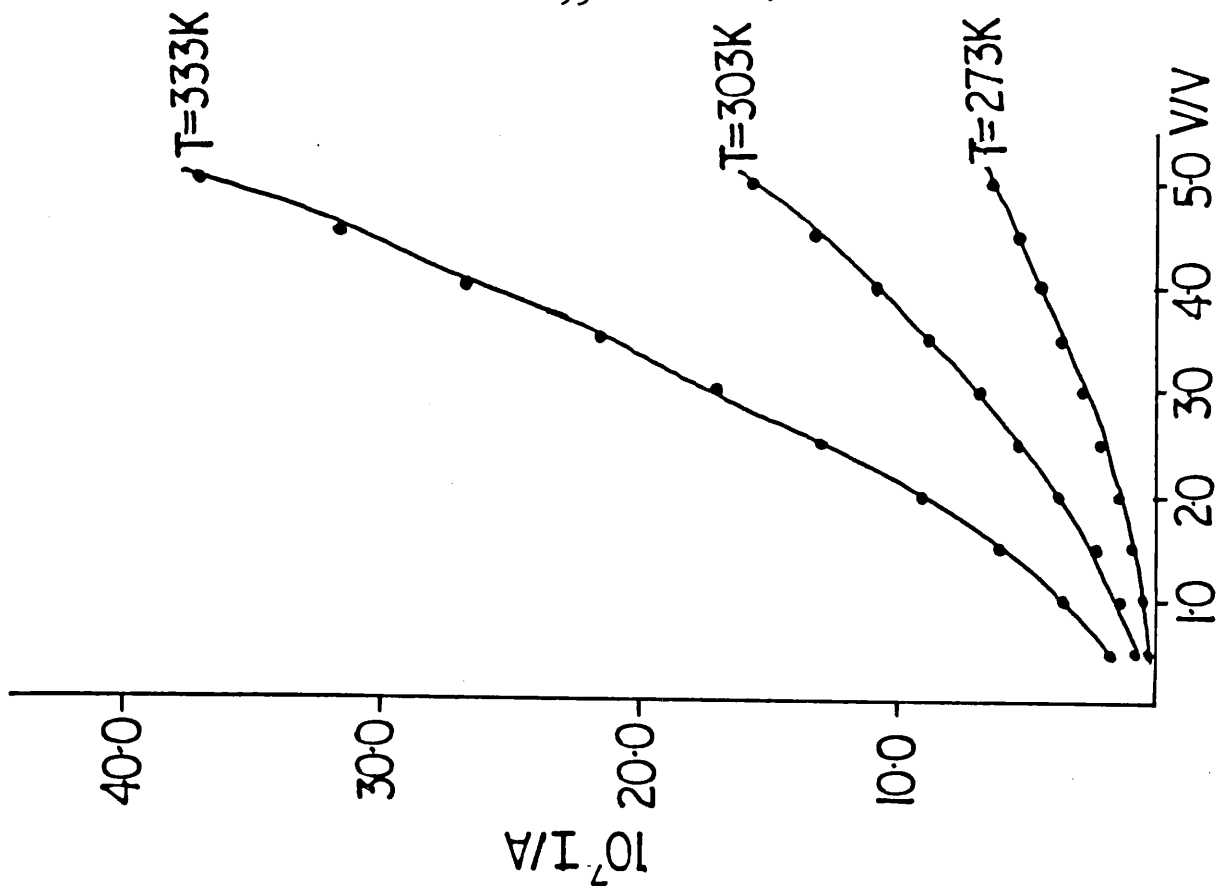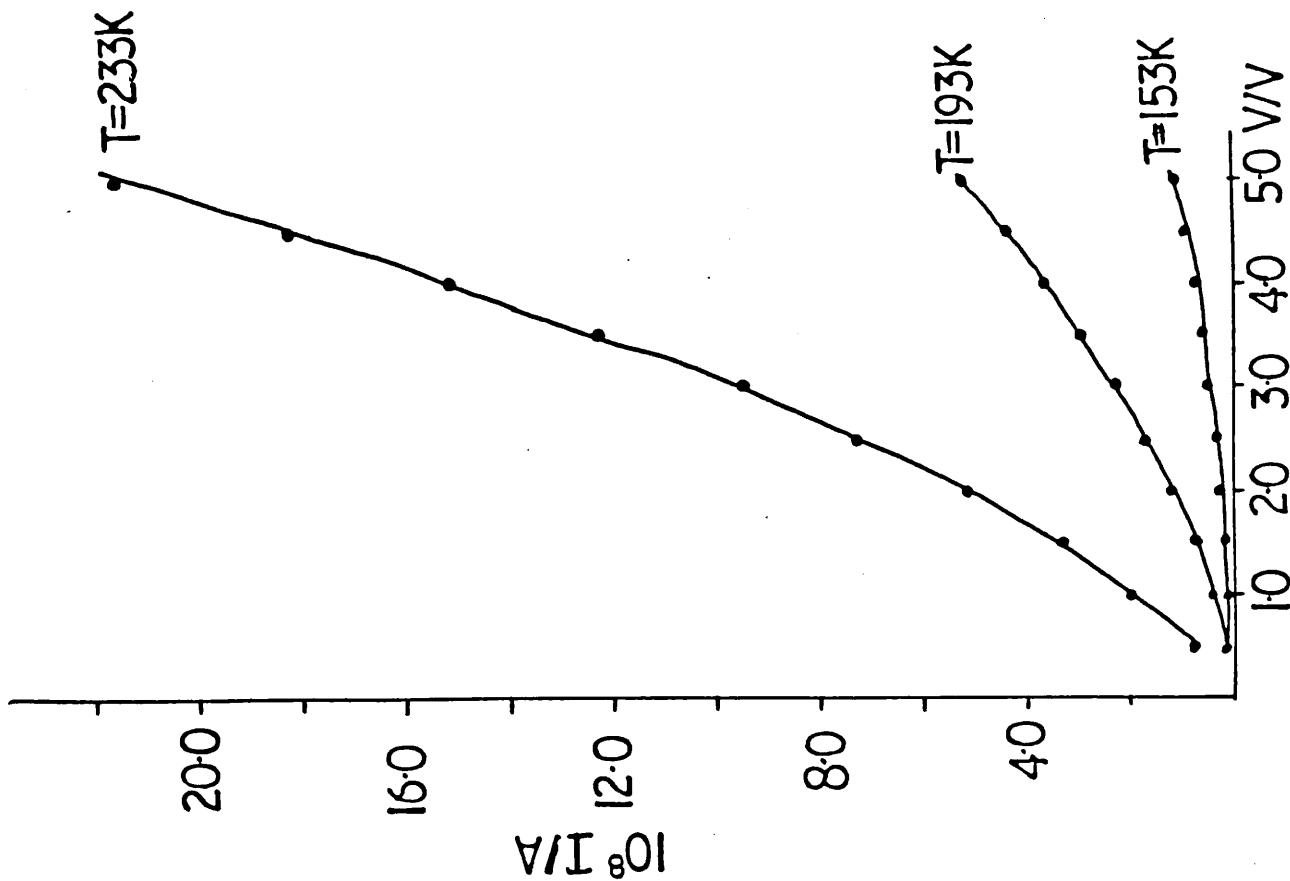
HPT 332/PRESSURE

Figure 8.30
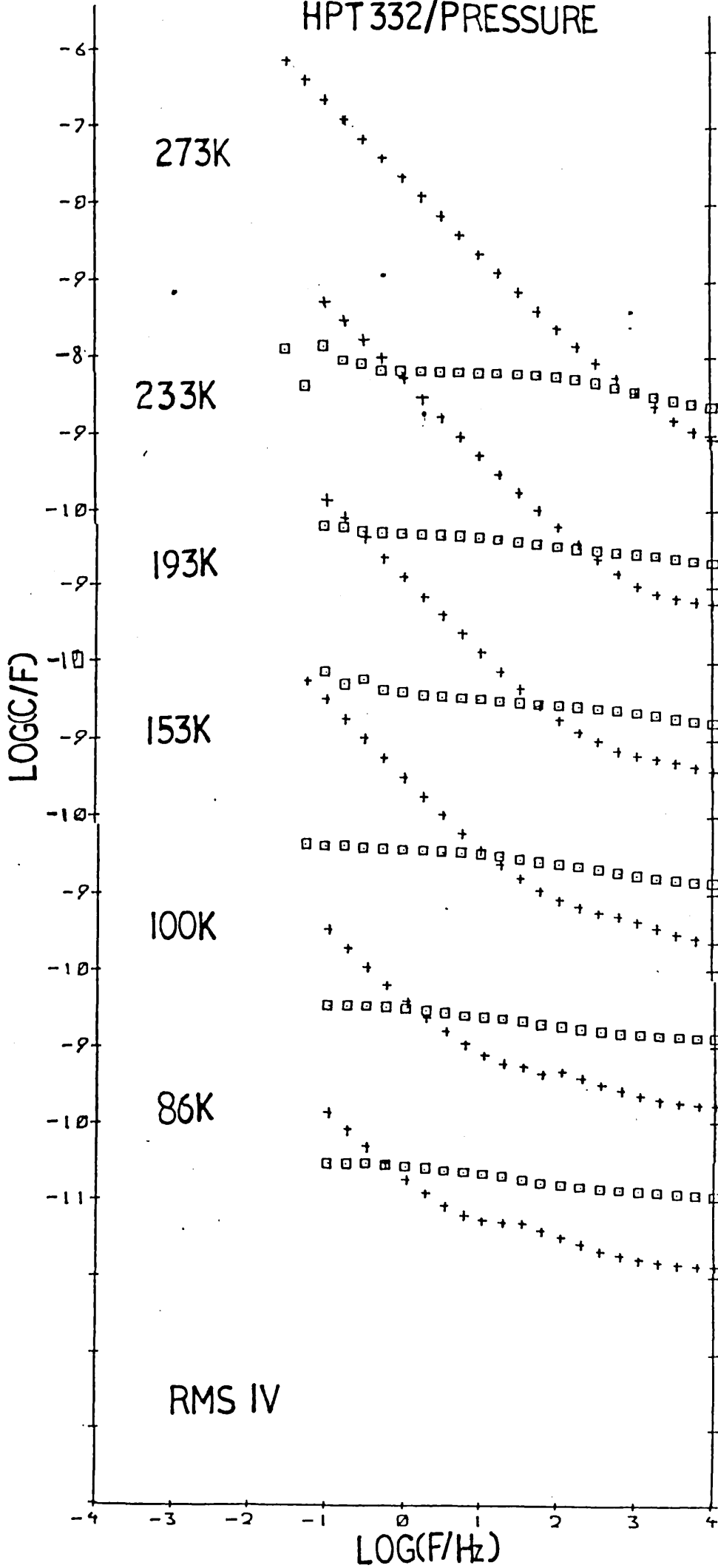
Figure 8.31

Figure 8.31

to obtaining d.c. conductivities, σ_o. If there is not a linear
relationship between current and voltage, as seen in Figure 8.30 then the
resistance, R, is not a constant (voltage independent) at a particular
temperature and hence neither is the conductance, G, nor conductivity,
σ_o. The literature is full of d.c. conductivity values calculated on
the strength of one isolated conductance measurement, neglecting the
nature of the contact.[37,48] These numbers mean nothing on their own.

Silver paint is the most commonly used material for contacts. We
have seen its diffusive properties, section 8.4. This has a number of
effects on d.c. conduction. Firstly, if the silver paint is diffusing
into the sample then we cannot accurately define either L or A from
equation (8.2). Secondly, the non-uniformity of the electrodes will give
rise to a non-uniform field across the sample, Figure 8.32. If one takes
an isolated point at which silver has diffused, then at that point there
will be a high field intensity (b). This then results in the drift of
ions, where present, towards their oppositely charged electrodes where
they are oxidised or reduced. This process, then, continues until, as in
the case of the metal ion, M^+((c) to (d)), it produces a thin metal
filament through the sample eventually short-circuiting the system. The
rate at which this process occurs is obviously dependent on a number of
factors, e.g. charge and size of the drifting ion, etc. This process
(electrophoresis) is not confined to charged species, formally neutral
entities behave in exactly the same way (dielectrophoresis).[82]

Blocking contacts (section 8.1.2) and electron injection (section
5.4.5) from electrodes are two other significant effects that are very
often overlooked. One might have a highly conducting material, yet if

(a)

(b)

(c)

(d)
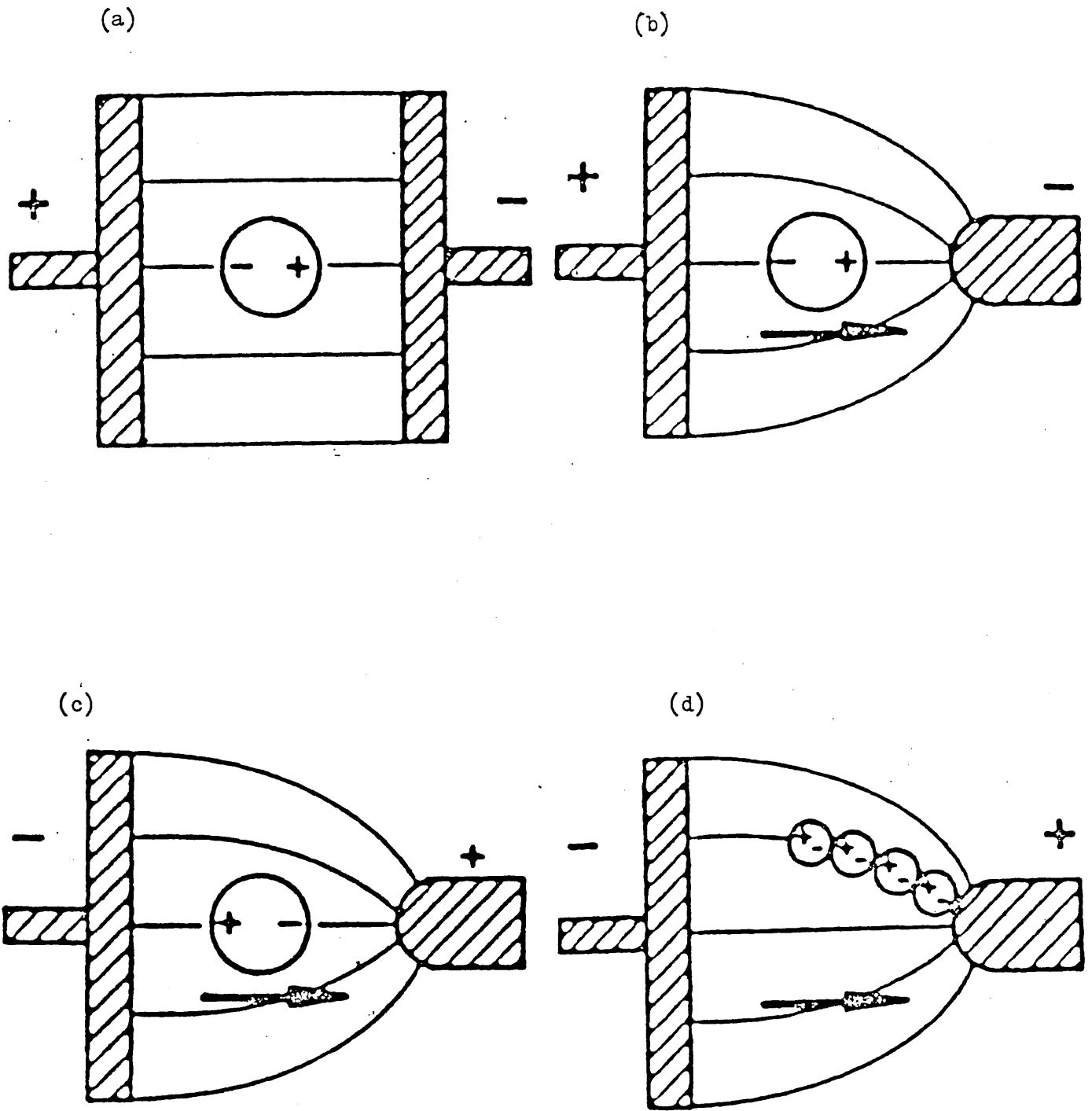
Figure 8.32

blocking contacts are in effect, and the charge carriers are being prevented from entering the external circuit, then there is no current and, of course, no way of measuring conductivity. Similarly one might have an insulating material and electrons are being injected into its conduction band from the electrode which then gives rise to a significant amount of conductivity.

Sample purity is a major problem. In order to present d.c. conductivity data we have to assume our materials to be intrinsic (pure), therefore enabling us to use equation (8.3). The solid-state physicists refer

$$\sigma_0 = A \exp(-\Delta\varepsilon/2kT) \qquad\qquad 8.3$$

to impurity levels in parts per billion, and their effects at such levels are significant. Germanium, for example, containing a few p.p.b. of arsenic, Figure 5.2, becomes an n-type extrinsic semi-conductor. The majority of the literature on organic materials quotes d.c. conductivities and activation energies as being for intrinsic material.[37-48] It is highly unlikely that any of these materials are truely intrinsic; their conductivity is extrinsic resulting from the promotion of charge-carriers to and from impurity levels within the forbidden gap. The development of ultra-purification techniques is a must.

So, although our d.c. measurements do provide a general qualitative guide, we have to be aware of their limitations and try wherever possible to support them with data acquired from other techniques. Dielectric spectroscopy allows us to study both the contact and bulk properties of our materials and quite obviously has enormous potential as an analytical tool for studying solid-state conduction.

CHAPTER 9

Conclusions

As far as the photographic side of our work was concerned the initial objectives were, in the main, achieved.

The step-wise condensation oligomer prepared in Chapter 3 has been patented[83] as a new anti-halation underlayer system. Further work is now in progress to synthesise dimeric material, Scheme 9.1, which is easily isolable and more readily characterised.
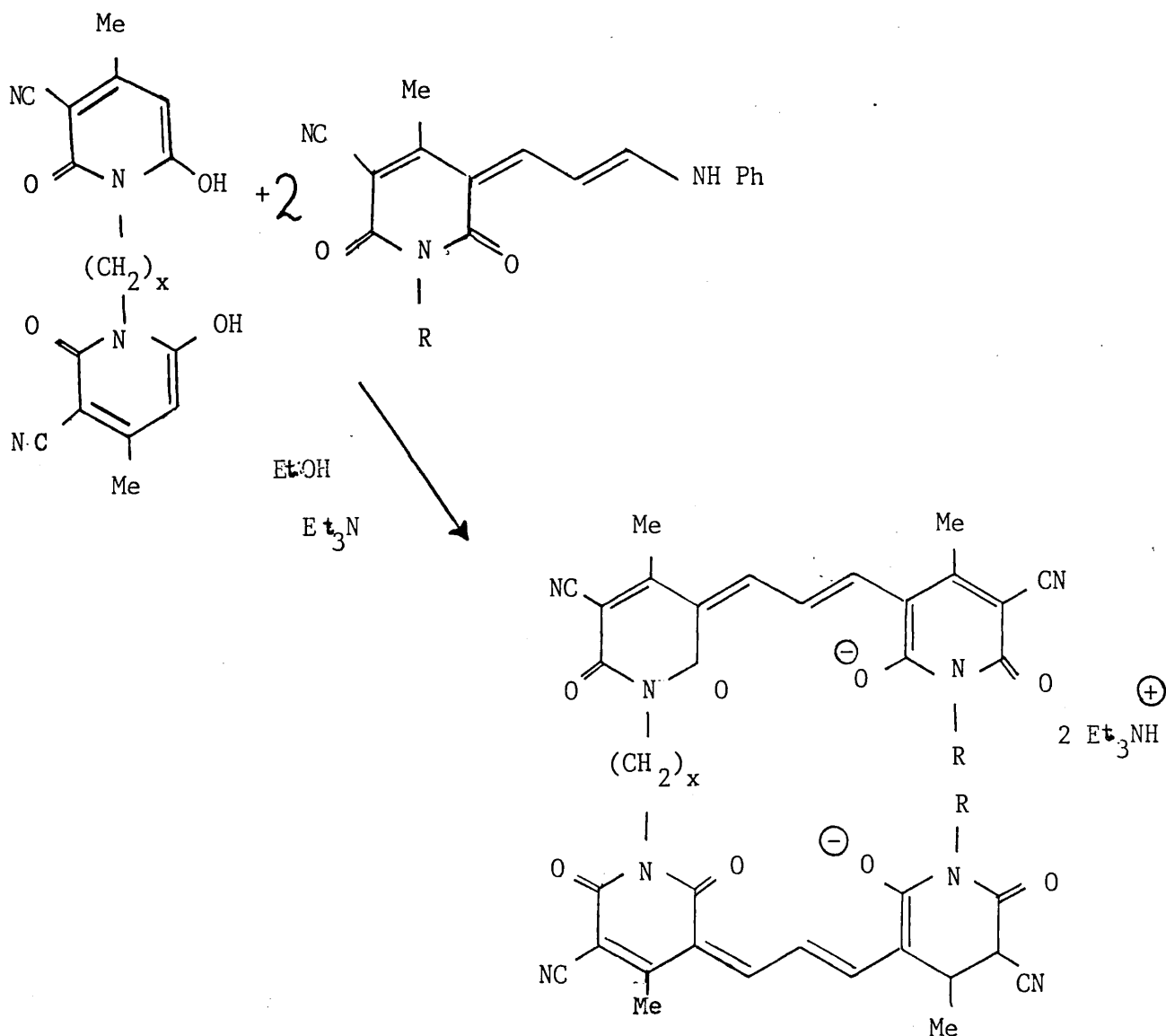
Scheme 9.1

The bleaching reaction studies for the sulphite ion case pointed to the major process being Michael-type conjugate attack of the methine bridge. Further investigation is necessary to elucidate fully the mechanistic details, in particular, for nucleophiles other than the sulphite ion.

Our more extensive solid-state studies revealed a number of interesting features.
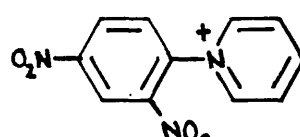
We observed a second example of anionic stacking in a herringbone arrangement first seen in MI 1579. We encountered selective peak splitting in the solid state ^{13}C n.m.r. spectra of MI 1579 and HPT 297. The reason for this is not clear.

The electrical properties of the oxonol dyes were varied. We found materials ranged from insulators to semi-conductors and their conductivities from being ionic to electronic in nature. More importantly, however, these measurements gave us an appreciation of the importance of contact effects and sample purity and as a result the limitations associated with d.c. conductivity data.

The effects on structure of cation variation is striking, however, these structural differences appear to have little effect on conductivity, Table 9.1. This is not surprising as all of those materials whose structure is known are insulating with large interplanar distances providing little hope of a pathway for intermolecular electronic charge transfer.

Table 9.1

Me ... Me
NC ... CN
O ... N ... O ... $^-$O ... N ... O
Et ... M ... Et
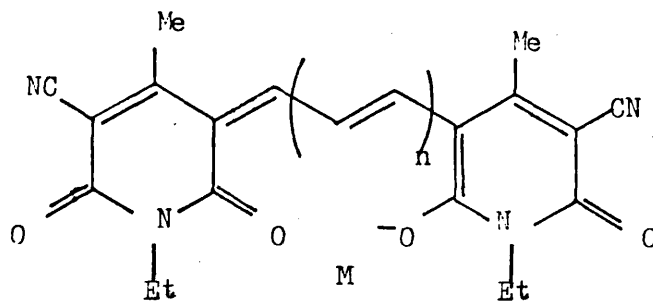
M	n	Interplanar Distance/Å [a]	Angle of twist/°	[b] Conductivity at 373 K/Ω^{-1}cm^{-1}
Et$_3$$\overset{\oplus}{N}$H	1	3.76	12.2	5.75 x 10^{-11}
Ph$_4$$\overset{\oplus}{P}$	"	4.06	40.4	7.24 x 10^{-11}
Bu$_4$$\overset{\oplus}{N}$	"	3.57, 5.56	25.6	6.92 x 10^{-11}
H$_2$CC-CO$_2$(CH$_2$)$_2$$\overset{\oplus}{N}HMe_2$ (with Me below)		4.54	14.1	9.98 x 10^{-10}
O$_2$N—C$_6$H$_3$(NO$_2$)—N$^+$-pyridinium	"			5.47 x 10^{-12}
Ph$_3$$\overset{\oplus}{P}$Me	"			4.82 x 10^{-8}
TTF$^{+\cdot}$	"			$\simeq$ 10^{-3} (c)
Et$_3$$\overset{\oplus}{N}$H	2			6.12 x 10^{-7}

(a) angle between the two planes defined by the two hydroxypyridone rings

(b) compacted powders

(c) room temperature (estimated by measurement of resistance at 0.1 V, see section 8.8, Chapter 8)

Enriching the dye structures with potential charge carrying
π-electrons via both the anion and cation had little effect. It seems
likely that the incorporation of these bulky aryl groups was counter-
productive pushing the molecules within the anionic stacks even further
apart. Introducing additional π-electrons by increasing the methine chain
length, however, produced three to four order of magnitude increases in
conductivity. Increasing the chain length above five carbon atoms becomes
difficult as these larger straight chained dyes are very unstable. It is,
however, possible to stabilise the bridge by rigidising it, e.g. with a
cyclohexene ring, Scheme 9.2. There is a vast amount of literature
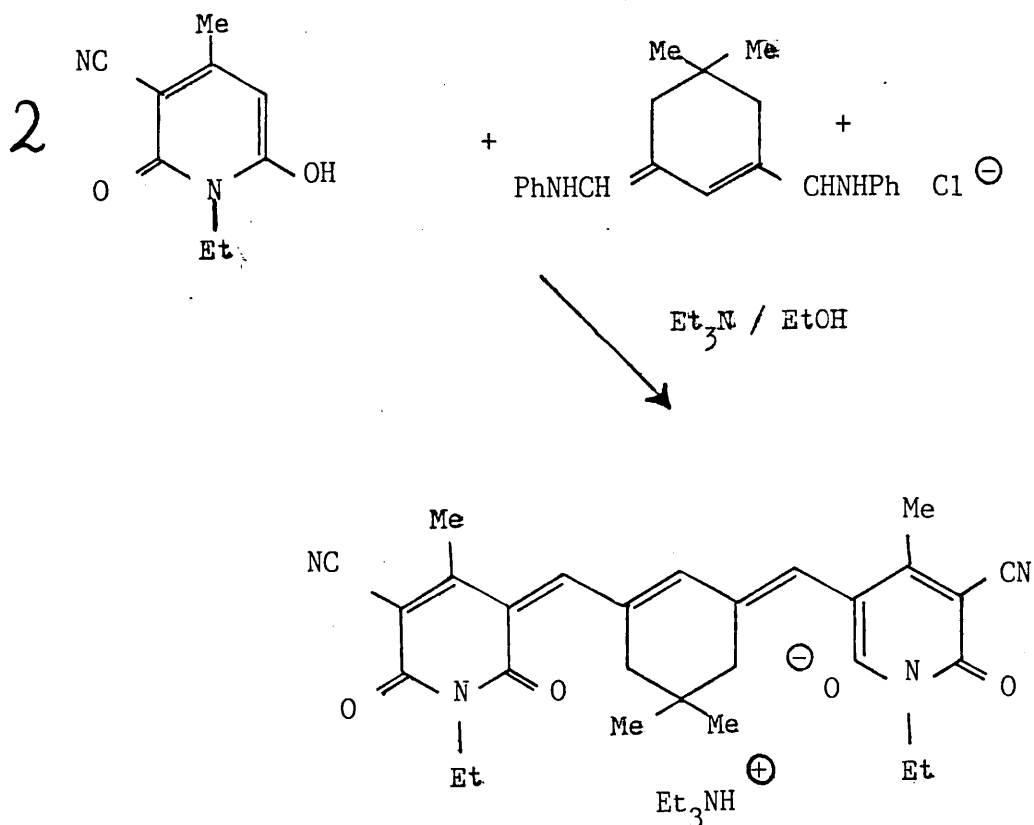
Scheme 9.2

covering the cyanine dye sensitisers with rigidised chains.[84-88] Oxonol

dyes of this type are now being synthesised.

The incorporation of cations with their own inherent conductivity

led us to prepare a TTF (tetrathiafulvalene)-oxonol dye salt which not

only appeared to be relatively highly conducting but was also reversibly

bleached. This material has a number of potential commercial applications

and has been patented[89]. The preparation of TTF-straight-chained penta-

and rigidised-penta- and heptamethine oxonol dyes are now being

investigated, as are other radical cation dye salts.

The reason for the three-order of magnitude difference in

conductivity between HPT 289 (M = Ph_4P^+) and HPT 297 (M = Ph_3PMe),

Table 9.1, has remained unsolved. Attempts are under way to grow good

quality crystals of HPT 297 for X-ray crystal structure determination. We

would then, hopefully, be in a better position to offer a possible

explanation.

CHAPTER 10

Experimental

10.1. <u>Syntheses</u>

10.1.1. Instrumentation

Routine ^{1}H and ^{13}C n.m.r analyses were carried out on the

Perkin Elmer R24-B and the Jeol FX-90Q instruments. Infra-red analyses of

nujol and/or hexachlorobutadiene mulls were carried out on the

Perkin-Elmer 197 machine. Elemental analyses of novel compounds were

carried out on the Perkin Elmer 240 Elemental Analyzer.

10.1.2 Aluminium Isopropoxide, $Al(iOPr)_3$.[12]

Isopropanol was dried by refluxing it over freshly calcined calcium

oxide for 4 hrs. Aluminium turnings (55.0 g, 2.0 mol) were placed in a

2 litre flask with 1 litre of dry isopropanol. Mercuric chloride (0.2 g,

0.7 mmol) was added and the mixture heated to reflux with good cooling of

the reflux condenser (two double surface condensers were used). The

hydrogen evolution soon became very violent and the flask was placed into

an ice/water bath. At the end of the stormy evolution of the hydrogen the

flask was heated on a water bath until the metal had vanished (12 hours).

On standing the mixture at room temperature overnight a grey sludge was

formed and this was covered by a nearly colourless solution. This was

diluted with isopropanol to 2 litres, to yield an approximately 1.0 M

solution.

10.1.3 α-Methyl-(m-nitrobenzyl) alcohol[12]

$$1 \; CH_3$$
$$2 \; CHOH$$

(structure: benzene ring with positions 3,4,5,6,7,8 and NO₂ at position 5)
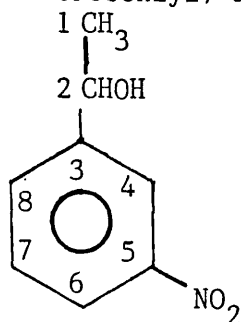
m-Nitroacetophenone (99.0 g, 0.6 mol) was reduced by 300 ml of the

1M-aluminium isopropoxide solution to yield 54.3 g (54%) of the alcohol

(recryst. toluene, m.p. = 61.0-62.5°, lit. m.p. = 62.0°; [1]H n.m.r.

$\delta(CDCl_3$, ppm.) 1.66 (d) $c^1 H_3$, 2.86 (s) OH, 5.04 (q) $c^2 H$,

7.92 (m) $C_6 H_4$; ^{13}C nmr. $\delta(CDCl_3$, ppm) 25.68 (c^1), 69.57 (c^2),

120.69, 122.57, 129.79, 132.20 (c^4, c^6, c^7, c^8), 148.45 (c^5);

infra-red 3300-3220 (O-H), 2985 $(c^1- H)$, 1535 (N-O), 1345 (N-O) cm^{-1}.

10.1.4 m-Nitrostyrene[13]

$$CH=CH_2$$

(structure: benzene ring with positions 1,2,3,4,5,6 and NO₂ at position 3)
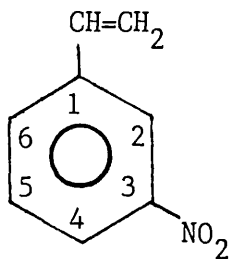
Used α-methyl-(m-nitrobenzyl) alcohol (50.0 g, 0.3 mol)

tert-butylcatechol (0.05g, 0.3 mmol) and A.R. orthophosphoric acid

(400 ml, 3.5 mol). The solution was maintained at 75-80° for 10 min and

then diluted with an equal quantity of water and steam distilled for 5

hrs. The m-nitrostyrene was then obtained from the distillate by

extraction with A.R. benzene, the benzene solution being dried over

potassium carbonate and the benzene removed by distillation. Pure

m-nitrostyrene was obtained by vacuum distillation under nitrogen yielding

18.6 g (42%), b.p. = 81-82°/1.0 mm Hg, lit. m.p. 81-82°C/1.0 mm Hg;
^{1}H nmr δ(CDCl$_3$, ppm) 6.58 - 8.25 (m) (C^{7}H, C^{8}H$_2$, C$_6$H$_4$);
^{13}C nmr δ (CDCl$_3$, ppm) 112.83, 113.54, 114.84, 117.06 (C^2,C^4,C^5,
C^6), 129.41 (C^8), 137.09 (C^7), 138.78 (C^1), 146.45 (C^3); i.r.
3085 (C^7-H), 3010 (C^2-H), 1632 (C^7=C), 1530 (N-O), 1355 (N-O), 925
(C^7-H) cm^{-1}.

10.1.5   m-Aminostyrene[14]
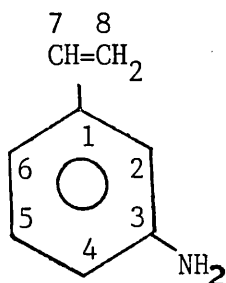
m-Nitrostyrene (15.3 g, 0.1. mol), stannous chloride (92.0 g, 0.4
mol) and concentrated hydrochloric acid (92 ml, 1.0 mol) in ethanol (50
ml) were refluxed for 30 mins cooled, and then poured into aqueous sodium
hydroxide (136.0 g in 460.0 ml). The oil which separated from the steam
distillate (steam distillation time of 4 hrs) was extracted with benzene.
The extract was dried over potassium carbonate, and the benzene distilled
off after the addition of a little quinol. Distillation of the product
under nitrogen gave 4.52 g (38%), b.p. = 68°C/0.8 mmHg, lit. b.p. =
68°C/0.8 mmHg; ^{1}H nmr δ(CDCl$_3$, ppm) 3.53 (s) NH$_2$, 6.44 - 7.26
(m)/C^{7}H$_1$C^{8}H$_2$,C$_6$H$_4$); ^{13}C nmr δ (CDCl$_3$, ppm) 112.70, 113.48,
114.71, 116.80 (C^2,C^4,C^5,C^6), 129.35 (C^8), 137.02 (C^7), 138.58
(C^1), 146.65 (C^3); i.r. 3440-3360 (N-H), 3025 (C-H), 2975 (C-H), 1620
(C^7=C), 1492 (C===C), 1300 (C-N) cm^{-1}.

10.1.6 Cyanoacetamide[10] $\overset{1}{N}\overset{2}{C}CH_2\overset{3}{C}ONH_2$

Ethyl cyanoacetate (75.3 ml, 0.7 mol) and concentrated aqueous ammonia solution (60 ml, 0.9 mol) were used. After drying the crude white amide weighed 50.3 g. An additional 6.3 g of amide was obtained by evaporating the original mother liquor to dryness under reduced pressure. This gave a total yield of 56.6 g (75%) (recryst. methylated spirit, m.p. = 118-119°, lit. m.p. = 119-120°; ^1H nmr $\delta(d^6$-DMSO, ppm) 3.65 (s) C^2H_2, 7.46 (d, broad) NH_2; ^{13}C nmr $\delta(d^6$-DMSO, ppm) 25.48 (C^2), 116.27 (C^1), 164.58 (C^3); i.r. 3400-3200 (N-H) 2955 (C-H), 2925 (C-H), 2255 (C≡N), 1680 (C=O), 1408 (C-N), 1375 (C-N) cm^{-1}.

10.1.7 $\underline{N}$-Ethyl cyanoacetamide

$$\overset{1}{N}C-\overset{2}{C}H_2-\overset{3}{C}\overset{\displaystyle O}{\underset{\displaystyle NH-\overset{4}{C}H_2\overset{5}{C}H_3}{\big\backslash}}$$
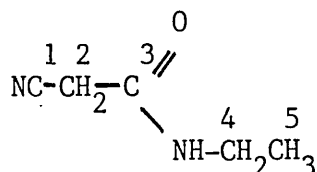
Used methyl cyanoacetate (308.5 ml, 3.5 mol) and ethylamine (253.1 ml, 4.5 mol). The total yield of amide was 211.1 g (54%) (recryst. methylated spirit, m.p. = 71.5-72.5°C, lit. m.p. = 72.0 °C; ^1H nmr $\delta(d^6$-DMSO, ppm) 1.07 (t) C^5H_3, 3.16 (q) C^4H_2, 3.58 (s) C^2H_2, 8.17 (s) NH; ^{13}C nmr $\delta(d^6$-DMSO, ppm) 14.44 (C^5), 25.95 (C^2), 35.38 (C^4), 114.97 (C^1), 161.15 (C^3), i.r. 3250 (N-H), 2250 (C ≡ N), 1680 (C=O), 1250 (C-N) cm^{-1}.

10.1.8   N-Butyl cyanoacetamide[17].

$$\underset{1}{NC}-\underset{2}{CH_2}-\underset{3}{C}\overset{\displaystyle O}{\underset{\displaystyle NH-\underset{4}{CH_2}\underset{5}{CH_2}\underset{6}{CH_2}\underset{7}{CH_3}}{\Big\langle}}$$
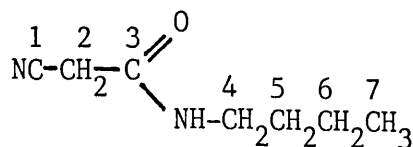
Ethyl cyanoacetate (49.0 g, 0.43 mol) was dripped into N-butylamine (31.6 g, 0.43 mol) over a 40 min period, the temperature rose to 45°. The mixture was then heated to 80° for 1 hr. The product crystallised out on cooling and on filtering weighed 60.0 g (98%) (recryst. toluene; m.p. = 68.5°, lit. m.p. = 69.0°; ^1H nmr $\delta(d^6$-DMSO, ppm) 0.81-0.87(m) C^7H_3, 1.30(m) (C^6H_2, C^5H_2), 3.02(m) C^4H_2, 3.48(s) C^2H_2, 8.10(s) NH; ^{13}C nmr $\delta(d^6$-DMSO, ppm) 12.36 (C^7), 18.47 (C^6), 24.26 (C^5), 29.85 (C^4), 37.85 (C^2), 114.91 (C^1), 160.89 (C^3).

10.1.9   N-Phenyl cyanoacetamide[17]

$$\underset{1}{NC}-\underset{2}{CH_2}-\underset{3}{C}\overset{\displaystyle O}{\diagdown}$$
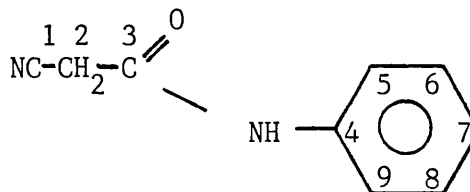
A mixture of aniline (40.91 ml, 0.45 mol) and methyl cyanoacetate (308.5 ml, 0.35 mol) in toluene (50 ml) was refluxed for 20 hrs. The crude amide filtered off after cooling weighed 18.2 g (32%) (recryst. methylated spirit, m.p. = 199-201°, lit. m.p. = 199-200°; ^1H nmr $\delta(d^6$-DMSO, ppm) 3.90 (s) C^2H_2, 7.33 (m) C_6H_5, 10.44 (s) OH; ^{13}C nmr (poor signal to noise); i.r. 3270-3210 (N-H). 3140 $(C^5$-H); 2250 (C ≡ N), 1665 (C=O), 1560 $(C^5\!\!=\!\!C)$, 760 $(C^5$-H) cm^{-1}.

10.1.10   N-(p-Tolyl)cyanoacetamide
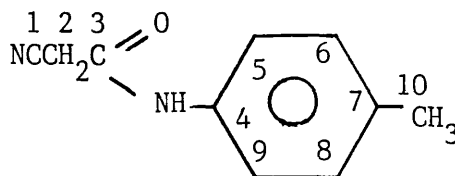
A mixture of p-toluidine (10 g, 0.1 mol) and methyl cyanoacetate (10.6 ml, 0.12 mol) in toluene (30 ml) was refluxed for 48 hrs. The reaction mixture was allowed to cool, the light brown residue was filtered off, 5.15 g (33%) (recryst. methylated spirit, m.p. = 186.0-187.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 2.29 (s) CH_3, 3.88 (s) CH_2, 7.33 (m) C_6H_4, 10.18 (s) OH; ^{13}C nmr δ(d^6-DMSO, ppm) 20.35 (C^{10}), 26.52 (C^2), 115.81 (C^1), 119.32, 129.14 (C^5,C^6,C^8,C^9), 132.98 (C^7), 135.78 (C^4), 160.55 (C^3); i.r. 3270-3210 (N-H), 3140, 3090 (C^5-H), 2955, 2925 (C^2-H), 2255 (C $\equiv$ N), 1665 (C=O) cm^{-1}; Calcd for $C_{10}H_{10}N_2O$: C, 68.94; H, 5.80; N, 16.08; Found: C, 68.92; H, 5.79; N, 15.97.

10.1.11   N-(p-Anisyl)cyanoacetamide)
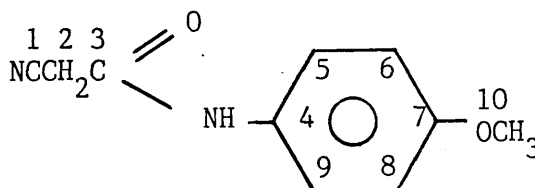
A mixture of p-anisidine (10 g, 0.08 mol) and methyl cyanoacetate (9.2 ml, 0.09 mol) in toluene (30 ml) was refluxed for 48 hrs. The reaction mixture was allowed to cool, the greyish residue was filtered off 4.64 g (31%) (recryst. methylated spirit, m.p. = 131-133°; ^{1}H nmr

δ(d^6-DMSO, ppm) 3.78 (s) OCH$_3$, 3.89 (s) CH$_2$, 7.27 (m) C$_6$H$_4$, 10.36 (s) OH; ^{13}C nmr δ(d^{6}DMSO, ppm) 26.59 (C^2), 55.07 (C^{10}), 113.86 (C^6,C^8), 115.81 (C^1), 120.88 (C^5,C^9), 131.29 (C^7), 155.61 (C^4), 160.29 (C^3); i.r. 3310-3215 (N-H), 3150-3100 (C^5-H), 2950-2930 (C^2-H), 2250 (C $\equiv$ N), 1658 (C=O), 1032 (C-O); Calcd for C$_{10}$H$_{10}$N$_2$O$_2$: C, 63.14; H, 5.31; N, 14.73; Found: C, 62.93; H, 5.27; N, 14.64.

10.1.12   N,N'-Dicyanoacetyl-1,3-diaminopropane
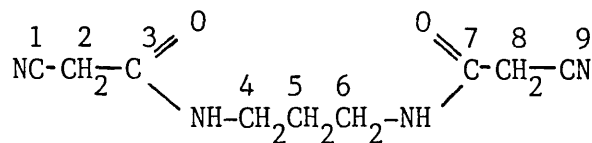
A mixture of ethyl cyanoacetate (30.51 g, 0.27 mol) and 1,3-diaminopropane (10 g, 0.14 mol) in ethanol (20 ml) was refluxed with stirring for 4 hrs. The reaction was allowed to cool and the solid residue was filtered off and dried over P$_2$O$_5$. The yellow solid weighed 7.46 g (27%) (recryst. ethanol m.p. = 158-159^0; ^{1}H nmr δ(d^6-DMSO, ppm) 1.64 (m) C^{5}H$_2$, 3.16 (m) C^{4}H$_2$, 3.64 (s) C^{2}H$_2$, 8.17 (t) OH; ^{13}C nmr δ (d^6-DMSO, ppm) 27.83 (C^5) 31.09 (C^2), 39.54 (C^4), 118.52 (C^1), 164.59 (C^3), i.r. 3284 (N-H), 2956 (C-H), 2260 (C $\equiv$ N), 1651 (C=O) cm^{-1}; Calcd. for C$_9$H$_{12}$N$_4$O$_2$: C, 51.91; H, 5.82; N, 26.91; Found: C, 51.60; H, 5.85; N, 26.59.

10.1.13 $\underline{N},\underline{N}'$-Dicyanoacetyl-1,4-diaminobutane

$$NC-\underset{1}{CH_2}-\underset{2}{C}\underset{3}{\overset{\displaystyle O}{\diagup}}\quad\quad\quad\underset{\displaystyle \diagdown}{\overset{O}{\diagup}}\underset{8\ 9}{C-CH_2}-\underset{10}{CN}$$

$$\underset{\displaystyle \diagdown}{NH-\underset{4}{CH_2}\underset{5}{CH_2}\underset{6}{CH_2}\underset{7}{CH_2}-NH}\diagup$$
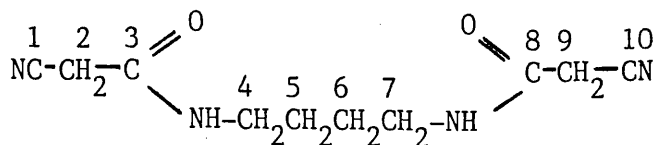
A mixture of 1,4-diaminobutane (20 g, 0.23 mol) and

ethylcyanoacetate (51.3 g, 0.46 mol) in ethanol (50 ml) was refluxed for 4

hrs. to yield 42.7 g (85%) of a yellow solid (recryst. ethanol m.p. =

147.0-148.0°C; ^{1}H nmr δ(d^6-DMSO, ppm) 1.78 (m) C^{5}H$_2$, 3.40 (m)

C^{4}H$_2$, 3.88 (s) C^{2}H$_2$, 8.36 (t) OH; ^{13}C nmr δ(d^6-DMSO, ppm)

25.23 (C^5), 26.14 (C^2), 38.76 (C^4), 115.96 (C^1), 161.86 (C^3);

i.r. 3279 (N-H), 2950 (C-H), 2256 (C $\equiv$ N), 1660 (C=O) cm^{-1}; Calcd. for

C$_{10}$H$_{14}$N$_4$O$_2$: C, 54.04; H, 6.36; N, 25.21; Found: C, 54.61; H, 6.18;

N, 24.82.

10.1.14 $\underline{N},\underline{N}'$-Dicyanoacetyl-1,6-diaminohexane

$$NC-\underset{1}{CH_2}-\underset{2}{C}\underset{3}{\overset{\displaystyle O}{\diagup}}\quad\quad\quad\underset{\displaystyle \diagdown}{\overset{O}{\diagup}}\underset{10\ 11}{C-CH_2}-\underset{12}{CN}$$

$$\underset{\displaystyle \diagdown}{NH-\underset{4}{CH_2}\underset{5}{CH_2}\underset{6}{CH_2}\underset{7}{CH_2}\underset{8}{CH_2}\underset{9}{CH_2}-NH}\diagup$$
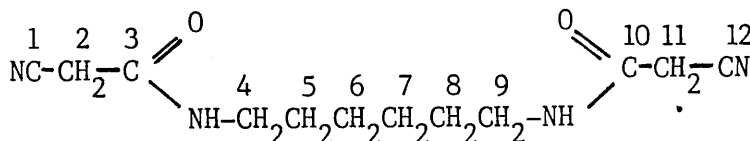
A mixture of 1,6-diaminohexane (58.0 g, 0.5 mol) and ethyl

cyanoacetate (113.0 g, 1.0 mol) in ethanol (100 ml) was refluxed for 4 hrs

to yield 98.7 g (79%) of a buff precipitate (recryst. ethanol m.p. =

149.0-151.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 1.33 (s, broad), 3.12 (m)

C^{4,5,6}H$_2$, 3.60 (s) C^{2}H$_2$, 8.18 (m) OH; ^{13}C nmr δ(d^6-DMSO, ppm)

25.30 (c^6), 25.95 (c^5), 28.68 (c^2), 39.21 (c^4), 115.82 (c^1),

161.80 (c^3), i.r. 3289 (N-H), 3096 (C-H), 2960 (C-H), 2255 (C ≡ N), 1665

(C=O) cm^{-1}; Calcd. for $C_{12}H_{18}N_4O_2$: C, 57.57; H, 7.26; N, 22.39:

Found C, 57.51; H, 7.24; N, 22.24.

10.1.15 3-Cyano-2,6-dihydroxy-4-methyl pyridine[11].
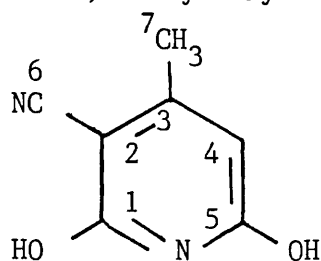
A mixture of cyanoacetamide (16.8 g, 0.2 mol), ethyl acetoacetate

(25.4 ml, 0.2 mol) in methanol (45 ml) was warmed to obtain solution and a

paste of potassium hydroxide in methanol (13.8 g, 0.25 mol) was added.

After acidification, filtration and drying the crude white hydroxypyridone

weighed 19.0 g (63%) (recryst. aqueous ethanol, m.p. = 313.0-315.0°,

lit. m.p. = 316-319°, ^{1}H n.m.r. δ(d^6-DMSO, ppm) 2.28 (s) CH_3, 5.67

(s) CH, 10.56 (s) OH; ^{13}C nmr. δ(d^6-DMSO, ppm) 20.82 (c^7), 89.02

(c^4), 92.73 (c^3), 116.92 (c^6), 160.16 (c^2), 160.88, 161.72

(c^1,c^5), i.r. 3350-2300 (O-H), 2215 (C ≡ N), 1610 (C═C),

1300 (C-O) cm^{-1}.

10.1.16   1-Ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one[11]
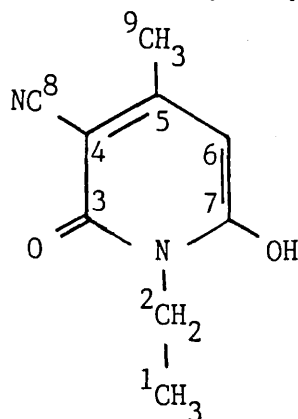
To a solution of N-ethyl cyanoacetamide (35.8 g, 0.32 mol) and

ethyl acetoacetate (41.6 ml, 0.32 mol) in methanol (70 ml) was added

potassium hydroxide in methanol (22.0 g, 0.4 mol). The crude white

hydroxypyridone weighed 21.3 g (38%) (recryst. ethanol; m.p. = 245.0 –

246.0°, lit. m.p. = 246.0-248.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 1.14 (t)

c^1H_3, 2.24 (s) c^9H_3, 3.97 (q) CH_2, 5.71 (s) CH, 10.68 (s) OH;

^{13}C nmr. δ(d^6-DMSO, ppm) 12.944 (c^1), 20.48 (c^9), 35.83 (c^2),

88.64 (c^6), 92.02 (c^5), 117.38 (c^8), 158.03 (c^4), 160.17

(c^3,c^7); i.r. 3080-2300 (O-H, C-H), 2220 (C $\equiv$ N), 1640 (C=O), 1610

(C===C), 1290 (C-N) cm^{-1}.

10.1.17   1-Butyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one
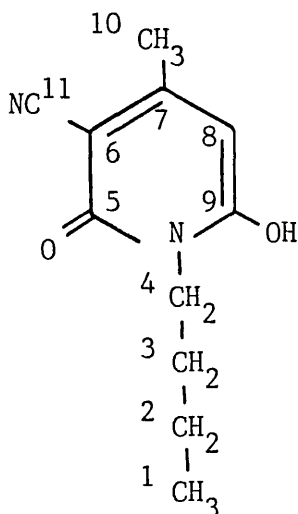
N-Butyl cyanoacetamide (28.0 g, 0.2 mol) and ethyl acetoacetate
(26.0 g, 0.2 mol) were added to a solution of sodium (4.6 g, 0.2 mol) in
200 ml methanol and the mixture refluxed for 7 hrs. On cooling the solid
deposited was filtered off. The filtrate was then diluted with its own
volume of water and the hydroxypyridone precipitated out with 25.0 ml
concentrated hydrochloric acid. On drying the white solid weighed 21.1 g
(51%) (recryst. ethanol; m.p. = 212.5 - 214.0°; lit. m.p. 212.0°; ^{1}H
nmr δ(d^6-DMSO, ppm) 1.24 (m) C_4H_9, 2.30 (s) $c^{10}H_3$, 3.98 (m)
C_4H_9, 5.72 (s) CH, 13.40 (s) OH; ^{13}C nmr δ(d^6-DMSO, ppm) 12.62
(c^1), 18.67 (c^2), 19.58 (c^{10}), 28.62 (c^3), 39.54 (c^4), 88.12
(c^8), 90.98 (c^7), 116.41 (c^{11}), 157.18 (c^6), 159.33 (c^5,c^9);
i.r. 3094 - 2961 (O-H), 2936-2877 (C-H), 2219 (C$\equiv$N), 1662 (C = O), 1611
(C$=$C) cm^{-1}.

10.1.18   1-Phenyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one
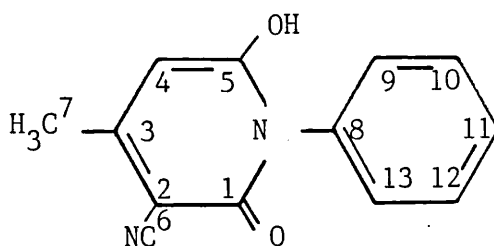
Sodium (0.6 g, 25 mmol) was dissolved in methanol (25 ml) while
stirring. After cooling the paste, N-phenyl cyanoacetamide (4.0 g,
25 mmol) and ethyl acetoacetate (3.3 g, 25 mmol) were added. The reaction
mixture was refluxed with stirring for 7 hrs. The solution was then
allowed to cool and was diluted with its own volume of water. On adding

1.0 ml of concentrated hydrochloric acid the phenyl hydroxypyridone

precipitated out and a further 2 ml of acid was added. The buff coloured

filter cake was then washed with several portions of cold water, followed

by ether, and dried by suction to yield 3.1 g (54%) (recryst. toluene m.p.

= 316.0- 318.0°; ^{1}H nmr. δ(d^6-DMSO, ppm) 2.31 (s) CH_3, 5.70 (s)

C-H, 7.42 (m) C_6H_5; ^{13}C nmr (poor signal to noise); i.r. 3080 (O-H),

2220 (C$\equiv$N), 1660 (C=O), 760 (C-H) cm^{-1}; Calcd. for $C_{13}H_{10}N_2O_2$:

C, 69.01; H, 4.46; N, 12.38; Found: C, 69.29; H, 4.55; N, 12.52.

10.1.19   1-(p-Tolyl)-3-cyano-6-hydroxy-4-methyl pyrid-2-one
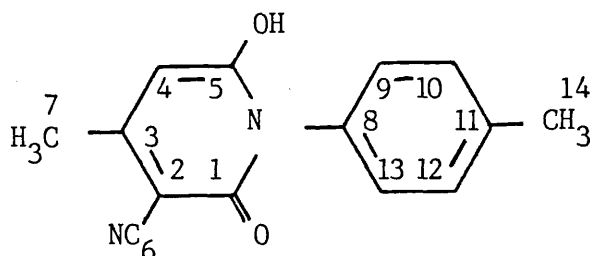
Procedure as for 10.1.18 above, dissolving sodium (0.3 g, 0.01 mol)

in methanol (12 ml) and adding p-tolyl cyanoacetamide (2.0 g, 0.01 mol)

and ethyl acetoacetate (1.5 g, 0.01 mol). On acidification 1.4 g (57%) of

an olive green precipitate was obtained (recryst. toluene m.p. > 350°;

^{1}H nmr δ(d^6-DMSO, ppm) 2.29 (s) c^7H_3, 2.37 (s) $c^{14}H_3$, 5.89 (s)

CH, 7.23 (m) C_6H_4; ^{13}C nmr δ(d^6-DMSO, ppm) 20.28, 20.54

(c^7,c^{14}), 87.91 (c^4), 92.40 (c^3), 117.50 (c^6), 122.96 (c^{11}),

127.91, 129.21 (c^{10},c^{12}), 129.86 (c^8), 132.65, 137.47 (c^9,c^{13}),

158.67 (c^2), 160.81 (c^1,c^5); i.r. 3070 (O-H), 2200 (C$\equiv$N), 1658

(C=O), 1612 (C==C) cm^{-1}; Calcd for $C_{14}H_{12}N_2O_2$: C, 69.98; H,

5.04; N, 11.66; Found: C, 69.72; H, 4.92; N, 11.59.

10.1.20   1-(p-Anisyl)-3-cyano-6-hydroxy-4-methyl pyrid-2-one
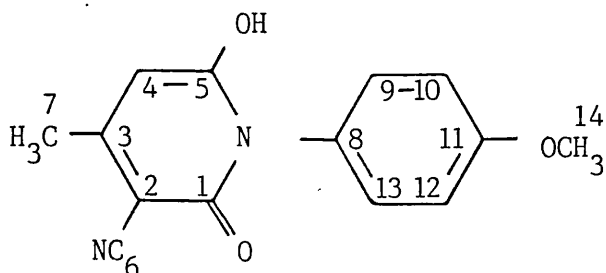
Procedure as for 10.1.18 dissolving sodium (0.2 g, 8.0 mmol) in

methanol (10 ml) and adding p-anisyl cyanoacetamide (1.5 g, 8.0 mmol) and

ethyl acetoacetate (1.0 ml, 8.0 mmol). On acidification 1.4 g (67%) of a

buff precipitate was obtained (recryst. toluene, m.p. = 265.0-267.0°;

^{1}H nmr δ(d^6-DMSO, ppm) 2.28 (s) c^{7}H$_3$, 3.80 (s) c^{14}H$_3$, 5.80 (s)

c^{4}H, 7.08 (m) C$_6$H$_4$; ^{13}C nmr δ(d^{6}DMSO, ppm) 20.67 (c^7), 55.27

(c^{14}), 88.30 (c^4), 92.40 (c^3), 113.86 (c^{11}), 114.06 (c^{10},c^{12}),

117.50 (c^6), 127.71 (c^8); 129.21 (c^9,c^{13}), 158.86 (c^2), 160.94,

161.07 (c^1,c^5); i.r. 3070 (O-H), 2200 (C≡N), 1660 (C=O), 1610

(C═══C); Calcd. for C$_{14}$H$_{12}$N$_2$O$_3$: C, 65.61; H. 4.73; N, 10.93;

Found: C, 65.31; H, 4.68; N, 10.66.

10.1.21   1-(Dimethylaminopropyl)-3-cyano-6-hydroxy-4-methyl-
           pyrid-2-one[17]
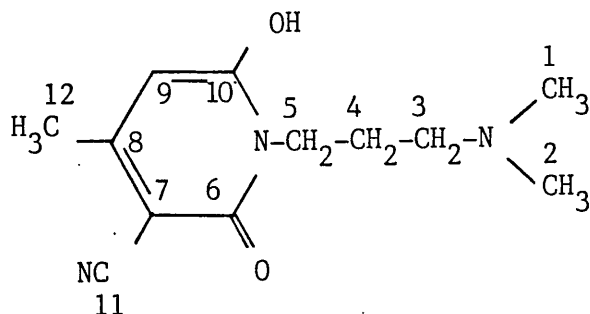
3-Dimethylaminopropylamine (125.0 ml, 1.0 mol) was added to ethyl

cyanoacetate (106.0 ml, 1.0 mol) over a 15 min period; temperature rose

to 65°. The solution was then heated to a gentle reflux and ethyl

acetoacetate (127.0 ml, 1.0 mol) was added. The mixture was then refluxed

for a further 15 hrs. On cooling the product crystallised out, was

filtered and dried to yield 95.3 g (41%) of a white powder (m.p. = 208.0 -

209.0°, lit. m.p. = 209°, ^{1}H n.m.r. δ(d^6-DMSO, ppm) 1.65 (m)

C^4H_2, 1.77 (s) $C^{12}H_3$, 2.55 (s) C^1H_3, 2.73 (t) C^3H_2, 3.62

(t) C^5H_2, 4.91 (s) C^9H, i.r. 3430 - 3027 (O-H), 2957 (C-H), 2188

(C≡N), 1613 (C≡C) cm^{-1}.

10.1.22   1-Methyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one
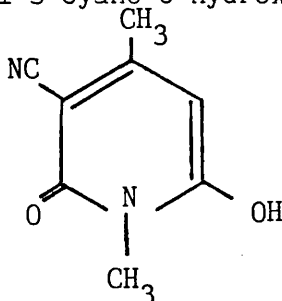
Supplied by Ilford Ltd. (m.p. = 276.0 - 277.0; lit. m.p.[17] =

275.0°).

10.1.23   1-Hexyl-3-cyano-6-hydroxy-4-methylpyrid-2-one
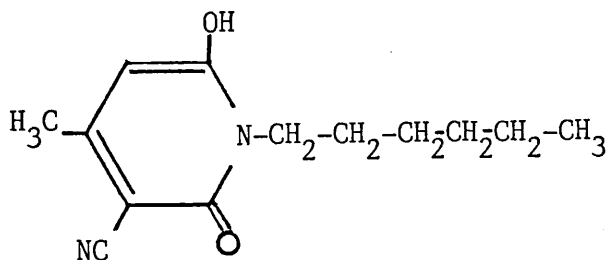
Supplied by Ilford Ltd (m.p. = 187.0 - 188.0°, lit. m.p.[17] =

187.0 - 188.0°).

10.1.24   1-Ethyl-3-amido-6-hydroxy-4-methyl pyrid-2-one
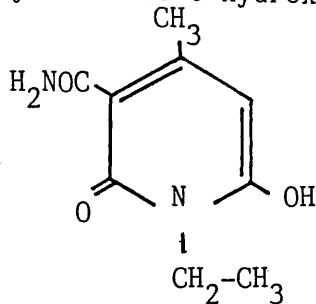
Supplied by Ilford Ltd. (m.p. = 158.5 - 159.5° lit. m.p.[17] = 159.0 - 160.0°).

10.1.25   N,N'-Trimethylene-bis-(3-cyano-6-hydroxy-4-methyl

pyrid-2-one)
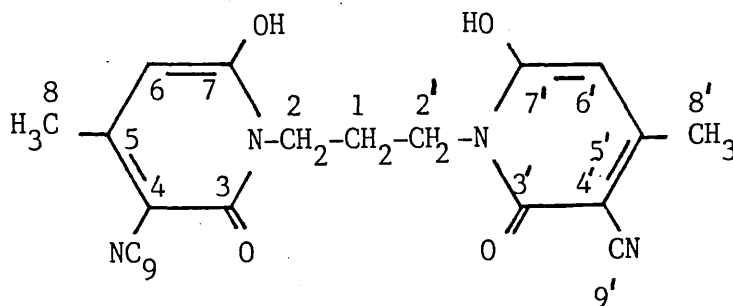
To a solution of sodium (1.1 g, 0.048 mol) in methanol (50 ml) was

added N,N'-dicyanoacetyl-1,3-diaminopropane (5.0 g, 0.048 mol) and

ethyl acetoacetate (6.3 g, 0.048 mol); the reaction mixture was then

refluxed for 18 hrs. After cooling any solid deposited was filtered off.

To the filtrate was added 80 ml water which was then acidified with 5 ml

concentrated hydrochloric acid. The resulting precipitate was filtered

off and dried over P_2O_5. The pale yellow solid weighed 5.45 g (67%)

(recryst. ethanol, m.p. = 251.0 -253.0° (decomp); ^{1}H nmr δ(d^6-DMSO,

ppm) 1.88 (m) C^{1}H$_2$, 2.25 (s) CH$_3$, 4.00 (m) C^{2}H$_2$, 5.65 (s) CH,

7.84 (s) OH; Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.75; N, 16.47;

Found C, 59.45; H, 4.77; N, 16.56.

10.1.26   N,N'-Tetramethylene-bis-(3-cyano-6-hydroxy-4-methyl

pyrid-2-one)

OH   HO

6 7   1' 2'   7' 6'   8'
8   2   1   5'   CH₃
H₃C   5   N-CH₂-CH₂-CH₂CH₂-N   5'
4   3   3' 4'
NC   0   0   CN
9   9'
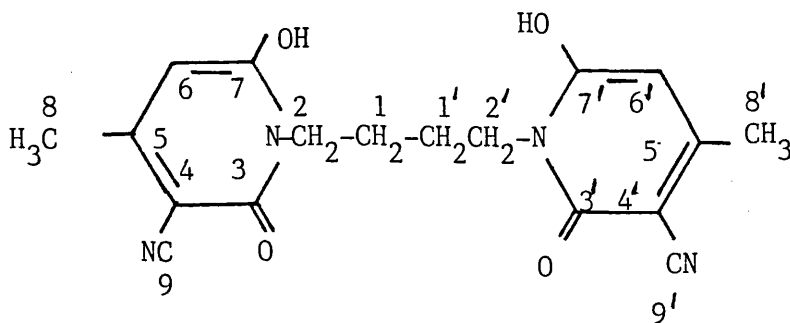
To a solution of sodium (2.1 g, 0.09 mol) in 100 cm³ methanol

was added N,N'-dicyanoacetyl-1-4-diaminobutane (10.0 g, 0.045 mol) and

ethyl acetoacetate (11.7 g, 0.09 mol). The mixture was refluxed for 18

hrs to yield 9.6 g (60%) of the yellow product after acidification

(recryst. ethanol m.p. = 272.0-275.0° (decomp); ¹H nmr δ(d⁶-DMSO,

ppm) 1.50 (m) C¹H₂, 2.16 (s) CH₃, 3.89 (m) C²H₂, 5.58 (s) CH,

7.52 (s) OH; ¹³C nmr δ(d⁶-DMSO, ppm) 20.55 (C⁸), 25.04 (C¹), 40.26

(C²), 88.18 (C⁶), 92.48 (C⁵), 117.64 (C⁹), 157.90 (C⁴), 160.56

(C³, C⁷); Calcd. for C₁₈H₁₈N₄O₄: C, 61.01; H, 5.13; N, 15.81:

Found C, 59.83; H, 5.41; N, 16.09.

10.1.27   N,N'-Hexamethylene-bis-(3-cyano-6-hydroxy-4-methyl

pyrid-2-one)

OH   HO

7 8   3   2   1   1' 2' 3'   8' 7'   9'
9   CH₃
H₃C   6   N-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-N   6'
5   4   4' 5'
NC   0   0   CN
10   10'
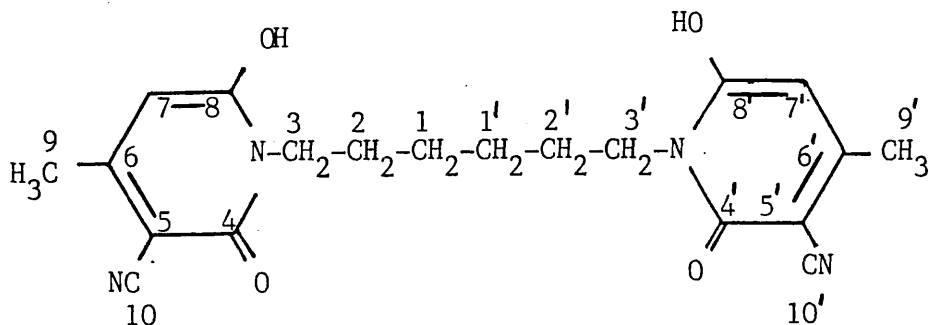
N,N'-Dicyanoacetyl-1,6-diaminohexane (125.0 g, 0.05 mol) and

ethyl acetoacetate (130.0 g, 1.0 mol) were added to a solution of sodium

(23.0 g, 1.0 mol) in 500 cm^3 methanol and the mixture refluxed for 18

hrs. On cooling and after acidification 138.2 g (72%) of this yellow

product was obtained (recryst. ethanol m.p. = 236.0 - 238.0° (decomp);

^{1}H nmr δ(d^6-DMSO, ppm) 1.42 (m) c^{1,2}H$_2$, 2.26 (s) CH$_3$, 3.94 (m)

c^{3}H$_2$, 5.75 (s) CH, 8.54 (s) OH; ^{13}C nmr δ(d^6-DMSO, ppm) 20.68

(c^9), 26.14, 27.57 (c^1,c^2), 40.91 (c^3), 88.51 (c^7), 93.13

(c^6), 117.84 (c^{10}), 158.29 (c^5), 160.95 (c^4,c^8); i.r. 3791

(O-H), 2937 (C-H), 2217 (C≡N) 1634 (C═C) cm^{-1}; Calcd. for

C$_{20}$H$_{22}$N$_4$O$_4$: C, 62.81; H, 5.81; N, 14.65: Found: C, 62.84; H, 6.09,

N, 15.06.

10.1.28   β-Anilinoacrolein anil hydrochloride [15].
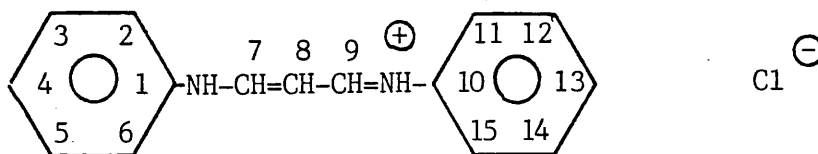
Aniline (31.3 ml, 0.33 mol) and tetramethoxypropane (26.8 ml, 0.16

mol) in 100 ml ethanol were stirred together at room temperature. The

mixture was cooled to 0° and concentrated hydrochloric acid (38.0 ml,

0.4 mol) was added dropwise so as not to allow the temperature to rise

above 10°C. The reaction mixture was left to stand overnight and was

then refluxed for 2 hrs. After cooling the product was collected by

filtration, washed with 40 ml cold ethanol and dried over P$_2$O$_5$ to

yield 26.7 g (65%) (m.p. = 227.0-228.0°; lit. m.p. = 229.0-230.0°,

^{1}H nmr δ(d^6-DMSO, ppm) 3.57 (s) NH, 6.64 (t) c^{8}H, 7.37 (m) C$_6$H$_5$,

9.19 (m) c^{7}H; i.r. 3108 (c^2-H), 3060 (c^7-H), 1632 (c^7═c^8), 1567

(c^2 ═══ c^3) cm^{-1}.

10.1.29   3-(3'-Acetanilidoallylidiene)-1-ethyl-4-methyl-5-cyano

pyrid-2,6-dione[16].
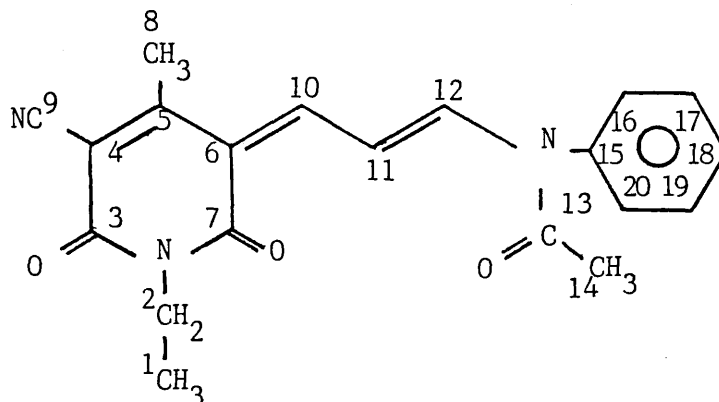
A mixture of 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (4.5 g,

0.03 mol) and β-anilinoacrolein anil hydrochloride (6.5 g, 0.03 mol)

suspended in 30 ml acetic anhydride was stirred at 75° for 1 hr. After

filtering, the black solid was washed with acetic acid and dried, yielding

8.1 g (93%) (m.p. = 208.0-210.0°; lit. m.p. = 208.0-210.0°; ^{1}H nmr

δ(d^6-DMSO, ppm) 1.14 (t) C^{1}H$_3$, 2.21 (s) C^{8}H$_3$, 2.46 (s)

C^{14}H$_3$, 3.90 (q) CH$_2$, 6.53 (m) C^{10}H, 7.43 (s) C$_6$H$_5$, 9.01 (t)

C^{11}H, 12.66 (d) C^{12}H; ^{13}C nmr δ(d^6-DMSO, ppm) 12.88 (C^1), 18.41

(C^8), 20.29 (C^{14}), 35.57 (C^2), 98.52 (C^5), 110.36 (C^6), 117.32

(Ar), 117.90 (C^9), 120.83 (C^{11}), 125.64, 129.54, 138.52 (Ar), 157.05

(C^{10},10^{12}), 157.77 (C^4), 158.35 (C^{13}), 160.04, 161.86 (C^3,C^7);

i.r. 3190 (C^{16}-H), 2941 (C^1-H), 2206 (C≡N), 1633 (C=O) 1567

(C═C) cm^{-1}.

10.1.30   N-(2,4-Dinitrophenyl)pyridinium chloride[17].
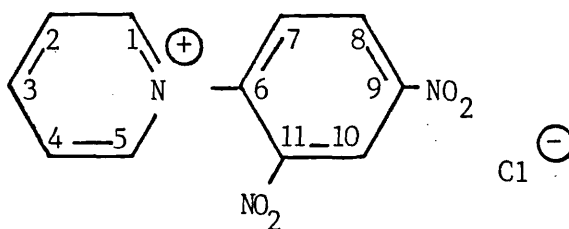
A mixture of pyridine (36.2 ml, 0.45 mol) and 1-chloro-2,4-dinitrobenzene (91.5 g, 0.45 mol) in 400 ml toluene was refluxed for 3 hrs. After cooling and filtering the buff precipitate was washed with three 50 ml portions of cold acetone and allowed to dry. The product weighed 56.8 g (45 %) m.p. = 203.0 - 203.5° (subl.) lit. m.p. = 204.0°. ^{1}H nmr δ(D_2O; ppm) 8.49 (m) $C^{7,8,10}$H, 9.02-9.48 (m) C^{1-5}H; ^{13}C nmr δ(D_2O, ppm) 125.05, 131.10, 133.25, 133.83 (CH), 141.12, 145.34 (C^9,C^{11}) 147.88, 151.85 (CH), 152.11 (C^6); i.r. 3118, 3072, 3058 (C-H), 1610, 1563 (C === C), 1544, 1343 (N-O) cm^{-1}.

10.1.31 Glutaconic dialdehyde dianil hydrochloride[17].
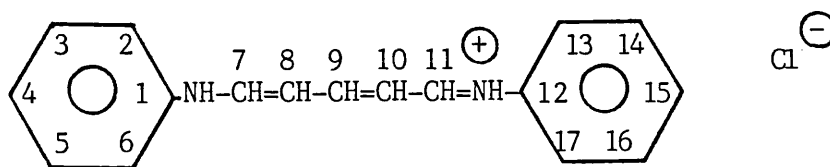
N-(2,4-Dinitrophenyl)pyridinium chloride (42.3 g, 0.15 mol) was suspended in 200 ml ethanol and cooled in an ice bath. Aniline (41.1 ml, 0.45 mol) was then added dropwise over a 30 min period. The reaction mixture was then refluxed for 1 hr, cooled and the red precipitate filtered off and washed with 3 x 25 ml portions acetone and dried to yield 40.8 g (96%) (recryst. ethanol m.p. = 148.0 - 149.0°, lit. m.p. = 148.0-150.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 3.52 (s) NH, 6.67-9.36 (m) C_6H_5, CH; ^{13}C nmr δ(d^6DMSO, ppm) 119.85 (Ar), 123.17 (Ar), 128.83 (C^8 or C^9), 129.02 (Ar), 135.39 (C^8 or C^9), 149.89 (C^7); i.r. 3450 (N-H), 3106 (C^2-H), 3072 (C^7-H), 1631 (C^7= C^8), 1566 (C^1=== C^2) cm^{-1}.

10.1.32   2-Methyl-3-ethyl benzothiazolium iodide[17].
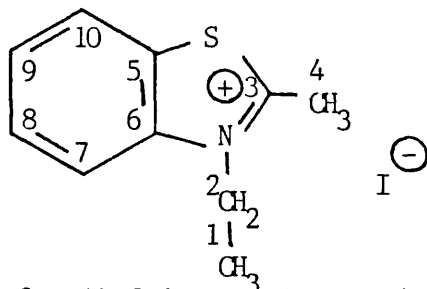
A mixture of 2-methyl benzothiazole (10.0 ml, 0.08 mol) and ethyl

iodide (10.0 ml, 0.13 mol) was refluxed for 6 hrs on a water bath. The

product was then filtered off, washed with ether and allowed to air dry,

yielding 3.2 g (13%) of a pale green solid (m.p. = 194.0-196.0°; lit.

m.p. = 196.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 1.58 (t) C^1H_3, 3.32 (s)

C^4H_3; 4.84 (q) CH_2, 8.16 (m) C_6H_4; ^{13}C nmr δ(d^6-DMSO, ppm)

13.06 (C^1), 16.97 (C^4), 44.67 (C^2), 116.46, 124.46, 127.71, 128.82

(C^7, C^8, C^9, C^{10}), 129.08 (C^5), 140.20 (C^6), 176.42 (C^3);

i.r. 3070 (C^7-H), 2975, 2925 (C^1H), 1615 (C === C) cm^{-1}.

10.1.33   1-Ethyl-2-methyl-β-naphthothiazolium tosylate
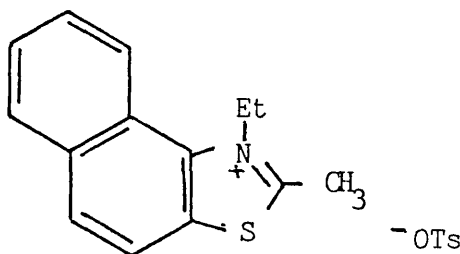
Supplied by Ilford Ltd. (m.p. = 151.0-154.0°)

10.1.34   Ethylene bis-(triphenylphosphonium) bromide
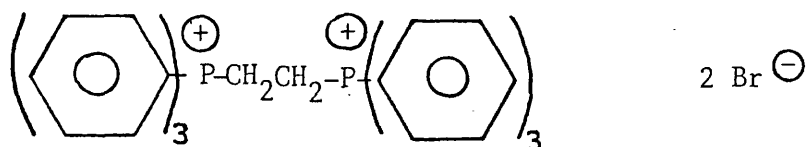
A mixture of triphenylphosphine (20.0 g, 0.076 mol) and

1,2-dibromoethane (60.0 g, 0.32 mol) was heated at 140° for 30 mins.

The white product was then filtered off and dried and weighed 26.0 g (48%)

(m.p. = 305.0 - 306.0°, lit. m.p.[90] = 308.0 - 315.0°); ^{1}H nmr

$\delta(D_2O$, ppm) 3.82 (s, broad) CH_2, 7.69 (m) Ph_3.

10.1.35   Allyl triphenylphosphonium bromide
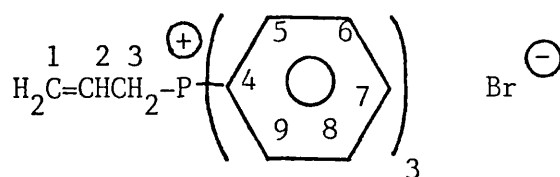
A mixture of triphenylphosphine (20.0 g, 0.076 mol) and allyl

bromide (13.2 ml, 0.15 mol) (redist. 25° at 162 mmHg) in 100 ml benzene

was refluxed for 2 hrs. The white crystalline product was filtered off

and washed with several portions of benzene and after drying weighed

27.6 g (95%) m.p. = 213.0 - 214.0° ; lit. m.p.[91] = 209.0°;

^{1}H nmr $\delta(d^6$-DMSO, ppm) 4.48 (m), 4.74 (m), 5.31 (m), C^1H_2, CH^2,

C^3H_2, 7.56 (m) Ph_3.

10.1.36.   Dibenzotetrathiafulvalene[18,92,93].
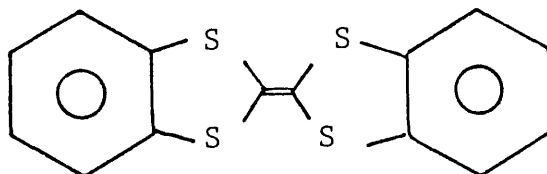
A solution of anthranilic acid (42.5 g, 0.3 mol) in dioxane (100

ml) was added dropwise over a period of 1.5 hrs to a stirred and gently

refluxing solution of isoamyl nitrite (43.3 g, 0.4 mol), isoamyl alcohol

(54.6, 0.6 mol) and carbon disulphide (150 ml) in 1,2-dichloroethane (800

ml). After the addition was completed, the mixture was refluxed for ½ hr.

The resultant red reaction mixture was washed successively with water,

aqueous sodium carbonate, and water and dried over anhydrous magnesium

sulphate. Solvent and excess reagents were removed under reduced pressure

and the red viscous oily residue was purified by distillation in vaccuo

yield; 32.0 g (44%) pale yellow oil, b.p. = 121° 0.1 mmHg. The black

crystalline distillation residue was washed with benzene to give

4.7 g dibenzotetrathiafulvalene.

A further 1.5 g pure dibenzotetrathiafulvalene was obtained from

the thermal decomposition of the 2-alkoxy-1,3-benzodithiole (yellow oil)

at 200° for 1 hr, after recrystallisation from benzene, total yield =

6.2 g (14%); m.p. = 233.0 - 235.0°, lit. m.p. = 234°, Calcd. for

$C_{14}H_8S_4$: C, 55.25, H, 2.63. Found: C, 55.27, H, 2.74.

Oxonols

Many of the dyes in this section have identical anions. As a

result, only very small differences in the anion peaks chemical shifts in

the ^{1}H and ^{13}C n.m.r. spectra and absorption band frequencies, in

the i.r. spectra, are observed, as the cation varies. Therefore the

n.m.r. and i.r. spectral characterisations of the first member of each

anion class are reported in full, subsequent members show only assignments

of the peaks and bands which are in addition to those of the anion.

10.1.37   HPM (1)
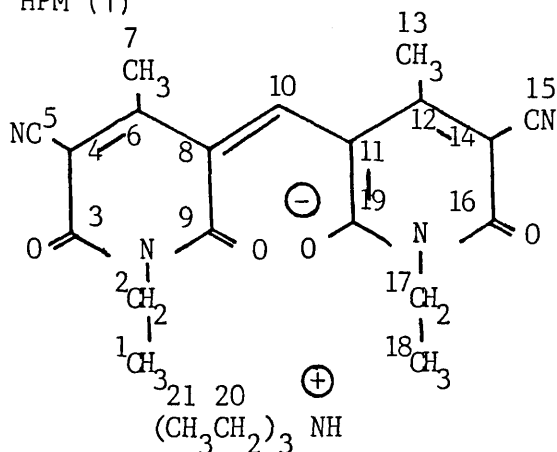
A mixture of 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (5.0 g, 0.028 mol), triethyl orthoformate (2.1 g, 0.014 mol) and triethylamine (1.42 g, 0.014) in 50 ml ethanol was refluxed for 3 hrs. The reaction mixture was allowed to cool, the product filtered off and dried to yield 3.5 g (53%) (recryst. ethanol (purple needles)); m.p. = 185.0 - 186.0° (decomp); ^{1}H nmr δ(d^{6}-DMSO, ppm) 1.21 (m) $C^{21}H_{3}$, $C^{1}H_{3}$, 2.33 (s), $C^{7}H_{3}$, 3.15 (m) $C^{20}H_{2}$, 3.82 (q) $C^{2}H_{2}$, 8.00 (s), $C^{10}H$; uv/visible; λ_{max} (EtOH) 549 nm (ε_{max}, 8.90 x 10^{3} mol^{-1}dm^{3}cm^{-1}) Calcd. for $C_{25}H_{33}N_{5}O_{4}$: C, 64.21, H, 7.13. N, 14.98. Found C, 63.92; H, 6.85, N, 14.70.

10.1.38.   HPT (302)
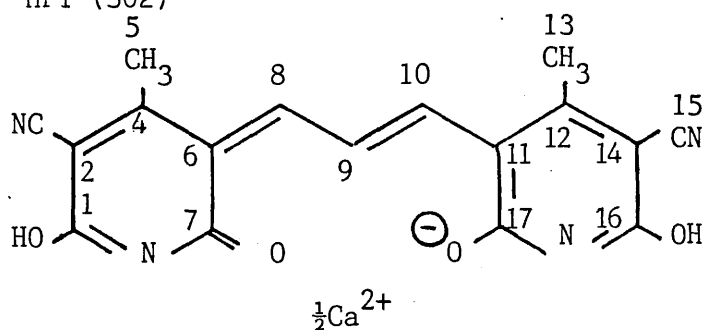
A mixture of 3-cyano-2,6-dihydroxy-4-methyl pyridine (5.0 g, 0.03 mol), tetramethoxypropane (TMP) (2.3 ml, 0.015 mol) and calcium hydroxide (0.52, 0.007 mol) in 40 ml 9:1 ethanol:acetic acid was refluxed for 1 hr.

After cooling, filtering and drying the blue precipitate weighed 5.0 g

(94%) (m.p. > 360.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 2.18 (s) CH_3, 5.45

(s) NH, 7.75 (d) C^8H, 8.93 (t) C^9H; ^{13}C nmr δ(d^6-DMSO, ppm) 18.92,

20.67 (C^5,C^{13}), 92.34, 94.74 (C^4,C^{12}), 110.93 (C^6,C^{11}),

117.76, 118.15 (C^3,C^{15}), 120.95 (C^9), 156.91, 158.80 (C^8,C^{10}),

160.29 (C^2,C^{14}), 162.24, 162.50, 162.83, 163.22 (C^1, C^7, C^{16},

C^{17}); i.r. 3600-3000 (O-H, N-H), 2210 (C≡N), 1625 (C=O), 1608 (C═══C),

1460 (C^5-H), 1360 (C-N), 1308 (C-O), u.v./visible λ_{max} (H_2O) 588

(ϵ_{max} 4.26 x 10^4), 545 nm (sh, 1.91 x 10^3 mol^{-1} dm^{3}cm^{-1}).

10.1.39. HPT (339)

$$M = (C^{21}H_3C^{20}H_2)_4 \; N; \; n = 1$$
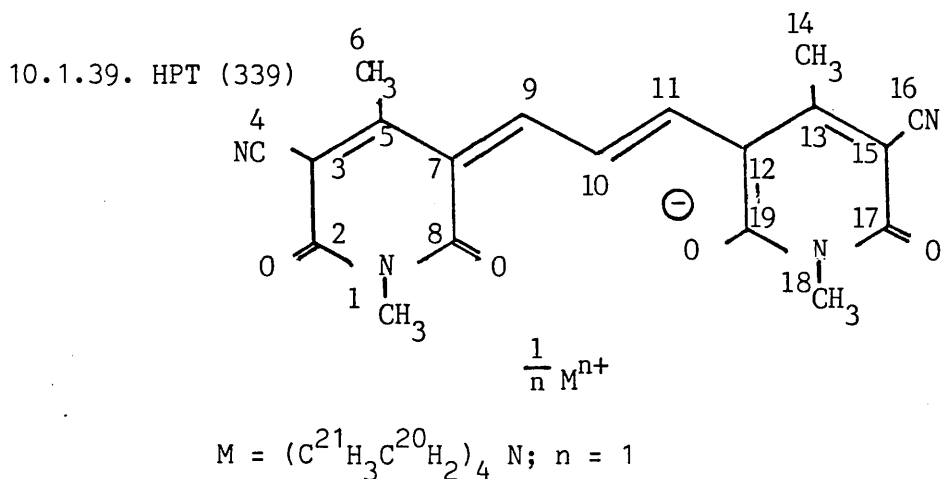
A mixture of 1-methyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (1.0

g, 0.006 mol), 1,1',3,3'-tetramethoxypropane (TMP) (0.5 g, 0.003 mol) and

tetraethylammonium iodide (0.8 g, 0.003 mol) in 20 ml ethanol was refluxed

for 12 hrs. The reaction mixture was allowed to cool and the blue

crystalline material filtered off and dried, yielding 1.1 g (79%)

(recryst. methanol (blue needles)) m.p. = 270.0-271.0°C; ^{1}H

nmr δ(d^6-DMSO, ppm) 0.44 (m) $C^{21}H_3$, 1.71 (s) C^6H_3, 2.43 (s)

C^1H_3, 2.52 (m) $C^{20}H_2$; 7.10 (d) C^9H, 8.36 (t) C^{10}H; ^{13}C nmr

δ(d^6-DMSO, ppm) 7.02 (C^{21}), 18.59 (C^6,C^{14}), 25.94 (C^1, C^{18}),

51.43 (C^{20}), 92.08 (C^5,C^{13}), 110.35 (C^7,C^{12}), 117.70

(c^4, c^{16}), 120.88 (c^{10}), 157.43 (c^9, c^{11}), 158.02 (c^3, c^{15}),

161.79 162.44 $(c^2, c^8, c^{17}, c^{19})$; Calcd. for $C_{27}H_{35}N_5O_4$: C,

65.69; H, 7.16; N, 14.19: Found; C, 65.92; H, 7.08; N, 14.18.

10.1.40. HPT (326)

$$M = (CH_3CH_2CH_2CH_2)_4N \; ; \quad n = 1$$
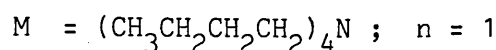
Procedure as for 10.1.39 using 1-methyl-3-cyano-6-hydroxy-4-methyl

pyrid-2-one (4.6 g, 0.029 mol), TMP (2.3 g, 0.014 mol) and tetrabutyl-

ammonium bromide (4.5 g, 0.014 mol) in 50 ml ethanol. Reflux time = 4

hrs. Yield = 6.43 g (77%), (recryst. methanol (dark green cubes); m.p. =

249.0 - 250.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 1.00 (m), $c^{23}H_3$, 1.49 (m)

$c^{21,22}H_2$, 3.22 (m) $c^{20}H_2$; ^{13}C n.m.r. δ(d^6-DMSO, ppm) 19.12

(c^{23}), 23.02 (c^{21}, c^{22}), 57.55 (c^{20}); u.v/visible λ_{max}(EtOH)

599 (ε_{max} 1.29 x 10^5), 555 nm (sh, 3.37 x 10^4 mol^{-1} dm^3cm^{-1});

Calcd. for $C_{35}H_{51}N_5O_4$: C, 69.38; H, 8.50; N, 11.56: Found: C,

68.90; H, 8.53; N, 12.09..

10.1.41. HPT (340)

$$M = \left(\!\left\langle\!\left\langle\bigcirc\right\rangle\!\right\rangle\!\right)_3 PCH_3 \qquad\qquad ; \quad n = 1$$

Procedure as for 10.1.39 using 1-methyl-3-cyano-6-hydroxy-4-methyl

pyrid-2-one (5.0 g, 0.03 mol), methyltriphenylphosphonium bromide (5.5 g,

0.015 mol) and TMP (2.5 g, 0.015 mol) in 50 ml ethanol. Reflux time = 2

hrs. Yield = 5.8 g (60%), (recryst. ethanol (green cubes)); m.p. 205.5 -

207.0°, ^{13}C nmr δ(d^6-DMSO, ppm) 6.84, 7.97 (c^{20}), 118.99, 120.95,

129.93, 130.21, 133.32, 134.75 (Ph$_3$); Calcd. for $C_{38}H_{33}N_4O_4P$: C, 71.23; H, 5.20; N, 8.75: Found C, 70.82; H, 5.45; N, 8.80.

10.1.42. HPT (261).

M = Ca ; n = 2
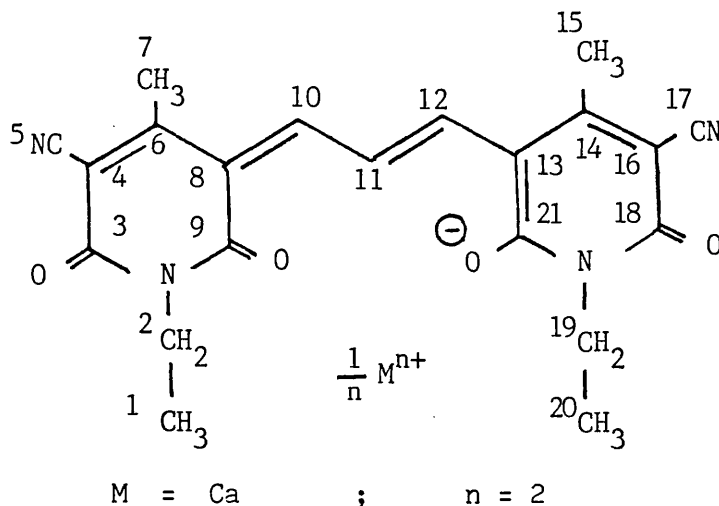
A mixture of 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (5.0 g, 0.028 mol), 1,1',3,3'-tetramethoxypropane (2.4 ml, 0.014 mol) and calcium hydroxide (0.52 g, 0.007 mol) in 50 ml of 9:1 ethanol:acetic acid was refluxed for 2 hrs. The reaction mixture was allowed to cool and the green precipitate filtered off and dried, yielding 4.7 g (82%) (m.p. > 360.0°; lit. m.p.[17] > 360.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 1.09 (t) c^{1}H$_3$, 2.44 (s) c^{7}H$_3$, 3.90 (q) CH$_2$, 7.71 (d) c^{10}H, 9.0 (t) c^{11}H; ^{13}C n.m.r. δ(d^6-DMSO, ppm) 13.08 (c^1,c^{20}), 18.55 (c^7,c^{15}), 33.82 (c^2,c^{19}), 92.21 (c^6,c^{14}), 110.40 (c^8,c^{13}), 117.72 (c^5,c^{17}), 120.93 (c^{11}), 157.36 (c^{10},c^{12}), 158.13 (c^4,c^{16}) 161.39, 161.97 (c^3,c^9,c^{18},c^{21}); i.r. 2975-2930 (C-H, ali), 2200 (C≡N), 1660 (C=O), 1615 (C=C, ar), 1265 (C-N) cm^{-1}.

10.1.43. HPT (336)

M = Co ; n = 2

Procedure as for 10.1.42 using 3-cyano-6-hydroxy-4-methyl
pyrid-2-one (2.5 g, 0.014 mol), TMP (1.2 ml, 0.007 mol) and cobaltous
acetate tetrahydrate (0.9 g, 0.004 mol) in 20 ml ethanol. Reflux time =
1 hr. Yield = 2.0 g (68%) (dark blue powder; m.p. = 344.0-345.5°, lit.
m.p.[17] = 346.0° u.v./visible λ_{max} (H$_2$O) 589 (ε_{max},
8.32 x 10^4), 548 (sh, 3.53 x 10^4 mol^{-1} dm^3 cm^{-1}).

10.1.44.   HPT   (335)

$$M = Ni \quad ; \quad n = 2$$

Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl
pyrid-2-one, (2.5 g, 0.014 mol), TMP (1.2 ml, 0.007 mol) and nickel
acetate tetrahydrate (0.9 g, 0.004 mol) in 20 ml ethanol. Reflux time =
1 hr. Yield = 1.64 g (56 %) (dark blue powder; m.p. > 350.0°, lit.
m.p.[17] > 360°; u.v./visible λ_{max}(H$_2$O) 589 (ε_{max}, 1.13 x 10^5),
545 nm (sh, 5.29 x 10^4 mol^{-1} dm^3 cm^{-1}).

10.1.45.   HPT   (334)

$$M = Al \quad ; \quad n = 3$$

Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl
pyrid-2-one (2.5 g, 0.014 mol), TMP (1.2 ml, 0.007 mol) and aluminium
acetate tetrahydrate (0.44 g, 0.0012 mol) in 20 ml ethanol. Reflux time =
1 hr. Yield = 2.2 g (77%), (dark blue powder; m.p. > 350.0°, lit.
m.p.[17] > 360°;u.v./visible λ_{max} (H$_2$O) 589 (ε_{max}, 6.44 x 10^4),
548 nm (sh, 2.44 x 10^4 mol^{-1} dm^3 cm^{-1}).

10.1.46.   MI1579

$$M = (CH_3CH_2)_3NH \quad ; \quad n = 1$$
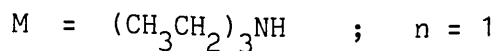
Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl
pyrid-2-one (35.6 g, 0.20 mol), TMP (16.7 ml, 0.10 mol) and triethylamine
(13.9ml, 0.10 mol) in 100 ml ethanol. Reflux time = 6 hrs. Yield = 33.4
(68%), (recryst. methanol (black needles) m.p. = 259.0-260.0°; lit.
m.p.[17] = 259.0-260.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 1.21 (m) $C^{23}H_3$,
3.12 (m) $C^{22}H_2$; ^{13}C nmr δ(d^6-DMSO, ppm) 8.52 (C^{23}), 45.91
(C^{22}).

10.1.47.   HPT   (288)

$$M = (CH_3CH_2CH_2CH_2)_4N \quad ; \quad n = 1$$
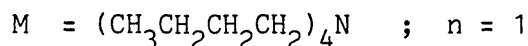
Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl
pyrid-2-one (6.6 g, 0.037 mol), TMP (3.0 ml, 0.019 mol) and tetrabutyl-
ammonium iodide (6.9 g, 0.019 mol) in 150 ml ethanol. Reflux time = 6
hrs. Yield = 5.9 g (50%), (recryst. methanol (metallic green needles);
m.p. = 186.0-187.0°, lit. m.p.[17] = 187.0°; ^{1}H nmr (d^6-DMSO, ppm)
1.09 (m) $C^{25}H_3$, 1.50 (m) $C^{23,24}H_2$, 3.31 (m) $C^{22}H_2$; ^{13}C nmr
δ(d^6-DMSO, ppm) 18.98 (C^{25}), 22.95 (C^{23},C^{24}), 57.61 (C^{22}).

10.1.48.   HPT   (289)

$$M = Ph_4P \quad ; \quad n = 1$$
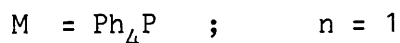
Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl
pyrid-2-one (4.5 g, 0.025 mol), TMP (2.1 ml, 0.0125 mol) and tetraphenyl-
phosphonium bromide (5.3 g, 0.0125 mol) in 20 ml ethanol. Reflux time = 6
hrs. Yield = 8.5 g (92%), (recryst. methanol (gold octahedra) m.p. =
254.0-255.0°, lit. m.p.[17] = 254.0-255.0°.

10.1.49.   HPT (297)
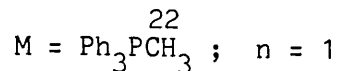
$$M = Ph_3\overset{22}{P}CH_3 \; ; \quad n = 1$$

Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (5.0 g, 0.028 mol), TMP (2.3 g, 0.014 mol) and methyl-triphenylphosphonium bromide (5.0 g, 0.014 mol) in 100 ml ethanol. Reflux time = 8 hrs. Yield = 8.31 g (89%), (recryst. methanol (dark blue needles) m.p. = 220.0 - 221.0° (decomp), lit. m.p.[17] = 221.0°, ^{1}H nmr δ(d^6-DMSO, ppm) 3.16 (d) C^{22}H$_3$, 7.84 (m) Ph$_3$, ^{13}C nmr δ(d^6-DMSO, ppm) 9.70 (d) (C^{22}), 119.79, 129.74, 130.26, 132.86, 133.31, 134.94 (Ph$_3$).

10.1.50.   HPT (299)
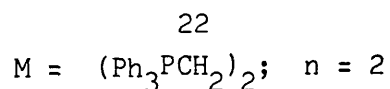
$$M = (Ph_3\overset{22}{P}CH_2)_2; \quad n = 2$$

Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one, (5.0 g, 0.028 mol), TMP (2.3 g, 0.014 mol) and ethylene bis(triphenylphosphonium) dibromide (5.0 g, 0.007 mol) in 50 ml ethanol. Reflux time = 22 hrs. Yield = 7.2 g (77%), (recryst. ethanol (silver needles) m.p. = 270.5-271.5° (decomp); ^{1}H nmr δ(d^6-DMSO,ppm) 3.55 (s) C^{22}H$_2$, 7.84 (s, broad)Ph$_3$;u.v./visible λ_{max} (H$_2$O) 589 (ε_{max}, 9.40 x 10^4), 546 nm (sh, 4.33 x 10^4 mol^{-1} dm^3 cm^{-1}); Calcd. for C$_{40}$H$_{36}$N$_4$O$_4$P: C, 71.95; H, 5.45; N, 8.39: Found C, 71.92; H, 5.46; N, 8.43.

10.1.51.   HPT (327)
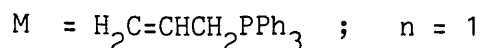
$$M = H_2C=CHCH_2PPh_3 \quad ; \quad n = 1$$

Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl

pyrid-2-one (5.0 g, 0.028 mol), TMP (2.3 g, 0.014 mol) and allyl

triphenylphosphonium bromide (5.4 g, 0.014 mol) in 75 ml ethanol.   Reflux

time = 5 hrs.   Yield = 6.1 g (63%), (recryst. ethanol (green needles);

m.p. = 206.5-207.5°; ^{1}H nmr δ(d^6-DMSO, ppm) 3.81 (m), 3.89 (m), 5.47

(m), CH_2, CH, C H_2, 7.85 (m) Ph_3; u.v./visible λ_{max} (EtOH)

601 nm (ε_{max}, 1.13 x 10^5 mol^{-1} dm^3cm^{-1}); Calcd. for

$C_{42}H_{39}N_4O_4P$: C, 72.60; H, 5.67; N, 8.07: Found C, 72.67; H, 5.64;

N, 8.00.

10.1.52.   HPT 328)
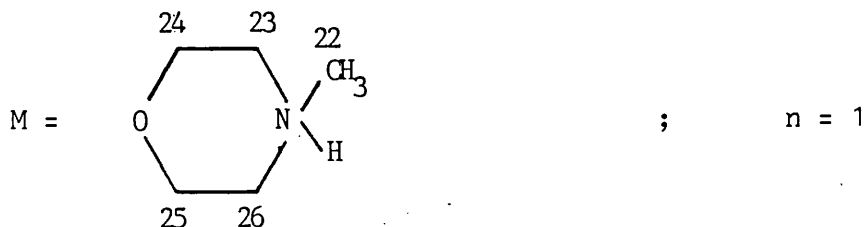
M =   (morpholine ring structure with positions 24, 23, 22, O, N, CH$_3$, H, 25, 26)   ;   n = 1

Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl

pyrid-2-one (5.0 g, 0.028 mol), TMP (2.3 g, 0.014 mol) and n-methyl

morpholine (1.43 g, 0.014 mol) in 50 ml ethanol.   Reflux time = 17 hrs.

Yield = 5.0 g (72%), (recryst. methanol (purple needles); m.p. =

271.0-272.0° (decomp); ^{1}H nmr δ(d^6-DMSO, ppm) 2.83 (s) $C^{22}H_3$,

3.47 (m), 3.91 (m), $C^{23,24,25,26}H_2$, u.v./visible λ_{max} (H_2O) 589

(ε_{max}, 1.15 x 10^5), 545 nm (sh, 3.4 x 10^4 mol^{-1} dm^3 cm^{-1};

Calcd. for $C_{26}H_{31}N_5O_5$: C, 63.27; H, 6.33; N, 14.19: Found C,

63.29; H, 6.13; N, 14.03.

10.1.53   HPT   (324)

$$M = \quad \text{(see structure)} \quad ; \quad n = 1$$
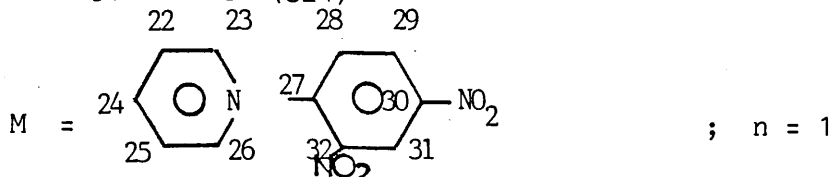
Procedure as for 10.1.42 using 1-ethyl-3-cyano-6-hydroxy-4-methyl

pyrid-2-one (2.5 g, 0.014 mol), TMP (1.15 g, 0.007 mol) and $\underline{N}$-(2,4-

dinitrophenyl)-pyridinium chloride in 50 ml ethanol. Reflux time = $4\frac{1}{2}$ hrs.

Yield = 3.4 g (76%), (recryst. ethanol (green cubes); m.p. =

261.5° (decomp); ^{1}H nmr δ(d^6-DMSO, ppm) 8.95 (m) C^{22-26}H,

$C^{28,29,31}$H; u.v./visible λ_{max} (H_2O) 589 (ε_{max} 9.49 x 10

547 nm (sh, 4.65 x 10^4 mol^{-1} dm^3 cm^{-1}); Calcd. for

$C_{32}H_{27}N_7O_8$; C, 60.28; H, 4.27; N, 15.38: Found C, 60.37; H, 4.54;

N, 15.21.

10.1.54.   HPT   (314)

$$M = H_2C = \underset{\underset{CH_3}{|}}{C} - CO_2CH_2CH_2 \underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{N}} - CH_3 ; \quad n = 1$$
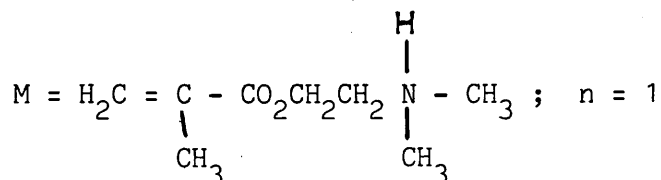
Procedure as for 10.142 using 1-ethyl-3-cyano-6-hydroxy-4-methyl

pyrid-2-one (10.0g, 0.056 mol), TMP (4.6 g, 0.028 mol) and dimethyl-

aminoethyl methacrylate (4.4 g, 0.028 mol) in 80 ml ethanol. Reaction

time = kept at 60°C for 24 hrs. Yield = 5.8 g (38%), (recryst. ethanol

(blue needles); m.p. = 216.0-217.0°; ^{1}H n.m.r.δ(d^6-DMSO, ppm) 1.91

(s) $C^{27}H_3$; 2.90 (s) $C^{22}H_3$, 3.49 (m) $C^{25}H_2$, 4.42 (m) $C^{24}H_2$,

5.36 (s) NH, 5.75 (m) $C^{29}H_2$, 6.15 (m) $C^{29}H_2$; Calcd. for

$C_{29}H_{35}N_5O_6$: C, 63.37; H, 6.42; N, 12.74: Found C, 62.97; H, 6.43;

N, 12.54.

10.1.55.   HPT (298)
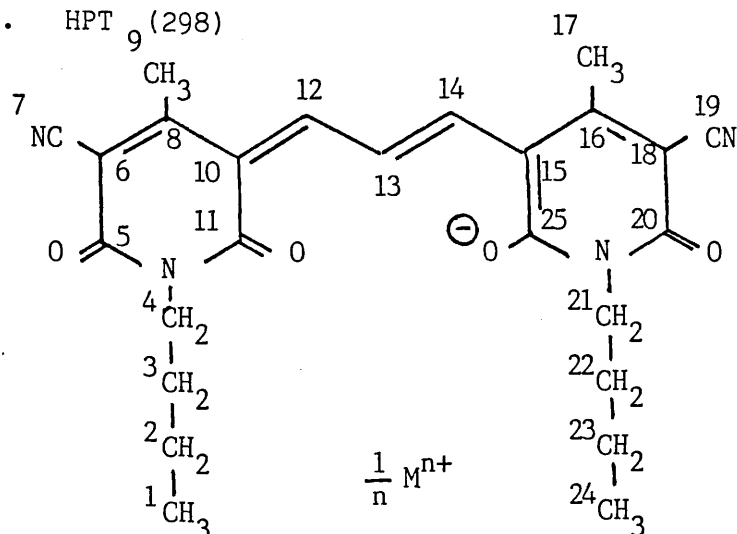
M = Na   ;   n = 1

A mixture of 1-butyl-3-cynao-6-hydroxy-4-methyl pyrid-2-one (10.0 g, 0.049 mol), 1,1',3,3'-tetramethoxypropane (4.0 ml, 0.024 mol) and sodium acetate (2.0 g, 0.024 mol) was refluxed for 20 hrs in 50 ml ethanol. On cooling an olive green precipitate was obtained which after filtering off and drying weighed 9.24 g (82%) (recryst. EtOH (green cubes) (m.p. = 349.0 -350.0°C; lit. m.p.[17] = 349.0-350.0°C; ^{1}H nmr δ(d^6-DMSO, ppm) 1.13 (m) c^1H_3, 1.62 (m) $c^{2,3}H_2$, 2.66 (s) c^9H_3, 4.08 (m), c^4H_2, 8.04 (d) $c^{12}H$, 9.38 (t) $c^{13}H$; ^{13}C nmr δ(d^6-DMSO, ppm). 13.58 (c^1,c^{24}), 18.40 (c^9,c^{17}), 19.76 (c^2,c^{23}), 29.52 (c^3,c^{22}), 38.49 (c^4,c^{21}), 92.08 (c^8,c^{16}), 110.22 (c^{10},c^{15}), 117.63 (c^7,c^{19}), 120.82 (c^{13}), 157.24 (c^{12},c^{14}), 157.95 (c^6,c^{18}), 161.46, 161.92 (c^5,c^{11},c^{20},c^{25}).

10.1.56.   HPT (309)

M = Li   ;   n = 1

Procedure as for 10.1.55 using 1-butyl-3-cyano-6-hydroxy-4-methyl

pyrid-2-one (10.0 g, 0.049 mol), TMP (4.0 ml, 0.024 mol) and lithium

carbonate (0.90g, 0.012 mol) in 50 ml ethanol. Reflux time = 20 hrs.

Yield 9.7 g (89%). (recryst. ethanol (green cubes); m.p.[17] > 360°.

lit. m.p. > 360° .

10.1.57.   HPT   (182)

M = $(CH_3CH_2CH_2CH_2)_4N$;   n = 1
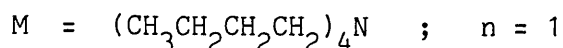
Procedure as for 10.1.55 using 1-butyl-3-cyano-6-hydroxy-4-methyl

pyrid-2-one (5.0 g, 0.024 mol), TMP (22.0 ml, 0.012 mol) and

tetrabutylammonium bromide (3.9 g, 0.012 mol) in 50 ml ethanol. Reflux

time = 7 hrs. Yield = 0.6 (7%) (recryst. ethanol (mauve powder); m.p.

178.0 - 180.0°; ^1H nmr $\delta(d^6$-DMSO, ppm) 1.00 (m) $C^{29}H_3$, 1.45 (m)

$C^{27,28}H_2$, 3.43 (m) $C^{26}H_2$; Calcd. for $C_{41}H_{63}N_5O_4$: C, 71.36;

H, 9.22; N, 10.15: Found C, 71.77; H, 8.89; N, 9.91.

10.1.58   HPT   (308)

M =

;   n = 1

Procedure as for 10.1.55 using 1-butyl-3-cyano-6-hydroxy-4-methyl

pyrid-2-one (2.5 g, 0.012 mol), TMP (1.0 ml, 0.006 mol) and n-methyl

morpholine (0.64 g, 0.006 mol) in 20 ml ethanol. Reflux time = 4 hrs.

Yield = 0.6 g (19%). (recryst. ethanol (two crystal habits; dark blue

needles (m.p.= 218.5-219.5°), green cubes (m.p. = 218.5-219.5°);

^{13}C nmr $\delta(d^6$-DMSO, ppm) 42.52 (C^{26}), 52.60 (C^{28},C^{29}), 63.33

(C^{27}, C^{30}); u.v./visible λ_{max}(EtOH) 602 (ε_{max}, 1.68 x 10^5) 555

nm (sh, 4.07 x 10^4 mol^{-1} dm^3 cm^{-1}). Calcd. for $C_{30}H_{36}N_5O_5$:

C, 65.55; H, 7.1; N, 12.74: Found C, 65.91; H, 7.20; N, 12.80.

10.1.59   HPT (179)
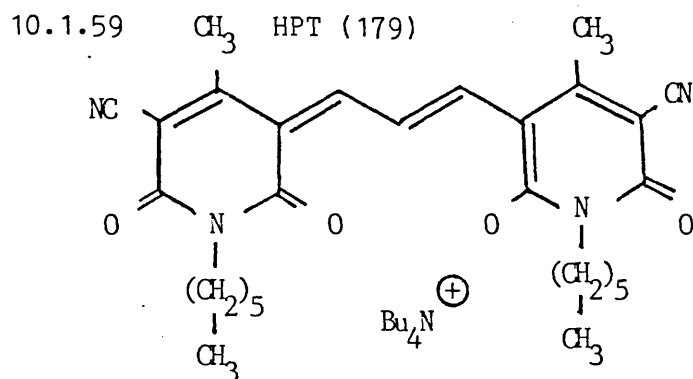
Supplied by Ilford Ltd. (λ_{max} (H_2O) 596 nm (ε_{max}, 1.74 x 10^5

mol^{-1} dm^3 cm^{-1})).

10.1.60   HPT (282)
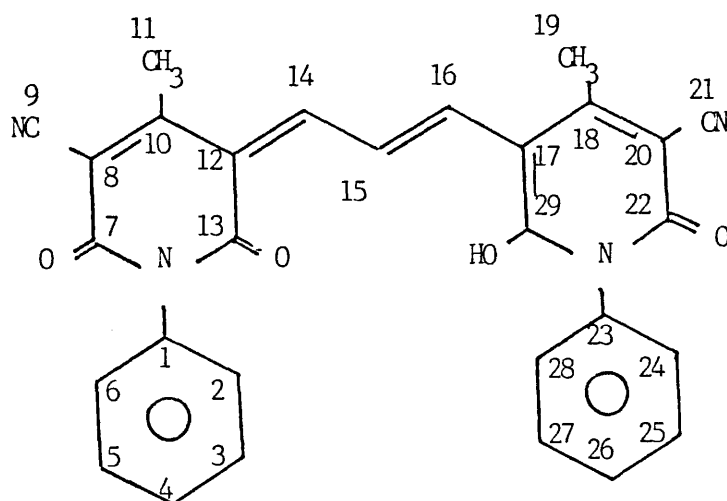
A mixture of 1-phenyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (2.5 g, 0.01 mol) and 1,1',3,3'- tetramethoxypropane (0.09 ml, 0.005 mol) in 20 ml acetic acid was refluxed for 1 hr. The product was precipitated out with ether, filtered and dried, yielding 0.6g (26%) (recryst. methanol, (dark purple powder). m.p. 261.0-263.0°; ^{1}H nmr δ(d^6-DMSO) 1.92 (s) $C^{11}H_3$, 7.39 (m) $C^{14}H$, Ph, 8.88 (t) $C^{15}H$; ^{13}C nmr δ(d^6-DMSO, ppm) 18.85, 21.00 (C^{11},C^{19}), 92.60 (C^{10},C^{18}), 110.80 (C^{12},C^{17}), 117.63, 119.84 (C^9,C^{21}), 123.94 (C^{15}), 127.45, 128.49, 129.01, 130.12 (Ph), 136.04, 136.49 (C^1,C^{23}), 157.30, 159.19 (C^{14},C^{16}), 161.72, 162.37 (C^8,C^{20}), 164.24, 165.82, 169.59, 172.00 (C^7,C^{13},C^{22},C^{29}); i.r. 3070 (O-H), 2220 (C≡N), 1660 (C=O) 1460 (C==C, Ph), 1350 (C-N) cm^{-1}; u.v/visible λ_{max} (H$_2$O) 591 (ε_{max}, 3.56 x 10^4), 548 nm (sh, 1.12 x 10^4 mol^{-1} dm^3 cm^{-1}); poor analysis.

10.1.61.   HPT (330)
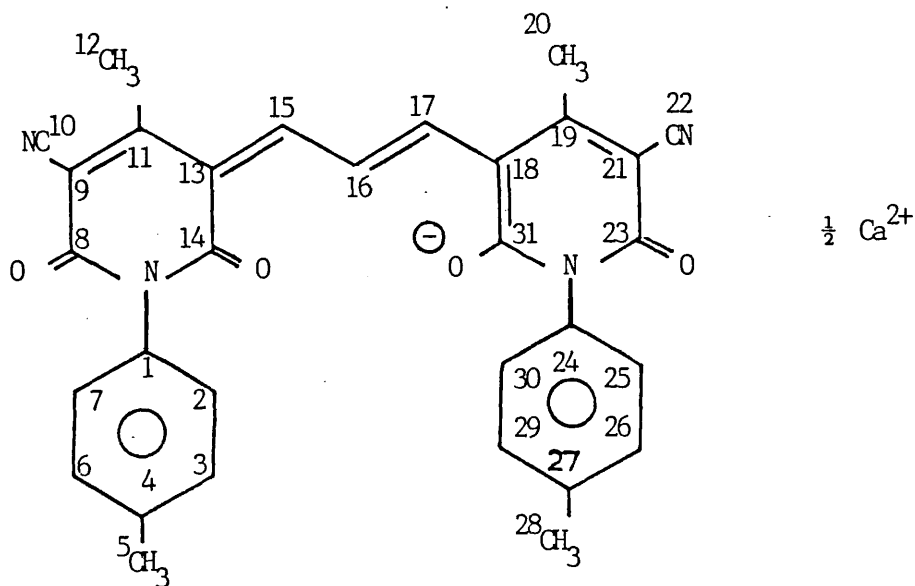
A mixture of 1-(p-tolyl)-3-cyano-6-hydroxy-4-methyl pyrid-2-one

(1.0 g, 0.004 mol), 1,1',3,3'-tetramethoxypropane (0.34 g, 0.002 mol) and

calcium hydroxide (0.08 g, 0.001 mol) in 20 ml 9:1 ethanol:acetic acid was

refluxed for 1 hr. The product was precipitated out with diethyl ether,

filtered and dried, yielding 0.7 g (65%) (recryst. methanol (pale blue

precipitate), m.p. 317.0-320.0°; ^{1}H n.m.r. δ(d^6-DMSO, ppm) 2.17 (s)

$C^{12}H_3$, 2.35 (s) C^5H_3, 7.13 (m) Ar, 7.85 (d) $C^{15}H$, 8.80 (t)

$C^{16}H$; ^{13}C nmr δ(d^6-DMSO, ppm) 18.79 (C^{12},C^{20}), 20.61

(C^5,C^{28}), 94.10 (C^{11},C^{19}), 110.67 (C^{13},C^{18}), 118.53

(C^{10},C^{22}), 120.81 (C^{16}), 128.23, 128.69, 129.14 (Ar), 133.43, 133.76

(C^4,C^{27}), 136.62, 137.01 (C^1,C^{24}), 157.24 (C^{15},C^{17}), 158.99

(C^9,C^{21}), 161.66, 162.31 (C^8,C^{14},C^{23},C^{31}), i.r. 3080 (C-H),

3025 (C-H), 2210 (C≡N), 1650 (C=O), 1608 (C=C) cm^{-1}; u.v./visible

λ_{max} (EtOH) 605 (ε_{max}, 3.76 x 10^4), 560 nm (sh, 9.68 x10^3 mol^{-1}

dm^3 cm^{-1}); poor analysis.

10.1.62.   HPT (331)
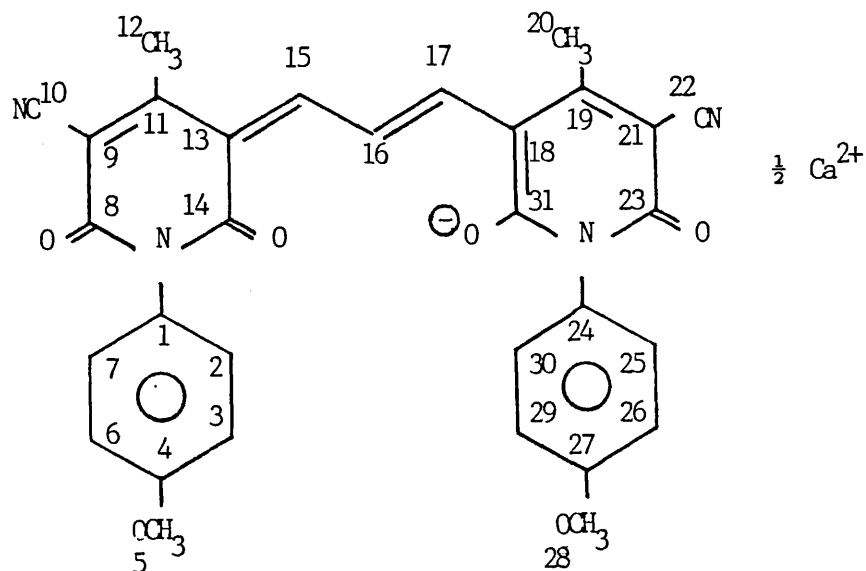
A mixture of 1-(p-anisyl)-3-cyano-6-hydroxy-4-methyl pyrid-2-one (1.0 g, 0.004 mol), 1,1',3,3'-tetramethoxypropane (0.32 ml, 0.002 mol) and calcium hydroxide (0.07, 0.001 mol)　　　　　　in 20 ml 9:1 ethanol:acetic acid was refluxed for 1 hr. The product was precipitated out with diethyl ether, filtered and dried yielding 0.7 g (60%) (recryst. methanol (pale blue powder); m.p. > 360.0°; ^{1}H nmr δ(d^6-DMSO, ppm) 2.26 (s) $C^{12}H_3$, 3.82 (s) OC^5H_3, 7.02 (m) Ar, 7.85 (d) $C^{15}H$, 8.90 (t) $C^{16}H$; i.r. 3070 (C-H), 3025 (C-H), 2210 (C≡N) 1660 (C=O), 1608 (C=C) cm^{-1}; u.v./visible λ_{max}(EtOH) 605 (ϵ_{max}, 2.53 x 10^4), 560 nm (sh, 6.53 x 10^3 mol^{-1}dm^3 cm^{-1}); poor analysis

10.1.63.　　　　　HPT (325)
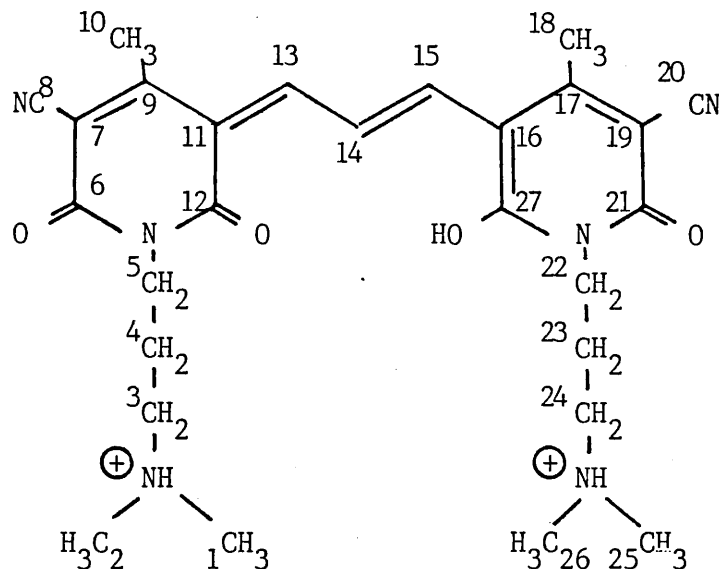
A mixture of 1-(dimethylaminopropyl)-3-cyano-6-hydroxy-4-methyl pyrid-2-one (2.5 g, 0.01 mol), 1,1',3,3'-tetramethoxypropane (0.9 g, 0.006 mol), hydroiodic acid (2.54 g, 0.02 mol) and iodine (2.87 g, 0.01 mol) was refluxed for 5 hrs in 50 ml ethanol. On cooling a dark green microcrystalline material precipitated out. After filtering and drying

it weighed 3.95 g (52%) (recryst. ethanol (green cubes); m.p. 227.0-

229.0° (decomp); ^{1}H n.m.r. δ (d^6-DMSO, ppm) 1.44 (m) C^{4}H$_2$,

1.90 (s) C^{10}H$_3$, 2.27 (s) C^{1}H$_3$, C^{2}H$_3$, 2.35 (m) C^{5}H$_2$, 3.40

(m) C^{3}H$_2$, 3.49 (s) NH, 7.25 (d) C^{13}H 8.47 (t) C^{14}H; ^{13}C nmr

δ(d^6-DMSO, ppm) 18.67 (C^{10},C^{18}), 23.02 (C^4,C^{23}), 36.03

(C^5,C^{22}), 42.34 (C^1,C^2,C^{25},C^{26}), 54.76 (C^3,C^{24}), 92.28

(C^9, C^{17}), 110.42 (C^{11},C^{16}), 117.51 (C^8,C^{20}), 121.15 (C^{14}),

157.64 (C^{13},C^{15}), 158.55 (C^7,C^{19}), 161.80, 162.25

(C^6,C^{12},C^{21},C^{27}); Found: C, 38.96; H, 5.19; N, 10.22, I, 39.02.

10.1.64   HPP (337)

M = (CH$_3$CH$_2$)$_3$NH   ;   n = 1
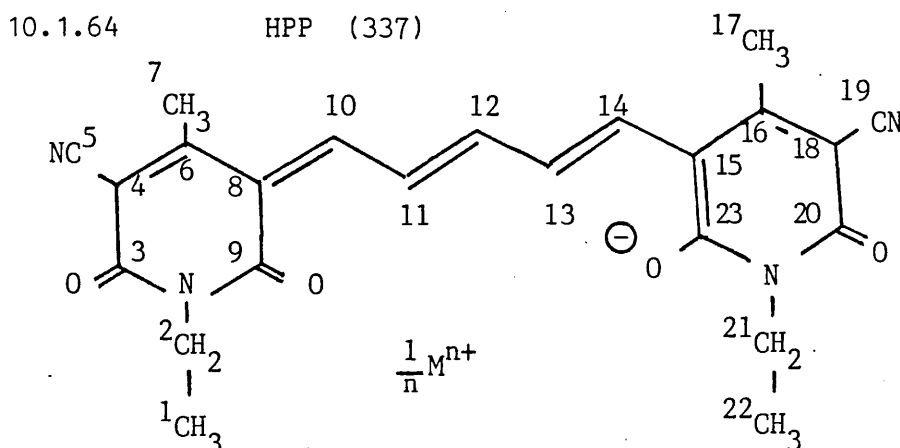
A mixture of 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (3.0 g,

0.02 mol) and glutaconic dialdehyde dianil hydrochloride (2.4 g, 0.01 mol)

in 20ml acetic anhydride
∧ was gently warmed (30-40°) with stirring until the solid starting

materials had dissolved. Triethylamine (2.3 ml, 0.216 mol) was then added

dropwise and the reaction mixture was heated to 95°C and maintained at

this temperature for 30 mins. On cooling a dark green precipitate was

obtained. On filtering and drying it weighed 1.5 g (37%) (recryst. acetonitrile (metallic green microcrystalline); m.p. = 138.0-139.0°; ^{1}H nmr δ(d^6-DMSO,ppm) 1.21 (m) C^1H_3, $C^{25}H_3$, 2.39 (s) C^7H_3, 3.81 (m) C^2H_2, $C^{24}H_2$, 7.75 (m) C^{10},$C^{11}H$, 8.92 (m) $C^{12}H$; ^{13}C nmr δ(d^6-DMSO, ppm) 8.51 (C^{25}), 12.93 (C^1,C^{22}), 18.46 (C^7,C^{17}), 33.74 (C^2,C^{21}), 45.90 (C^{24}), 91.88 (C^6,C^{16}), 110.41 (C^8,C^{15}), 117.63 (C^5,C^{19}), 123.50 (C^{12}) 146.13 (C^{11},C^{13}), 156.92 (C^{10},C^{14}), 157.89 (C^4,C^{18}), 161.21, 162.12 (C^3,C^9,C^{20},C^{23}); u.v./visible λ_{max} (H_2O) 680 nm (ε_{max}, 8.42 x 10^4 mol^{-1} dm^3 cm^{-1}); Calcd. for $C_{29}H_{37}N_5O_4$: C, 67.02; H, 7.19; N, 13.48: Found C, 66.70; H, 6.98; N, 13.38.

10.1.65.   HPP (323)
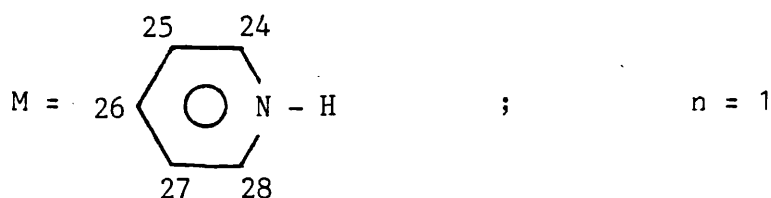
Procedure as for 10.1.64 however using pyridine (2.0 g, 0.025 mol) in place of triethylamine. Yield = 0.8 g (21%) (recryst. ethanol (green powder); m.p.209.0-211.0°; ^{13}C nmr δ(d^6-DMSO, ppm) 127.01 (C^{25}), 142.03 (C^{26}), 150.61 (C^{24}); u.v./visible λ_{max} (H_2O) 682 (ε_{max}, 1.04 x 10^5, 605 nm (sh, 4.46 x 10^3 $mol^{-1}dm^3cm^{-1}$); Calcd. for $C_{28}H_{27}N_5O_4$: C, 67.59; H, 5.48; N, 14.08: Found C, 67.60; H, 5.48; N, 14.06.

10.1.66.   HPP (322)

$$M = \quad \begin{array}{c} 26 \quad 25 \quad 24 \\ O \quad N \quad CH_3 \\ 27 \quad 28 \quad H \end{array} \quad ; \quad n = 1$$
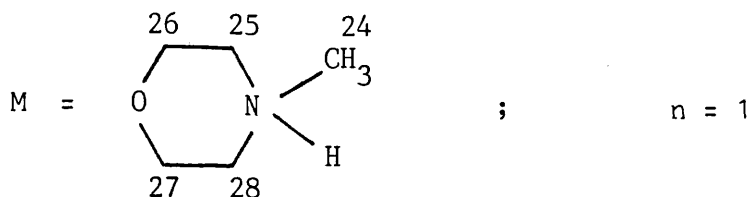
Procedure as for 10.1.64 however replacing the triethylamine with

N-methylmorpholine (2.8 ml,0.025 mol) . Yield = 2.85 g (70%) (recryst.

methanol (metallic green cubes); m.p. = 205.0-208.0°; ^{13}C nmr

$\delta(d^6$-DMSO, ppm) 42.42 (C^{24}, 53.00 (C^{26}), 63.31 (C^{25});

u.v./visible $\lambda_{max}(H_2O)$ 679 nm ε_{max}, 7.81 x 10^4

$mol^{-1}dm^3cm^{-1}$); Calcd. for $C_{28}H_{33}N_5O_5$: C, 64.71; H, 6.41; N,

13.48: Found C, 64.37; H, 6.39; N, 13.17.

10.1.67.   HPP (321)

$$M = \quad \begin{array}{c} CH_3 \\ N \\ H \end{array} \quad ; \quad n = 1$$
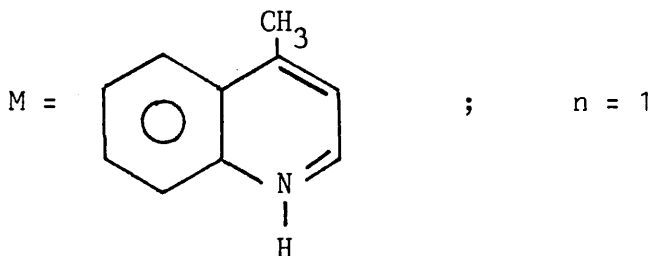
Procedure as for 10.1.64 however replacing the triethylamine with

lepidine (3.3 ml, 0.025 mol). Yield = 2.1 g (48%) (recryst. methanol

(dark green powder); m.p. = 211.0-212.0° (decomp); u.v./visible λ_{max}

(EtOH) 678 (ε_{max}, 1.33 x 10^5) 630 nm (sh, 2.50 x $10^4 mol^{-1}dm^3 cm$

Calcd. for $C_{33}H_{31}N_5O_4$: C, 70.57; H, 5.57; N, 12.47: Found: C,

70.77; H, 5.49; N, 12.51.

10.1.68.   HPT (320)
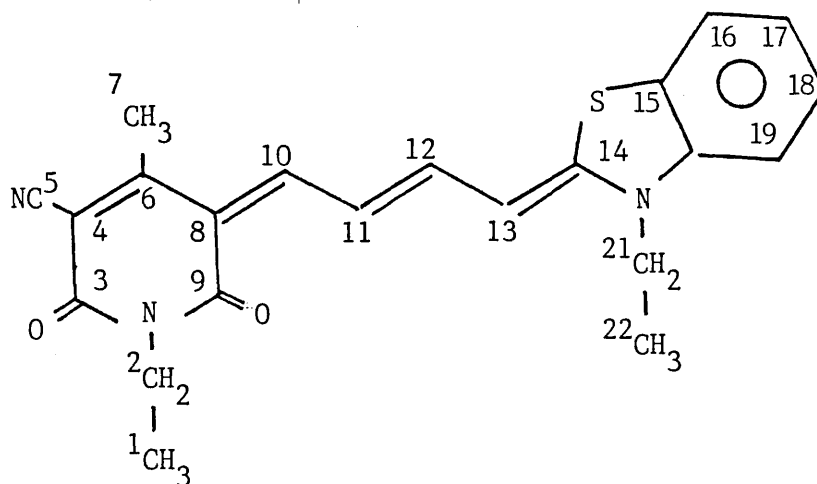
A mixture of 3-(3'-acetanilidoallylidiene)-1-ethyl-4-methyl-5-cyanopyrid-2,6-dione (2.5 g, 0.007 mol), 1-ethyl-2-methylbenzothiazolium iodide (2.2 g, 0.007 mol) and triethylamine (1.0 ml, 0.007 mol) in 9.0 ml pyridine was heated to 100° and was maintained at this temperature for 30 mins. After cooling, filtering and drying the green precipitate weighed 1.6 g (58%) (recryst. acetonitrile (green cubes); m.p. = 193.0-194.5° (decomp); ^1H nmr $\delta(d^6$-DMSO, ppm) 1.22 (m) C^1H_3, $C^{22}H_3$, 2.39 (s) C^7H_3; 3.47 (m) C^2H_2, 4.15 (m) $C^{21}H_2$, 6.79 (d) $C^{10}H$, 7.49 (m) $C^{16-19}H$, $C^{13}H$, 7.89 (m) $C^{11}H$, $C^{12}H$; ^{13}C nmr $\delta(d^6$-DMSO, ppm) 12.41 (C^{22}), 12.93 (C^1), 18.91 (C^7), 34.52 (C^2), 36.73 C^{21}), 92.87 (C^6), 112.75 (C^8), 117.24 (C^5), 122.64 (C^{11},C^{12}), 124.46 (C^{16-19}), 125.05 (C^{11},C^{12}), 127.58, 128.04, 129.34 (C^{16-19}), 138.31 (C^{15}), 140.52 (C^{20}), 149.95 (C^{13}), 157.52 (C^4), 161.07, 162.49 (C^3,C^9); uv/visible λ_{max} (H_2O) 646 nm (ε_{max}, 4.53 x 10^4 mol^{-1} dm^3 cm^{-1}: Calcd for $C_{22}H_{21}N_3O_2S$: C, 67.49; H, 5.42; N, 10.74: Found C, 66.76; H, 6.02; N, 11.01.

10.1.69.   HPT (319)
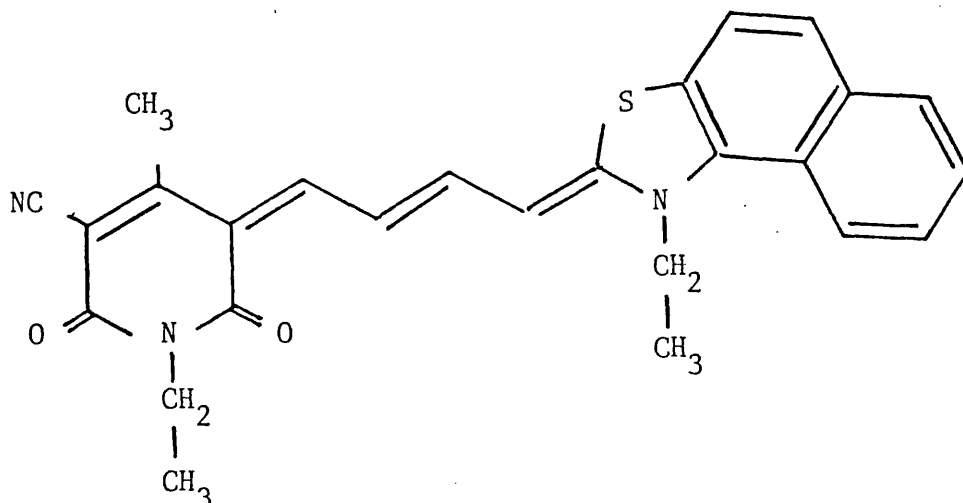
A mixture of 3-(3'-acetanilidoallylidiene)-1-ethyl-4-methyl-5-cyano
pyrid-2,6-dione (1.0 g, 0.003 mol), 1-ethyl-2-methyl-β-napthothiazolium
tosylate (1.2 g, 0.003 mol) and triethylamine (0.5 g, 0.004 mol) in 5.0 ml
pyridine was heated to 100 $^{\circ}$ and maintained at this temperature for 30
mins. After cooling, filtering and drying the precipitate weighed 0.54 g
(41%) (recryst. acetonitrile (dark purple powder) m.p. = 181.0-
183.0° (decomp); u.v./visible λ_{max} (H_2O) 665 nm (ϵ_{max},
8.27 x 10^3 mol^{-1} dm^3 cm^{-1}); poor analysis.

10.2. Polymeric Dye Systems as Bleachable Antihalation Underlayers

10.2.1. Instrumentation

A 35 ml dilatometer, a high pressure mercury photolysis lamp,

Bruker WM-250 MHz and WH-400 MHz n.m.r. spectrometers and a Perkin-Elmer

550S u.v./visible spectrophotometer.

10.2.2. Chain-growth polymerisation : hydroxypyridone oxonol

salts of polymerisable cation.

The following attempts were made to polymerise the oxonol dye (I),

scheme 3.1 and 10.2.1.

$$H_2C=C(Me)CO_2(CH_2)_2NHMe_2 \quad (I)$$
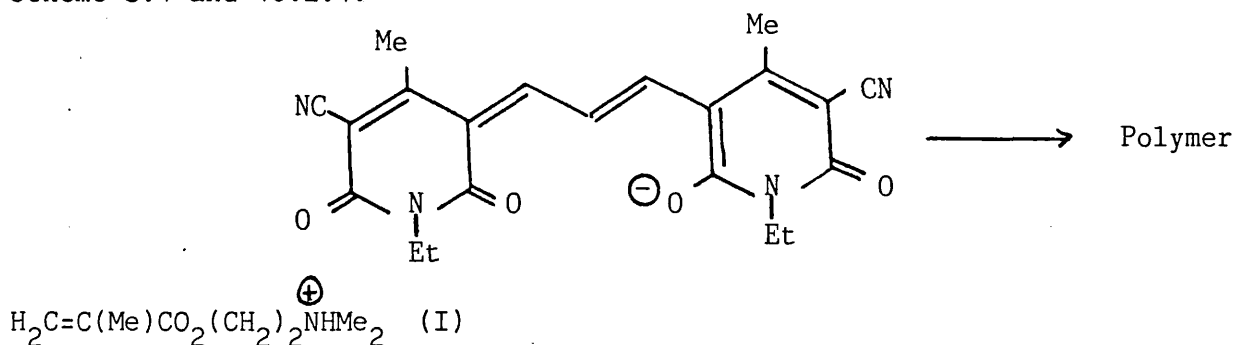
Scheme 10.2.1.

a)   Dye (I) (0.3 g, 0.55 mmol) and 4,4'-azobis(4-cyanopentanoic acid)

(ABCPA) (1.6 mg, 0.003 mmol) in 3 ml water were heated to 60° under

nitrogen overnight.

b)   Dye (I) (2.0 g, 3.6 mmol) and azobisisobutyronitrile (AIBN)

(3.0 mg, 0.021 mmol) in 10.0 g absolute ethanol was heated at 60°,

under nitrogen overnight.

c)   Dye (I) (0.5 g, 0.9 mmol) and AIBN (1.5 mg, 0.01 mmol) in 5.0 g

dimethylformamide, DMF, was heated at 60°, under nitrogen, overnight.

d)   Dye (I) (2.0 g, 3.6 mmol) and AIBN (3.0 mg, 0.02 mmol) in 10.0 g

DMF was heated at 60°, under nitrogen, overnight.

e)   Dye (I) (0.3 g. 0.55 mmol) heated at 160°, for 8 hours.

f)   Dye (I) (0.3 g, 0.55 mmol) exposed to ultra-violet light

(λ = 207 nm) over a weekend.

In each case ^{1}H nmr analyses revealed that no polymerisation had

taken place.

Dilatometric measurements were then undertaken to establish

whether or not dye (I) was an inhibitor to free-radical

polymerisation[23,24]. A stock solution of pre-distilled (38°, 79

mmHg) methyl methacrylate (70.0 g, 0.7 mol) and AlBN (0.2 g, 1.2 mmol)

in 200 g methyl ethyl ketone was prepared. A portion of this stock

solution (35 ml) was placed in a dilatometer which itself was placed in a

water bath at 60°. The contraction in volume over a period of 1 hr was

recorded. To a second portion of the stock solution (135 g) was added

dye (I) (0.1 g, 0.2 mmol) and 35 ml of this solution was placed in a

dilatometer, in a water bath at 60°, and the contraction in volume

measured over the same time period. The results are shown in figure 3.3,

Chapter 3.

10.2.3. Step-growth polymerisation

N,N'-Hexamethylene-bis-(3-cyano-6-hydroxy-4-methyl pyrid-

2-one) (20.0 g, 0.05 mol) was dissolved in 50.0 g DMF to yield a 40% w/w

solution. 1,1',3,3'-Tetramethoxypropane (8.6 g, 0.05 mol) and

triethylamine (6.8 g, 0.06 mol) were then added and the mixture heated at 130° for 48 hrs. Aliquots (5.0 ml) were taken from the reaction mixture every 4 hrs. These aliquots were diluted to 10 ml with DMF and were individually added dropwise to a vigorously stirred ethyl acetate (750 ml) solution. The precipitates were filtered off and dried.

Each of the samples was then characterised using ^{1}H nmr and uv/visible spectroscopy. Table 10.2.1 shows the assignment of the ^{1}H nmr spectrum for the 4 hour aliquot (III, x = 6, M = Et$_3$NH, m = 1, scheme 3.3).
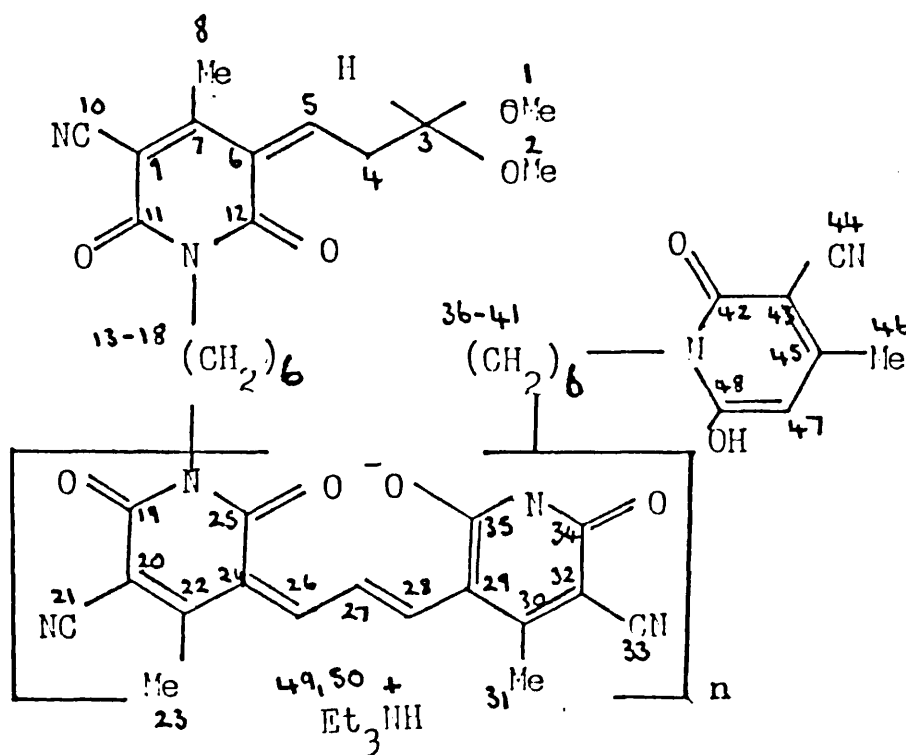
III

Table 10.2.1

$\delta(d^6\text{-DMSO, ppm})$	Assignment
1.19 (t)	$C^{49}H_3$
1.30 (s, broad) $\Big\}$	$C^{13-18}H_2$, $C^{36-41}H_2$
1.47 (s, broad)	
2.00 (s)	Unreacted hydroxypyridone
2.44 (s)	$C^{23,31}H_3$
2.51 (s)	$C^{46}H_3$
3.10 (s)	Unreacted TMP
3.26 (s)	$C^{1.2}H_3$
3.60 (s, broad) $\Big\}$	$C^{13-18}H_2$, $C^{36-41}H_2$
3.80 (s, broad)	
4.35 (m)	C^4H_2
5.11 (s)	$C^{47}H$
5.43 (t)	C^3H
6.97 (t)	C^5H
7.76 (d)	$C^{26,27}H$
8.43 (s)	$C^{48}\text{-OH}$
9.28 (t)	$C^{27}H$

The peaks selected for molecular weight distribution analyses ("end-group" analyses) were those at 7.7 (repeating unit) and 5.4 ppm (end-group). The ratio of their relative integrals for each of the aliquots is shown in table 3.1, Chapter 3. The uv/visible spectra of each of the aliquots (1 mg in 100 ml H_2O) are represented in figure 3.4, Chapter 3.

The most promising material was that formed after 4 hrs. Gelatin coatings containing this material were made up on triacetate base. That is, this sample (80 mg) was dissolved in 10 ml water. A portion of this solution (0.5 ml) was then added to a solution of 10% DIB gelatin (3.0 ml) and 1% saponin (surfactant) (1.0 ml) which was made up to 10 ml with water. This mixture was then coated on to triacetate base[17]. The coating then underwent a number of standard evaluation tests[17].

i)   Substantivity; the visible spectrum of the coating is recorded, it is then immersed in water for 30 mins after which time the spectrum is re-recorded. The dye was 88.7% substantive.

ii)   Bleachability; again the visible spectrum of the coating is recorded before and after, (a) being immersed in a 0.5 M Na_2SO_3 solution for 2 mins. The dye was 100% bleachable; and (b) being immersed in a solution of ID11 (standard Ilford developer) for 2 mins. Here dye was 97.8% bleachable.

The results of these tests are illustrated in figure 3.5, Chapter 3.

10.3. The Bleaching Reaction

The dye chosen for the investigation was HPT261, figure 10.3.1.

$\lambda_{max} = 589$ nm
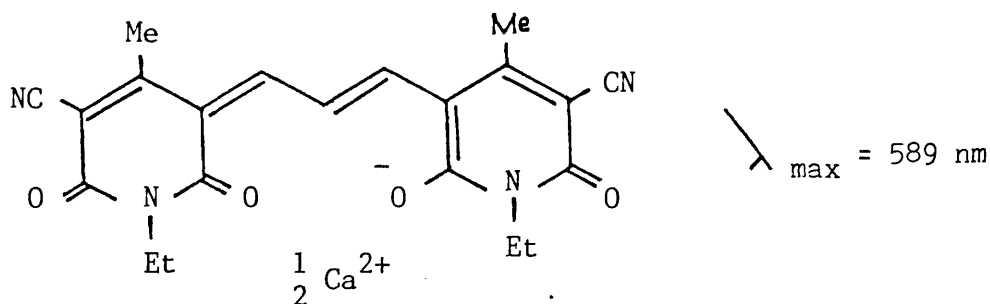
Figure 10.3.1.

10.3.1. Instrumentation.

Bruker WM-250 MHz and WH-400 MHz n.m.r. spectrometers, a Jeol FX-90Q n.m.r. spectrometer and a Varian SuperScan 3 u.v./visible spectrophotometer.

10.3.2. Kinetic studies of sulphite bleaching.

Two standard solutions were prepared, a 10^{-6} M aqueous solution of HPT 261 and a 10^{-2} M aqueous solution of sodium sulphite. 15 ml Aliquots of the standard dye solution were pipetted into a 16 ml quartz cell and varying amounts of the standard sulphite solution ranging from 0.05 - 0.4 ml were added, in each case the contents of the cell being made up to 16 ml with water. The change in absorbance with time on the addition of the sulphite solution was then measured. The results thus obtained are shown in section 4.2.1, Chapter 4.

The effect of pH on the rate of sulphite bleaching was also investigated. A citric acid/sodium hydroxide buffer was used,[94] thus for:

a)   pH = 2.1, 1.4 g citric acid was dissolved in 100 ml 10^{-6} M standard dye solution (0.06 M citric acid); 6 ml of this solution was then made up to 16 ml in the cell with 10 ml 10^{-2} M standard sulphite solution.

b)   pH = 3.2, 1.4 g citric acid was dissolved in 80 ml 10^{-6} M dye solution and was made up to 100 ml with 20 ml 0.2 M sodium hydroxide solution; 6 ml of this solution was then made up to 16 ml with 10 ml 10^{-2} M sulphite solution.   ·

c)   pH = 4.1, 1.4 g citric acid was dissolved in 60/40 ml solution of 10^{-6} M dye/0.2 M sodium hydroxide solution. 6 ml of this solution was then diluted to 16ml with 10 ml 10^{-2} M sulphite solution. Absorbance vs time plots and the pseudo-first order rate constants, thus obtained, for each of the pH values, can be seen in table 4.4. and figure 4.4., Chapter 4.

10.3.3. Qualitative studies

All studies were carried out in 0.2 mmol dimethyl sulphoxide solutions of HPT 261 with the addition of 4 molar excess of the bleaching agent. Where necessary a few drops of water were added to aid in solubilising the bleachant. The potential bleaching reagents investigated were potassium cyanide, sodium methoxide, sodium sulphide, ammonia, triethylamine, sodium hydroxide, potassium thiol, ethylamine, sodium azide, aniline, potassium thiocyanate, triphenylphosphine, sodium

thiosulphate and of course sodium sulphite. To test for reversibility of the reaction, molar equivalents of hydrochloric acid to bleachant were added. Excess acid resulted in protonation of the dye species.

10.3.4. NMR studies

0.2 mmol Solutions of HPT 261 were made up in either 50/50 D_2O/d^6-DMSO (NH_3, CN^-, S^{2-}), 50/50 d^4-MeOH/d^6-DMSO (CD_3O^-) or d^6-DMSO ($EtNH_2$), 4 Molar excesses of the nucleophiles were again used.

10.3.5. Trapping a bleached adduct

HPT 298 (2.0 g, 4.2 mmol) (II, scheme 4.4) and o-phenylene-diamine (2.3 g, 0.02 mol) were refluxed in absolute ethanol (50 ml) for 2 hrs. A pale blue solid had precipitated almost immediately on refluxing. This solid was filtered off from the hot ethanolic solution (1.3 g (55%); m.p. 312.0 - 314.0° (decomp) calcd for $C_3H_{33}N_6O_4$: C, 67.25; H, 6.01; N, 15.18: found C, 67.63, H, 6.19, N, 15.47). This materials insolubility in all of the common solvents made both recrystallisation and solution nmr spectroscopy studies impossible. The accurate top mass obtained from mass spectrometry was 544. Solid state ^{13}C nmr spectra of both the dye HPT 298 and its o-phenylenediamine bleached adduct were recorded.

10.4. Structural Studies in the Solid State

10.4.1. X-ray crystal structure analyses

10.4.1.1. Instrumentation

The radiation used was either Ni-filtered copper K_α radiation or Zr-filtered molybdenum K_α radiation. The diffractometer used was a CAD4-F instrument (ENRAF NONIUS DELFT) controlled by a PDP8-A mini-computer. All subsequent computational work was done on either an ICL 298 computer or an ICL 1906A machine using the "Crystals" series of programmes[95,96,97,98].

10.4.1.2. The structure of tetraphenylphosphonium 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one trimethine oxonol.

Crystal data - $C_{45}H_{39}N_4O_4P$, Monoclinic, M_w = 730, a = 12.634(6), b = 11.802(0), c = 12.875(9) Å, β = 95.69(3)°, U = 1909.1 Å^3, D_m = 1.3 gcm^{-3}, D_c = 1.3 gcm^{-3} for z = 4, C_uK_α radiation, λ = 1.5418 Å, Space group P2/c.

A selected crystal (octahedra with a gold metallic lustre) was mounted on an Enraf-Nonius CAD-4F diffractometer. The orientation routine and unit cell parameters were optimised by a least squares refinement using the angular coordinates of 25 reflections. An inspection of the intensities of reflections from the three zero-level zones (hk0, h0l, 0kl) revealed systematic absences consistent with the space group P2/c. Automatic data collection was implemented in the range $0 < 0 < 75°$. The angular coordinates of three reflections and the intensities of a further three were monitored throughout data collection to provide a check on variation in crystal orientation and intensity. In all, 5478 distinct reflections were measured with a net intensity greater

than zero. Lorentz and polarisation corrections were applied and the data merged to give 2679 independent structure amplitudes with $I > 3\sigma$ (I) , where I is the final observed intensity and σ (I) the standard deviation derived from counting statistics. The structure was solved by direct methods using MULTAN. Full matrix least-squares techniques were employed for the refinement. Hydrogen atoms were found from an electron density difference Fourier synthesis. In the final refinement the coordinates and anisotropic temperature factors of the carbon, oxygen, nitrogen and phosphorus atoms were refined with the coordinates and isotropic temperature factors of the hydrogen atoms. A three-term Chebyshev series was used as a weighting scheme. A final R-value of 6.1% was reached. The atom coordinates anisotropic temperature factors, bond lengths and bond angles are listed in Chapter 6. The hydrogen atom isotropic temperature factors and the structure factors are listed in appendix 1B.

10.4.1.3. The structure of tetrabutylammonium 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one trimethine oxonol.

Crystal data - $C_{37}H_{55}N_5O_4$, Monoclinic, M_w = 633, a = 8.399(5), b = 10.445(5), c = 21.265(7) $\overset{o}{A}$, β = 83.34(2) U = 1853.2 A^3, D_m = 1.3 gcm^{-3}, D_c = 1.3 gcm^{-3} for z = 4, Cu - K_α radiation, λ = 1.5418 $\overset{o}{A}$, Space group P2/n.

A selected crystal (needles with a metallic green reflex) was mounted on the diffractometer. The orientation matrix and unit cell parameters were optimised by a least squares refinement using the angular cordinates of 25 reflections, as before. The systematic absences observed were consistent with the space group P2/n. 4723 reflections

with a net intensity greater than zero were measured in the range

0 < 0 < 70°. The data was merged to give 1677 independent reflections

having I > 3 σ (I). The structure was solved by direct methods. The

hydrogen atoms were placed geometrically. In the final refinement, the

coordinates and anisotropic temperature factors of the carbon, nitrogen

and oxygen atoms were refined with the fixed coordinates and isotropic

temperature factors of the hydrogen atoms. A three-term Chebyshev series

was used as a weighting scheme. A final R-value of 8.3% was reached.

The atom coordinates, anisotropic temperature factors, bond lengths and

bond angles are listed in Chapter 6. The structure factors are listed

in Appendix 1B.

10.4.1.4.   The structure of dimethylammonium ethyl methacrylate

1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one

trimethine oxonol.

Crystal data - $C_{29}H_{35}N_5O_6$, Monoclinic, M_w = 549, a =

31.313(5), b = 7.436(3), c = 25.495(4), β = 100.63 (7)°

U = 5834.7 A^3, D_m = 1.3 gcm^{-3}, D_c = 1.3 gcm^{-3} for z = 8,

Cu - K_α radiation, λ = 1.5418 Å, Space group C2/c.

A selected crystal (dark blue needles) was mounted on the

diffractometer. The systematic absences observed were consistent with

the space group C2/c.   4141 reflections with a net intensity greater than

zero were measured in the range 0 < 0 < 45°. The data was merged to

give 1065 independent reflections having I > 3 σ (I). The structure was

solved by direct methods. The hydrogen atoms were placed geometrically.

In the final refinement, the coordinates and anisotropic temperature

factors of the carbon, nitrogen and oxygen atoms were refined with the

fixed coordinates and isotropic temperature factors of the hydrogen atoms. A three-term Chebyshev series was used as a weighting scheme. A final R-value of 6.5% was obtained. The atom coordinates, anisotropic temperature factors, bond lengths and bond angles are listed in Chapter 6. The structure factors are listed in Appendix 1B.

10.4.1.5. N-Methyl morpholinium 1-butyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one trimethine oxonol.

On recrystallisation from ethanol two crsytalline forms of this dye were obtained, a needle-like form (which crystallised out after a few hours) and a cuboid form (which crystallised after a few days), the needles being dark blue in colour and the cubes having a bright green metallic lustre.

An attempt was made to collect a data set on the cuboid form. However, preliminary photographs taken on the CAD4-F diffractometer revealed a diffraction pattern very similar to that one might observe for a powder, figure 10.4.1. This suggested a high degree of disorder at the data collection temperature (room temperature). Obtaining a solution would have been impossible from this standard of data.
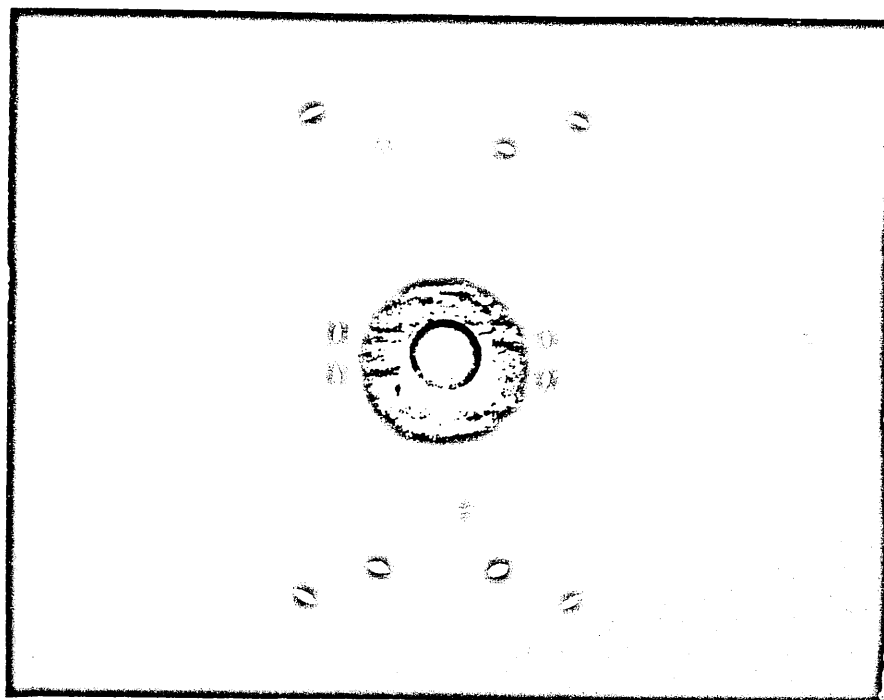
Figure 10.4.1

10.4.1.6. Methyl triphenylphosphonium 1-ethyl-3-cyano-6-hydroxy-4

methyl pyrid-2-one trimethine oxonol.

An attempt to collect a data set on the blue needles of this key

material was undertaken. The small size of the crystal led to very few

high intensity spots in the diffraction pattern, figure 10.4.2.
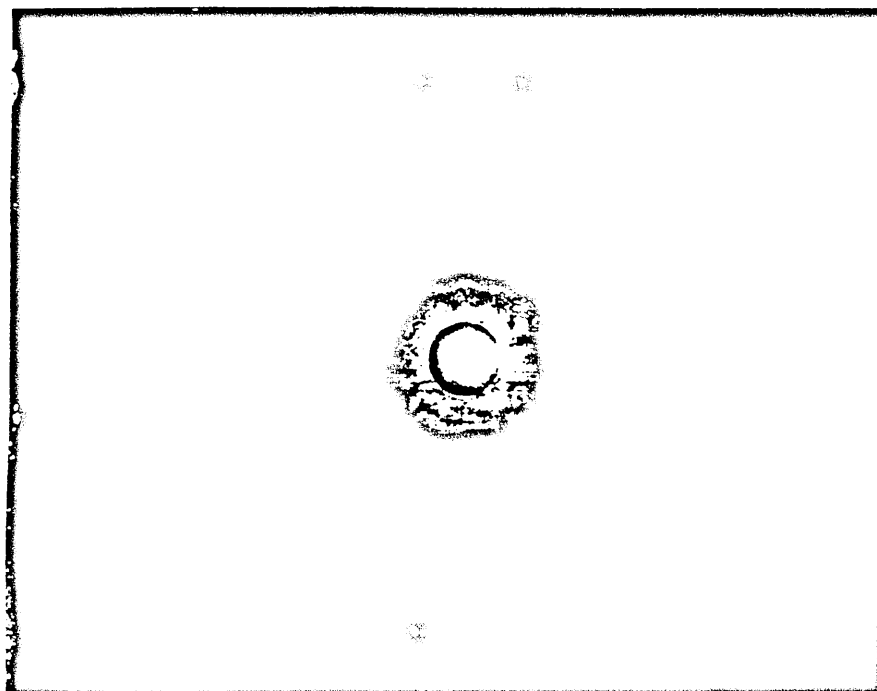
Figure 10.4.2

Obtaining a satisfactory solution from so few strong reflections would have been practically impossible.

10.4.2.   Solid state nmr spectroscopic studies

The high resolution ^{13}C nmr experiments were performed on Bruker CXP 200 and 300 spectrometers. High-power proton decoupling was used to eliminate ^{13}CH dipolar broadening along with high-speed "magic angle" spinning in a Delrin rotor to eliminate broadening from the carbon chemical shift anisotropy. In addition, matched spin-lock cross-polarisation was used to enhance the sensitivity.

10.5. Electrochemical Investigations: The Design of a Radical Cation-Dye Complex

10.5.1. Instrumentation

Varian E4 EPR spectrometer. Figure 10.5.1 shows a circuit diagram of the CV set up used (where AE = auxiliary electrode (platinum), RE = reference electrode (S.C.E.), WE = working electrode (platinum) and X and Y are the terminals of the XY-plotter (JJ Instruments, PL51). The potentiostat used was a Thompson Associates ministat and the ramp generator a Thompson Associates "16 bit" ramp generator (Model DRG 16).
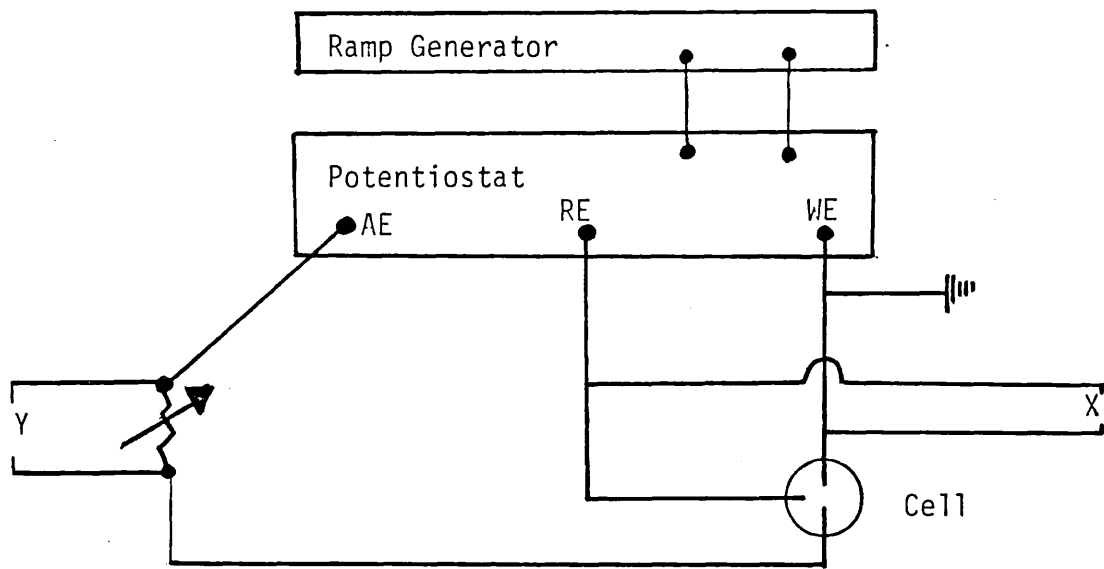
Figure 10.5.1

10.5.2.   Experimental

For all CV samples 1.0 mmol solutions were made up in acetonitrile with 10.0 mmol tetrabutylammonium perchlorate as supporting electrolyte. The voltage was scanned between -2.0 and 2.0 V at a rate of 1000 mV/s. A saturated calomel electrode was used as a reference. Platinum electrodes were used for both auxiliary and working electrodes.

10.5.3.   The preparation of the TTF-oxonol dye complex.

The complex was prepared by the electrolysis (2mA, 4 hr, Pt electrodes) of tetrabutylammonium 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one trimethine oxonol (0.32 g, 5.0×10^{-4} mol) and tetrathia-fulvalene (0.10 g, 5.0×10^{-4} mol) in acetonitrile (100 ml) and tetrabutylammonium perchlorate (1.5 g, 4.4×10^{-3} mol). The black crystalline material formed at the anode (m.p. = 230.0° (decomp.); uv/visible, λ_{max} (EtOH) 597 (ε_{max}, 4.72×10^{4}), 552 nm (sh, 1.16×10^{4} mol^{-1} dm^{3} cm^{-1}); Calcd. for $C_{27}H_{23}O_4N_4S_2$: C, 54.43; H, 3.90; N, 9.41; S, 21.53: Found: C, 54.61; H, 4.00; N, 9.44; S, 21.73).
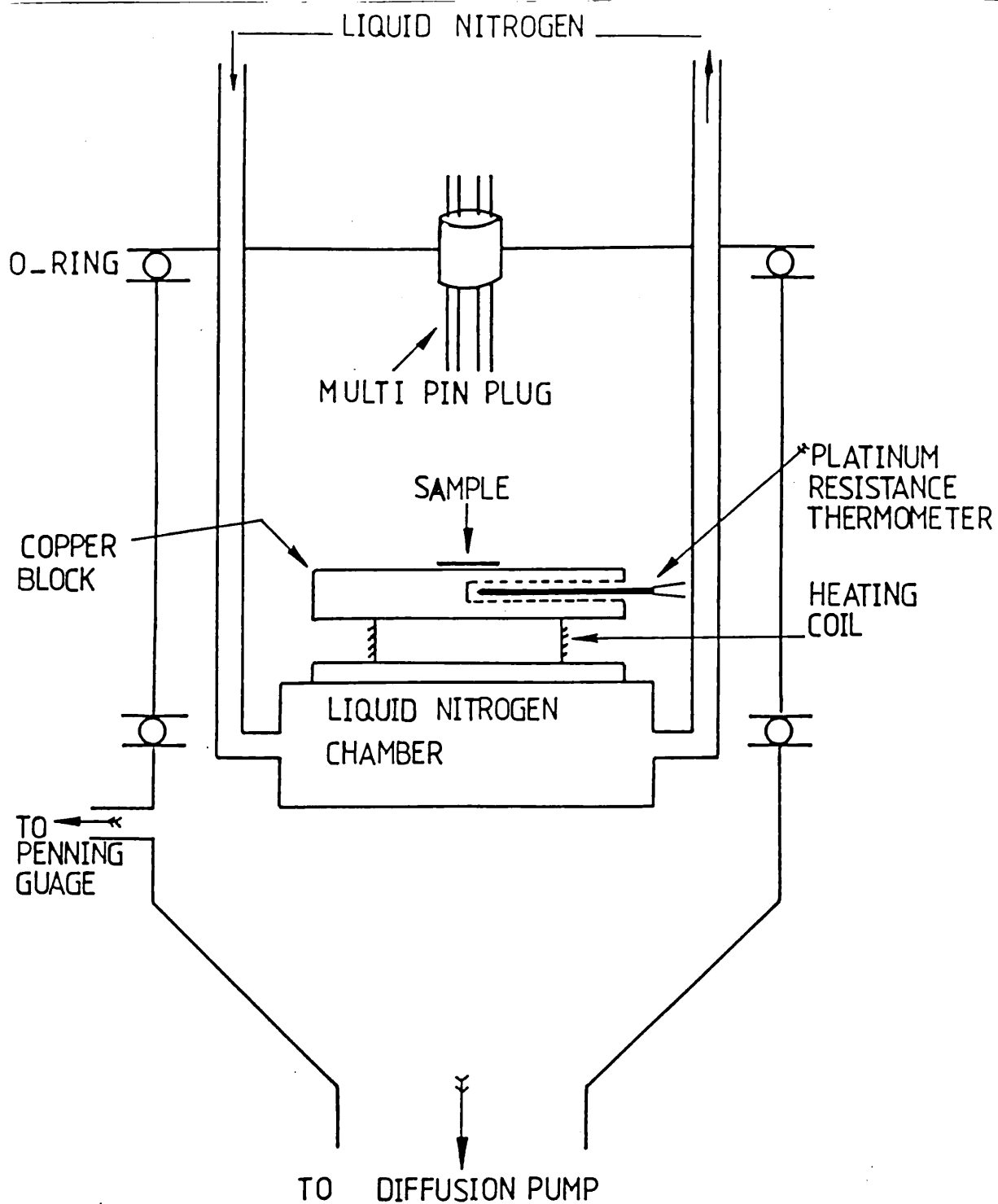
FIGURE. 10.6.2

SCHEMATIC DIAGRAM OF THE CRYOSTAT

10.6. D.c. Conductivity and Dielectric Spectroscopic Measurements

10.6.1. Sample preparation

All of the electrical measurements were carried out on samples in the form of compressed discs. For silver dag contacts, two paper reinforcers were placed on either side of the disc; two copper wires were then connected on either side by the silver dag, which filled the centre hole of the reinforcer figure 10.6.1.
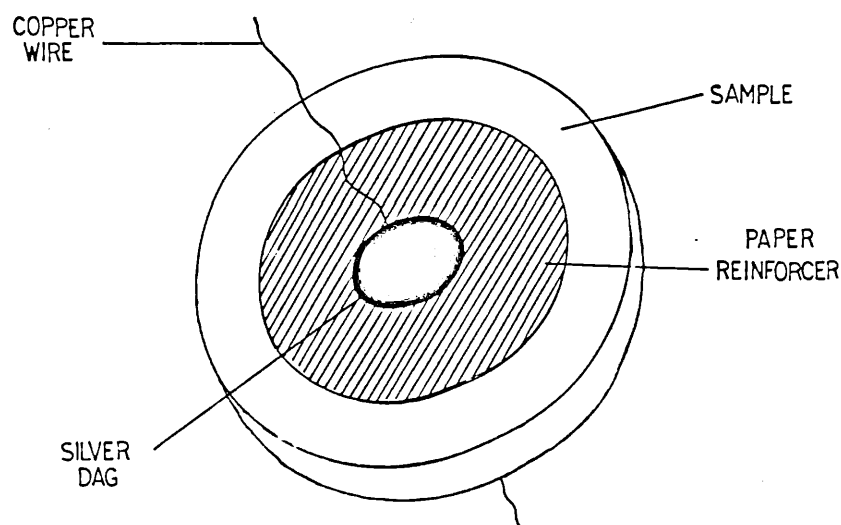
Figure 10.6.1

Of the other contacts used, the aluminium and indium were vacuum deposited on to an accurately defined area on either side of the sample discs, and the pressure contacts involved sandwiching the sample discs between two copper discs of known area. Each of these contacts was then connected to the external circuit via copper wire silver dagged to their surfaces.

10.6.2. Low temperature measurements

Measurements below room temperature were made in a liquid nitrogen cryostat system, figure 10.6.2. This system consists of a temperature

BNC. SOCKET

SCREW

SPRING

BRASS TOP

FURNACE

SILICA BARS
WITH
PLATINUM LEADS

SILICA TUBE

STAINLESS
STEEL
TUBE

PLATINUM TOP
ELECTRODE

THERMOCOUPLE

PLATINUM
BOTTOM
ELECTRODE
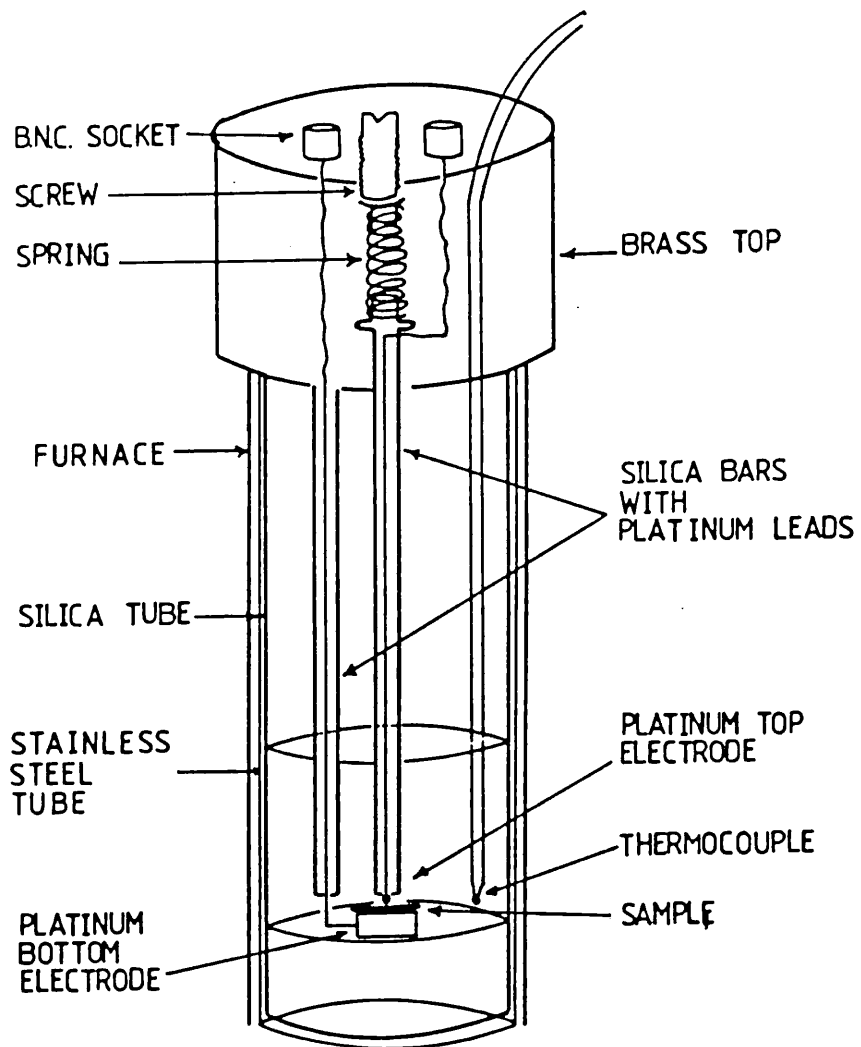
SAMPLE

FIGURE .10.6.3
HIGH TEMPERATURE SAMPLE HOLDER

controller and cooling-heating arrangement. The system used a vacuum of
5×10^{-2} mbar in order to avoid moisture condensation on the sample
during measurements. Temperature was controlled by balancing the heat
flow from the liquid nitrogen reservoir to the cold finger (a copper
block) by supplying the required amount of heat through a heating coil
wound around the latter. A Eurotherm model 070/008/010 controlled the
heating current and a platinum resistance thermometer was used to sense
the temperature of the copper block. To ensure that the temperature of
the sample was as close as possible to that of the copper-block, good
thermal contact was obtained by applying a thin coating of heat-sink
compound between the copper and a thin mica sheet which was used as an
electrical insulator.

10.6.3. High temperature measurements

High temperature work (above 373 K) was carried out by keeping the
sample in a non-inductive Severn Science vertical furnace.

The cylindrical core, which was fitted with a 30 cm long, 5.4 cm
diameter stainless steel cylinder, was wired to give a heat plateau at
the centre of the furnace tube. The metallic cylinder was earthed to
shield the sample from any electrical noise. The sample was placed in
the stainless steel cylinder as shown in figure 10.6.3. A
Chromel-Alumel thermocouple connected to the Eurotherm controller and
hung between the stainless steel cylinder and the furnace core at the
central position was used to control the temperature. The actual
temperature was measured by another Chromel-Alumel thermocouple attached
to the sample holder near the sample. There was always a slight

difference between the temperature set on the Eurotherm and that measured

by the thermocouple. The thermo-emf of the measuring thermocouple, with

reference to the ice point maintained by an Mk-11 ICEL unit, was

monitored by a SOLARTRON digital voltmeter having a reading accuracy of

$\pm$ 0.02%. Standard calibration tables were used to record the

temperature sensored by the thermocouple.

10.6.4. D.c. conductivity measurements

10.6.4.1. Instrumentation

A Kingshill stabilised power supply (MODEL 36V2C), two 610C

solid state electrometers (Keithley Instruments), a variable resistance

box (100 Ω - 1 MΩ), a non-inductive Severn Science vertical furnace, two

Chromel-Alumel thermocouples, a Eurotherm controller, an MK-11 ICEL unit,

a SOLARTRON digital voltmeter, and a liquid nitrogen cryostat system.

10.6.4.2. Experimental

Figure 10.6.4 shows the circuit used for all of the measurements.

V_1 measured the applied voltage and V_2 the voltage drop across a
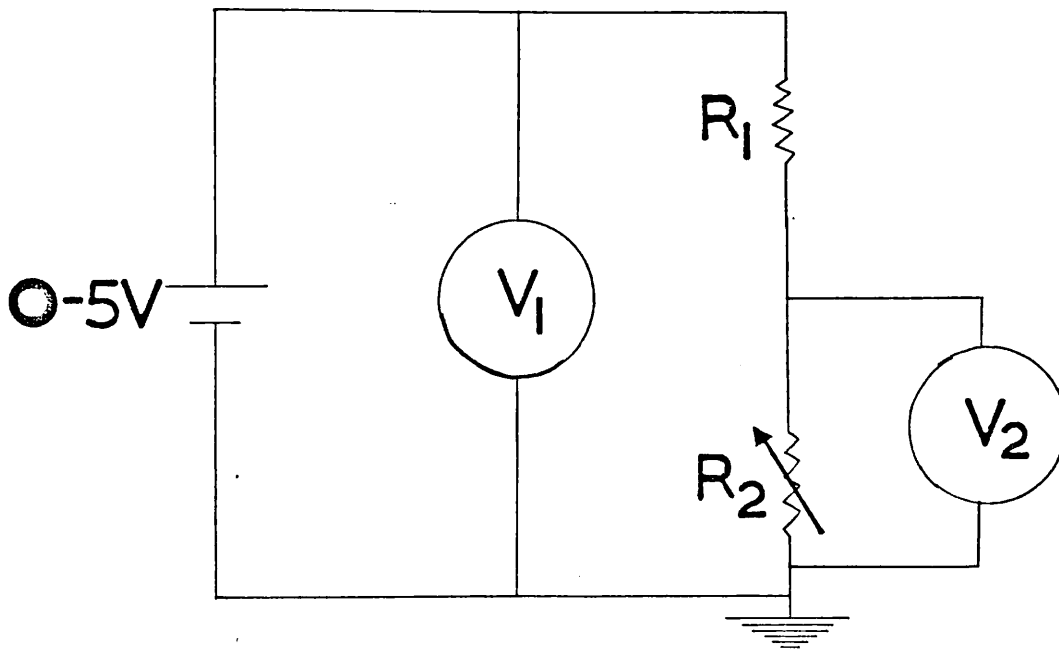
Figure 10.6.4
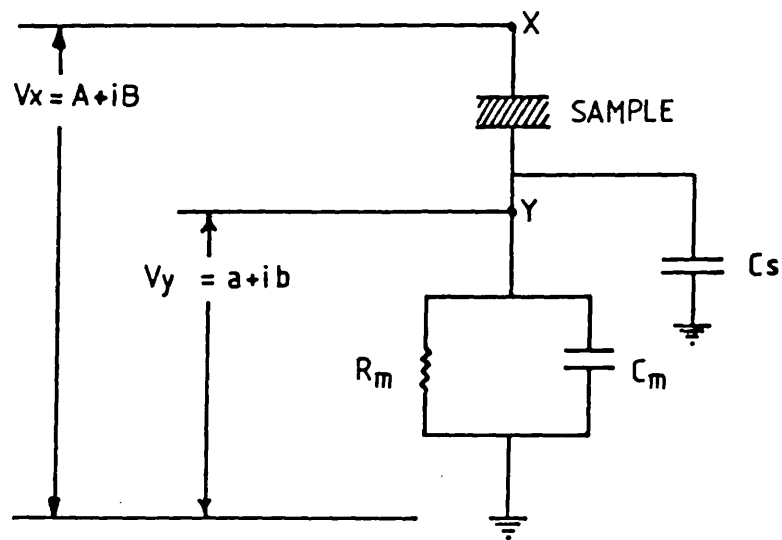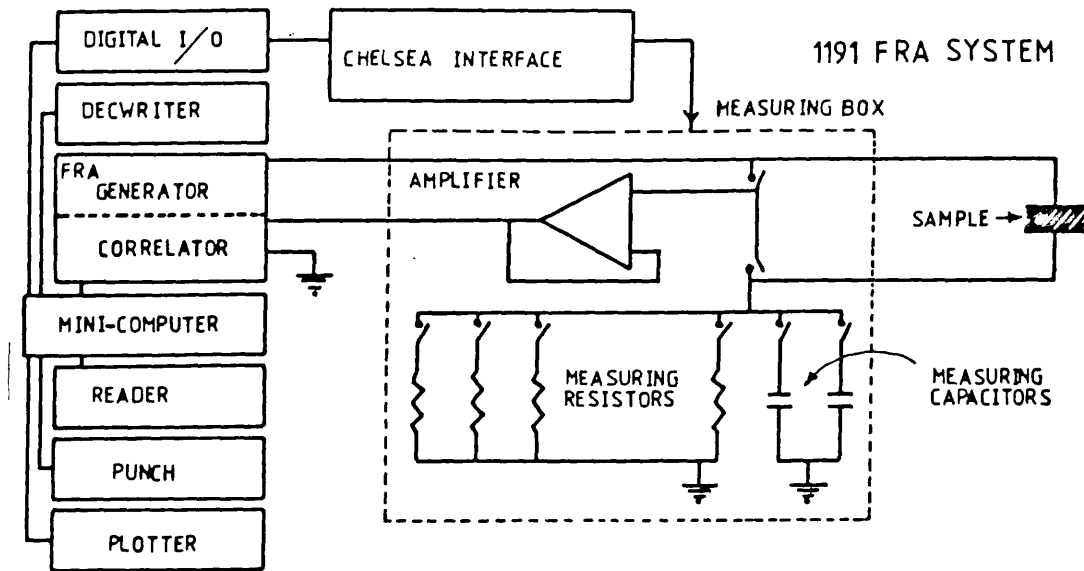
FIGURE 10.6.5
THE BLOCK DIAGRAM OF FRA SYSTEM WITH EQUIVALENT
CIRCUIT OF SAMPLE AND MEASURING RESISTOR/CAPACITOR
COMBINATION.

known resistance in series with our sample. The known resistance was kept small compared to the sample resistance to maintain as large a voltage drop across the sample as possible. From Ohms Law,

$$I_2 = \frac{V_2}{R_2} \quad \text{and} \qquad\qquad 10.6.1.$$

$$I_1 = \frac{V_1}{R_1} \qquad\qquad 10.6.2.$$

where I_1 and I_2 are the currents flowing through resistances R_1 (sample) and R_2 (known), respectively. As these resistances are in series ($I_1 = I_2$) and as R_2 is known and V_2 measured, I_2 and hence I_1 can be obtained. Measurements similar to these were made for a range of temperatures.

10.6.5. Dielectric measurements[99,100,101].

10.6.5.1. Instrumentation (Frequency Response Analyser) The basic component of the system is a SOLARTRON 1191-FRA. The full system consists of a generator, a correlator, a measuring box together with its interface and a PDP- 11/04 computer. The block diagram together with an equivalent circuit is shown in figure 10.6.5. A digitally synthesised sine wave signal which is produced by the generator in the form of a stair-case with 2000 steps per cycle is applied to the dielectric sample. The correlator measures directly the in-phase and quadrature components

of the received signals in comparison to the generator output. If the generator output is proportional to $\sin \omega t$ and the input to the correlator is $V \sin(\omega t + \Phi)$ then the in-phase and quadrature components of V are given by:

$$A = 2/NT \int_0^{NT} V \sin(\omega t + \Phi) \sin \omega t \, dt \qquad 10.6.3.$$

$$B = 2/NT \int_0^{NT} V \sin(\omega t + \Phi) \cos \omega t \, dt \qquad 10.6.4.$$

where $V = A + iB$, $\text{Arg } V = \Phi$, and N is the number of complete cycles, each of time $T = 2\pi/\omega$, over which integration takes place. If P is an integer greater than unity, then

$$1/NT \int_0^{NT} \sin(P\omega t + \Phi) \sin \omega t \, dt = 0 \qquad 10.6.5.$$

so that the system will not only reject the harmonics completely but also the noise.

The measuring box consists of 34 resistors in the range 10 to 10^{12} ohms. Each decade has three resistors of values 1,2 and 5×10^n ohms where n is the decade. To overcome any possible problem arising from the presence of stray capacitance (C_s), four measuring capacitances (C_m) are included in the measuring box.

The box also contains all the relays that are required to switch the signal to the sample and to choose the required measuring resistor and capacitor. An interface controls the relays in the measuring box using digital outputs from the computer. The signal received into the measuring box is fed via the relays to a high inpedance buffer amplifier before being transmitted back to the correlator.

10.6.5.2. Experimental

All the variables are controlled by the computer via the interface unit and the capacitance and conductance of the sample under investigation are calculated. V_x (= A + iB) is the value of the applied signal with the generator connected to the sample and the measuring resistor R_m. If the impedance of the sample is low it will reduce the amplitude of the applied signal. This can be overcome by modifying the program so that the amplitude of the signal actually applied to the sample is within 2% of the nominal value. In the second measurement V_y = (a + ib) is measured across the measuring resistor (R_m) only. In the third measurement the amplifier output V_z is then substracted from both V_x and V_y. It is desirable to make V_y small compared to V_x so that most of the signal is dropped across the sample and not across the measuring resistor. The values of C and G/ω are then obtained from V_x and V_y measurements by means of the relationships:

$$C = 1/\omega R_m \frac{Ab - aB}{(A-a)^2 + (b-b)^2} + C_m \frac{a(A-a) + b(B-b)}{(A-a)^2 + (B-b)^2} \qquad 10.6.6.$$

$$G/\omega = 1/\omega R_m \frac{a(A-a) + b(B-b)}{(A-a)^2 + (B-b)^2} - C_m \frac{Ab - aB}{(A-a)^2 + (B-b)^2} \qquad 10.6.7.$$

where $\omega = 2\pi f$.

The loss tangent is given by

$$\tan \delta = G/\omega C = \varepsilon''/\varepsilon \qquad 10.6.8.$$

In the case of low loss materials, $\tan \delta \ll 1$, the capacitance is recorded with higher accuracy than the conductance. For high loss materials, $\tan \delta \gg 1$, the reverse is true.

APPENDIX 1A

X-Ray Structure Determination[102]

1.1. The CAD4-F diffractometer

This instrument is employed to collect accurate X-ray diffraction intensity data for a crystal. It consists of a goniometer and X-ray counter controlled by a PDP8-A mini-computer[103]. The instrument uses either copper K_α or molybdenum K_α radiation. The sequence of operations leading up to data collection will be outlined below.

First the crystal is placed at the intersection of the four rotation axes of the instrument and the X-ray beam, where it can be accurately viewed through a telescope, figure 1.2(A). Having aligned the crystal the instrument is instructed to measure the setting angles of 25 reflections. These reflections can be obtained either from a Polaroid rotation photograph of the crystal about the ϕ axis or from a random search of reciprocal space. The instrument indexes these reflections and from them calculates the cell parameters and orientation matrix. The values of the cell parameters are then compared with the values derived from the photographic techniques. Any necessary transformations are performed at this stage (for example the instrument may have chosen the incorrect axis to be the unique axis in a monoclinic cell). Next a rapid data collection (probably from 10 to 12 or 13 degrees in theta) is initiated with the object of measuring some strong reflections from which to refine the cell parameters and orientation matrix. 25 such reflections are chosen from those collected and stored in the computer (in the "Ref dump"). They are all accurately recentred and a routine in the computer checks for zero-error in the detector position and outputs an accurate value of theta. The cell parameters and the orientation matrix are
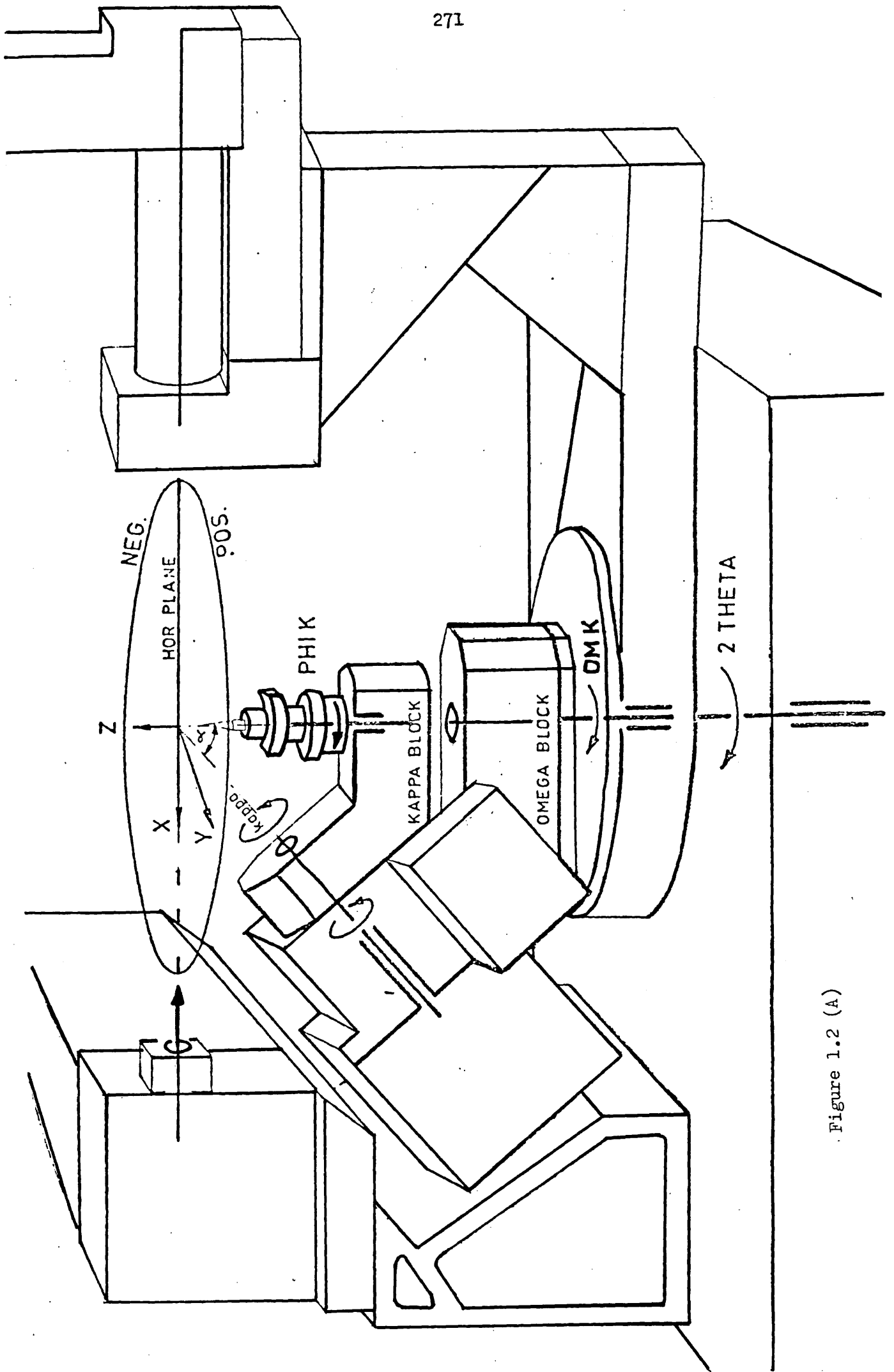
Figure 1.2 (A)

refined by a least squares calculation and accurate values are output to the terminal. Following this, the intensity profiles of a few reflections are examined in detail to determine the optimum intensity collection parameters for the detector (i.e. the aperture size, scan angle and the ratio of various motor drives during the scan). From the 25 reflections in the "Ref dump" a few are chosen as intensity and orientation standards to provide checks for crystal decay and change in alignment during data collection. At this stage a final review of the data collection parameters is made before initiating the full automatic data collection. The data so collected is stored on a magnetic disc in the computer and at the end of data collection it is transferred to, and stored on, 7-track magnetic tape from whence it can be read onto another computer (in Oxford, either the ICL 1906A or the ICL 2980) for data reduction and subsequent analysis.

1.2. Data reduction

The data reduction program takes the raw diffractometer data and outputs a set of sorted, scaled and merged structure factor amplitudes, $/F_{obs}/$. The structure factor is related to the observed intensity by the equation

$$/F_{hkl}/ = \sqrt{\frac{K.I_{hkl}}{L.p.}} \qquad \text{1.1(A)}$$

p is the polarisation factor which allows for partial polarisation of the X-ray beam of reflection. L is the Lorentz factor and arises because of the variation in time t for reciprocal lattice (r.l.) points to pass through the sphere of reflection. It depends on the position of the point in the r.l. and the direction from which it approaches the limiting

sphere, and is therefore also dependent on the method of intensity measurement. K is normally a constant for any given set of measurements. This term is normally omitted from further calculation and becomes integrated into the scale factor used to relate the observed structure factor amplitude to the absolute structure factor modulus, thus

$$/F_{relative}/ = k'/F_{observed}/ = \sqrt{I_{hkl}/L.p}$$
1.2(A)

After the above corrections have been applied the data is sorted, so that the reflections are placed in a pre-determined order with reflections having the same indices adjacent in the list. The systematic absences are checked for consistency with the space-group symmetry operators and are removed. Equivalent reflections for the space-group in question are merged to produce a single mean structure factor amplitude and the final list of reflections is stored in the computer. The cell parameters, symmetry elements and the atomic scattering curves are also entered to be on hand when required[95].

1.3. Fourier synthesis

At this stage in the structure determination the crystal data consists of a set of observed structure factor amplitudes. The structure factor (F_{hkl}) is the resultant of the j waves scattered in the direction of the hkl reflections by the j atoms of the unit cell.

$$F_{hkl} = \sum_{j} f_j exp2\pi i(hx_j + ky_j + lz_j)$$
1.3(A)

Alternatively the structure factor may be expressed in terms of the electron density in the unit cell as

$$F_{hkl} = \int_V \rho(x,y,z)\exp 2\pi i(hx + ky + lz)dv \qquad 1.4(A)$$

A relationship exists between the electron density and the structure factor in as much as each is the Fourier transform of the other.

$$\rho(x,y,z) = \frac{1}{v} \sum_h \sum_k \sum_l /F_{hkl}/\exp{-2\pi i(hx + hy + lz - \alpha'_{hkl})} \qquad 1.5(A)$$

The expression for the electron density above is a three-dimensional Fourier series using the structure factor amplitudes as coefficients and requires the phase α' of each reflection. The intensity measurements, however, only provide information on the amplitude of the structure factor and not on its phase. This is because the structure factor is proportional to the square-root of the intensity and not the intensity itself (which has been measured). This lack of any direct experimental measurement of the phase of a reflection is referred to as the phase problem. In order to overcome this problem a final structure can be used as a phasing model to calculate structure factors in a Fourier synthesis. These structure factors together with their signs are compared with the observed structure factors and, from the success of the comparison, adjustments are made to the model and the "adjusted" model used in a subsequent structure factor calculation. The two main approaches in use today to obtain the phasing model are the Patterson or heavy atom method and the Direct Method approach.

1.4.   The Patterson Function and the Heavy Atom Method

The Patterson Function is a three-dimensional Fourier series using $/F_{hkl}/^2$ as coefficients which gives rise to peaks corresponding to all the interatomic vectors.

$$P(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l /F_{hkl}/^2 \cos 2\pi(x,y,z) \qquad 1.6(A)$$

Thus for a molecule with N atoms in the unit cell the Patterson map will show N^2 peaks. Of these, N will be vectors of zero length from each atom to itself and will be concentrated as a very large peak at the origin, while the remaining N^2 - N will be vectors distributed throughout the cell. There is generally a great deal of overlapping in the Patterson map, caused by both the increased number of peaks and their increased width (compared to Fourier peaks). This can be corrected for in a "sharpened" Patterson map by modifying the observed structure factor amplitudes to those $/F_{hkl}/$'s expected for point atoms. The weight or height of a Patterson peak is proportional to the product of the atomic numbers of the atoms giving rise to it. If only one or two heavy atoms are present in a molecule the small number of large Patterson peaks so produced enables a solution of the map and positioning of these heavy atoms in the unit cell. The heavy atoms also contribute a large percentage to the structure factors (i.e. the scattering of X-rays by the electrons and so a phasing model based on the heavy atom positions can usually give a reasonable correlation between observed and calculated structure factors. The remaining non-hydrogen atoms can then usually be detected from a normal or difference Fourier.

1.5. Direct Methods

This approach attempts to obtain a phasing model directly from the observed structure factor amplitudes[104]. Sayre[105] showed that subject to certain restrictions where Φ_{hkl} is simply a scaling term.

$$F_{hkl} = \Phi_{hkl} \sum_{h'} \sum_{k'} \sum_{l'} F_{h'k'l'} \; F_{h-h'k-k'l-l'} \qquad 1.7(A)$$

This implies that any structure factor F_{hkl} is determined by the products of all the pairs of structure factors whose indices add to give (hkl). If F_{hkl} above is large then the series summation above must have tended strongly in one direction (+ or -) which can be determined by the parity agreement between products with large values for F. Thus for large values of F where S means "the sign of". The probability of the

$$S(F_{hkl}) \simeq S(F_{h'k'l'}) \; S(F_{h-h'k-k'l-l'}) \qquad 1.8(A)$$

equation above being true is an important consideration of the Direct Methods approach. This probability is given by the tangent formula below

$$P = \tfrac{1}{2} + \tfrac{1}{2} \tan h \left\{ \frac{1}{\sqrt{N}} \; / E_{hkl} E_{h'k'l'} E_{h-h'k-k'l-l'} / \right\} \qquad 1.9(A)$$

which contains the normalised structure factor amplitudes or E-values and where N is the number of atoms in the unit cell. In a determination by direct methods a small number of reflections are assigned phases and then used with equation 1.8(A) to build up a large enough set of phases which, when used in a Fourier synthesis, give a reasonable representation of the structure.

1.6. Completion of the Structure

When a phasing model has been obtained, by one of the methods described, the phases are used in combination with the observed (phaseless) structure factors as coefficients in a Fourier synthesis. The atomic positions so found may be used to calculate a more accurate set of phases which may then be used to calculate a more accurate set of atomic positions and so on.

A "difference" Fourier is often useful for locating atoms not found in the phasing model. This uses the quantities as coefficients in a

$$\Delta F = /F_{obs}/ - /F_{calc}/ \qquad\qquad 1.10(A)$$

Fourier synthesis.

The last stages of a structure determination involve "least squares" refinement of the atomic parameters. The function minimised in

$$D = \sum W_{hkl}(/F_{obs}/ - / kF_{calc.}/)^2 \qquad\qquad 1.11(A)$$

where W is the weight assigned to the observation.

The agreement between observed and calculated structure factors is expressed in terms of the residual index or 'R-value', given by

$$R = \frac{\sum / /F_{obs}/ - /F_{calc.}//}{\sum /F_{obs}/} \qquad\qquad 1.12(A)$$

This may be used during refinement as a guide to the correctness of the model.

APPENDIX 1B

X-Ray Structure Data

1.1. The isotropic temperature factors for the hydrogen atoms of I(b), with estimated standard deviations in parentheses.

Atom	U[iso]		
H(1)	0.089(24)	H(20)	0.084(19)
H(2)	0.101(24)	H(21)	0.078(19)
H(3)	0.089(26)	H(22)	0.099(21)
H(4)	0.092(18)	H(23)	0.121(21)
H(5)	0.057(16)	H(24)	0.052(15)
H(6)	0.074(18)	H(25)	0.042(14)
H(7)	0.108(22)	H(26)	0.049(17)
H(8)	0.131(24)	H(27)	0.064(21)
H(9)	0.047(13)	H(28)	0.150(28)
H(10)	0.054(19)	H(29)	0.082(21)

1.2.   Structure Factors for I(b)

```
H /FO/ /FC/ PHI        H /FO/ /FC/ PHI         H /FO/ /FC/ PHI          H /FO/ /FC/ PHI

** K= 0 L= 0 **       4  776  339  181      ..   45   ..  ...        ..  164   ..  ...
 1   36   29  346     5  193  187    2      11   54   ..  ...        10  ..   ..  ...
 2  242  243    2     6  376  363  181      ..   ..   57  ...        14  ..   ..  ...
 3  323  369  181     7   41   41    7
 4  212  215    2     8   94   89  184    ** K= 10 L= 0 **         ** K= 2 L= 1 **
 5  147  142  357     9   82   76  177     0   72   78    3       -15   41   40  ...
 6  113  109    3    10  205  194  182     2  130  130    2       -13   57   43  ...
 7  110  110  184    11   79   78  178     3  110   99  182       ..  164  167  ...
 8  102   99  183    12   69   60  184     4   94   87    2       -10   69   68  ...
 9  375  391    1    13   67   60    3     7   84   54  182        -9  215  210  182
11  214  202  182    14   45   38  184     8   92   90    2        -7   ..   ..  ...
12   41   36    5    15   51   51    3     9   60   36  182        -6  413  374    1
14   41   35    5                         10   63   60    2        -5  609  ..   181
15   70   67  182  ** K= 5 L= 0 **        11   44   47  353        -4  483  470    1
16   42   40    4     0  324  321    1                             -2 1018 1120    1
                     2  178  172  178   ** K= 11 L= 0 **          -1   31   59  173
** K= 1 L= 0 **       3  349  347  181     0   78   80    0         0  157  160    3
 0  124  121  357     4  215  208    2     1  113  109    1         1   43   44  191
 1  483  787    1     7   46   47  156     2  104   96  183         2  815  851    1
 2  214  210  182     8  123  119    3     5   66   63  180         3  552  552  357
 3  360  355  180    13   49   44  184     8   31   27  360         4  138  149  177
 4   31   33  170    14   38   34    3                             5  593  569  181
 5   85   72  176    15   22   22  186   ** K= 12 L= 0 **          6  258  284    1
 7  151  143    2                          0  134  132  181         7   78   91  357
 8  328  317  181  ** K= 6 L= 0 **         2   52   53  182         8  429  412    1
 9  116   47    5     0  107  100  182     4  124  117  181         9   41   40  188
10  221  214  181     1  238  232  180     5   35   40    3        10  213  206    2
11  213  227    1     2  156  148  181     7   99   94    1        11  201  187  182
13   42   11  177     3  131  116  179                            12  138  131    2
14   51   53  183     4  123  108  359   ** K= 13 L= 0 **         13   94   70  182
15   36   41    3     7   39   34    3     0   83   84    2        14   37   30    5
16   37   35  183     8   75   65  182     1  105   99  182        15   36   33  185
                    10  179   80  181     2   29   18    8
** K= 2 L= 0 **      11   33   38    3     3   82   80  182      ** K= 3 L= 1 **
 0  103  104  160    14   31   33  182     4   70   64    3       -13   32   30    4
 1  168  192  357                          5   76   64  183       -11   47   47    4
 2  794  826  180  ** K= 7 L= 0 **         6   44   43    3        -9  162  162    2
 3  605  603    0     0  233  223  181                            -8  161  156  192
 4   91   76    1     1  178  150  179   ** K= 14 L= 0 **          -7   61   68  ...
 5   92   74  357     2  228  214    0     3   37   ..   ..        -6  155  181  161
 6  214  208    1     4   83   73  359     4   37   35  184        -5  197  201  ...
 7   52   46    1     5   48   33    1     3   ..   24  176        -4   94   78  308
 7  131  127  181     6   93   71  359                            -3  267  255  179
13   90   54  360    10  174  158  181   ** K= 1 L= 1 **          -2  301  305  182
14   46   45  180    12   44   42  359    -16   70   70  181       -1  364  190  179
                                         -15   38   37    2       ..  460  457  357
** K= 3 L= 0 **    ** K= 8 L= 0 **        -14  138  136  181        1  354  339    1
 0  134  134    2     0  118  114    2    -13  163  154    1        2  631  629  181
 1  396  397  360     1   43   51  355    -12   94   84  182        3  297  305  ...
 2  112  107    3     2   30   33    8    -11  163  142    1        4   43   44  358
 3  261  262  359     3  128  122  182    -10   54   57  183        5  136  141  ...
 4  210  197    1     4   38   19   12     -8  146  142  182       ..  ..   ..   ...
 5  344  329  181     5   86   78  183     -7  129  128  178        7   43   40  ...
 6  113  100    2     6  110  103    2     -6  177  173  182        8  144  127  359
 7   48   36  355     7  138  151  359     -5  106  109  179       ..  ..   ..   ...
 8  120  120    2     8  196  179    1     -4   99   88  180       13  ..   ..   ...
 9  241  223  181     9   69   62  183     -3 1332 1340    0       15   25   ..   ..
10   35   37  177    10   42   49  177     -2  478  486  360
11  190  181  181    11   45   46  183     -1  844 1006    0     ** K= 4 L= 1 **
12   85   84    2    12   43   40    3      0  346  375  181       -15   ..   22  ...
13  117  109  181                          1  205  206  179       -14   43   53  ...
14   73   74    1  ** K= 9 L= 0 **         2  788  846  180       -11   44   ..  ...
                     0  123  105  183      3   69   67    5        ..   ..   ..  ...
** K= 4 L= 0 **       2  226  216  182      4  217  205  182        -9  137   ..  ...
 0   30   21  196     4  230  214  181      5  137  177  178        -7   71   72  ...
 1  132  136    3     6  135  129  182      6  277  283  181        -6   64   ..  ...
 2  313  212  181     7  215  202    1      7  257  246    1
 3  264  262    2     9  122  113    2
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   H  /FO/ /FC/ PHI        H  /FO/ /FC/ PHI        H  /FO/ /FC/ PHI        H  /FO/ /FC/ PHI

  -4    79   88    2      -3   177  184  182     -10    30   73  182      -1   262 1047
  -3   677  660  360      -2   178  133    2      -9    66   67    2       2   133  104  184
  -2   298  297  180      -1    76   68  355      -8    75   70  183           773  842  360
  -1   314  302  360       1    58   65  185      -7    77   23    3            53   55  187
   0   613  621    0       2    88   86    4      -6    48   43  184       4   505  554  182
   1    43   46  358       4   322  311    1      -5    88   84    3       5   353  453
   3    71   67  192       5   224  214  182      -4    38   39  355       6   167  148  183
   4   142  135    1       7   229  213  181      -3    47   47    5       7   422  397
   5   257  279  181       8   117  113    2      -2   105  105  182           287  211   18
   6    30   25    4      11    67   64  183      -1   168  162    2      10   174  187   18
   7    62   54  358      12    54   18    3       0   168  148  182      11    42   40
   8   239  226  180      13    66   65  183       1   243  237    1      13    49   43  179
   9    30   30  359                               2   102   93  182      14    37   31
  10    63   56  179    ** K=  8  L=  1 **         4   114  111  182
  13    55   49  359                               5    47   48    4    ** K=  1  L=  2 **
                        -12   120  116  181        6   106  103  182
** K=  5  L=  1 **      -11    46   44  178        7    62   61    3     -15    30   73  182
                       -10   150  138  181        8    44   38  184     -13    77   77  358
 -13   102   99  181     -7   262  258    1        9    67   61    3     -11    77   94  182
  -9    88   80  182     -6    48   53  183       10    52   49  183     -10   147  147    2
  -8    74   71    2     -5   111  108    2                              -9   208  200   18
  -7    73   59  182     -4   136  134  181    ** K= 12  L=  1 **        -8    73   44    4
  -5    46   14  357     -3    95   92    2                              -7   115  114  182
  -3   165  153  359     -2    72   58  183      -9    44   40  183      -6   267  261    1
  -2   358  348    0      0    94   79  358      -8    58   49    3      -5    30   38  188
  -1   432  405  360      3   147  154    1      -4    86   82    2      -4   335  321  179
   0   253  252    1      4    95   96  182      -3    45   42  357      -3  1499 1705  180
   1   178  186  181      5    71   71    2      -2   102   92    2      -1   322  349  181
   2    61   31  177      6   247  232  181      -1    97   86  182       0   892 1015    0
   3   113  105  182      7   199  188  180       0   167  161    1       1   568  579  181
   5    84   71  182      8   191  179  181       1    53   46  183       2   132  124  177
   6    79   79  179      9    52   48  178       2    35   33    5       3   109  108  357
   7   138  134  181     10    39   34  183       4    27   24    6       4    65   52  174
   9    77   71  182     13    37   34    3       6    47   48    3       5   105   76  357
  10    79   77  179                              7    40   33  184       6    34   24   12
  12    62   60    2    ** K=  9  L=  1 **        8    76   69    2       7   277  242  181
                                                  9    48   46  183       8   158  140    2
** K=  6  L=  1 **      -12    34   34  181                              10   102   97    2
                       -11    54   55  180    ** K= 13  L=  1 **        11    45   38  185
 -14    58   38  184    -10    31   32  181                              12    35   30    6
 -13    53   47    3     -9    84   78    1      -7    25   25    1      13    43   45  358
 -12    47   35  184     -7    75   69  180      -6    38   40  181      14    34   30    2
  -9    58   59  177     -5    56   54  180      -4    31   26  182      15    52   41  182
  -8   136  128  182     -4   122  112    0      -2    30   31  182
  -7   140  134    2     -3    78   72  180       0    38   33  181    ** K=  2  L=  2 **
  -5   108  104  183      2   113  110  181       2    33   46  359
  -5   388  362  180      3   103   91  180       3    69   69  180     -15    29   36  180
  -4   223  209  182      4   257  251    0       5    76   71    0     -14    43   43  360
  -3   355  345    1      5   171  151    1       6    34   37  360           29   32  179
  -2   138  132  358      6    39   33  181                             -12   111  107  360
  -1   140  126    3      7    75   74  180    ** K= 14  L=  1 **        -11    40   40
   0   183  186  182      8   120  113  181                             -10   173  167  181
   1   365  328  179      9    59   57  180      -4    46   45  182      -9    45   47    1
   2   477  447  181     10    75   75  181      -3    50   43    2      -8    37   50  182
   3   260  253    2     12    43   43    0      -2    33   35  182      -7   112   98  180
   4    41   43  187                              2    80   73  181      -6   375  357
   5    60   61    5    ** K= 10  L=  1 **                              -5   374  381
   7   117  108    3                           ** K=  0  L=  2 **        -4   146  161
   8   101   93  183    -10    82   83    2                             -3   125  147  183
  12    72   64  183     -9    97   95  182     -16    46   48  183      -2   535  533  179
  13    47   45    3     -8   123  118    1     -15    54   50    3      -1   550  579
  14    99   93  182     -7    55   56  183     -14   141  133  182       0   737 1004  180
                        -6    62   60    3     -12    66   59  357       1   491  491
** K=  7  L=  1 **       -5    54   49  184     -11   325  304    1       2    38   33  357
                        -3    54   51  184     -10   233  223  181       3   744  712  180
 -12    33   36    5     -1   138  138  182      -9   122  115    3       4   257  251  360
 -11   114  100  182      0    61   53    3      -8    35   34  170       5    78   95
 -10   136  149  179      1    64   50  184      -7   312  301    1       6   144  129
  -9   229   93  183      6   118  107    2      -6   131  134  183       8    71   45  181
  -8   139  129    2      9    83   78  182      -5   618  617  180       9    69   68    1
  -6   170  161    2     10    28   36    3      -4  1500 1602  180      11   150  147
  -5   187  146  182                             -3  1410 1600  180      12    78   72  181
  -4    66   55  179    ** K= 11  L=  1 **       -2   647  915  360
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H /FO/ /FC/ PHI   H /FO/ /FC/ PHI   H /FO/ /FC/ PHI   H /FO/ /FC/ PHI

** K= 3 L= 2 **
-15   64   63   1
-13 111 109   1
-12   49   43 183
-10   77   72 358
 -8   97   92 182
 -7   53   46   4
 -6 481 461 181
 -5 600 587   1
 -4 528 536 181
 -3 190 178   1
 -2 344 336 181
 -1 625 651   0
  0   34   30 183
  1 319 308 179
  2   21   23 352
  3 244 234   1
  4 174 167 181
  5 409 376   1
  6 343 328 360
  7 195 178   1
  8   92   81 358
 10   36   30 183
 11   33   30 179
 12   39   32 184
 13   42   35   3
 14   29   31 183

** K= 4 L= 2 **
-14   72   65   2
-12 106   93   2
-11 126 115 182
-10   40   34   7
 -8   49   50   6
 -7   92   99 183
 -6   48   45   7
 -5 233 229 182
 -4 167 153 178
 -3 318 322 181
 -2 180 174   2
 -1 140 112 183
  0   97   43 172
  1 244 263 358
  2 129 125   3
  3   86   85 354
  4 231 226   2
  6 338 317   1
  7   96   78 357
  8 183 173   2
  9 203 198 182
 10 147 138   2
 11 102   99 182
 12   66   58   3
 13   72   63 183
 14 108 111   2
 15   30   33 184

** K= 5 L= 2 **
-14   23   20 187
-13 102 102   2
-11   87   83   3
-10   90   92 184
 -9   79   76   3
 -8   41   44 355
 -7 187 177   2
 -6 190 176 359
 -5   54   57 175
 -4 199 193 182
 -3 190 189   2
 -2 375 356 357

 -1 544 534   1
  0 238 226 185
  1 126 115 177
  2 246 236 182
  3 397 391   1
  4 403 387 181
  5   98   93 175
  6   66   69 183
  7 246 234   1
  8   67   70 184
  9   57   47   5
 10   38   34 187
 11   67   59   4
 12   54   53 183
 13 117 107   2
 14   40   33 184

** K= 6 L= 2 **
-14   41   35   2
-13   47   45 359
-12   73   73   1
-11   44   52 182
 -9   96   96 181
 -7   58   53 182
 -6 138 128   1
 -4 261 244   1
 -3   47   48 183
 -2 244 229   1
 -1   64   65 183
  1 336 319 181
  2 100 102   2
  3 113   97 182
  4 110 103   2
  5 130 123 181
  6 137 124   1
  8   30   35 177
  9   76   68 359
 13   44   44 182
 14   65   62   1

** K= 7 L= 2 **
-14   51   45   1
-13 104   98   3
-12   33   29   2
-11   98   89 181
-10   87   86 180
 -9   43   31 182
 -8   54   58 179
 -7   82   74 181
 -6   86   76   1
 -5   92   89 359
 -4 110 107   1
 -3   70   66 353
 -2 190 175 180
 -1 230 223 181
  0 279 267   1
  1   74   71 181
  2 103   87   1
  3 139 130 181
  4 229 217   1
  5   58   56 360
  6 164 156   1
  7   88   84 359
  8   64   70 180
  9   66   62 181
 10   30   21   3
 11   64   60 181
 12   50   50 180

** K= 8 L= 2 **

-13   78   34   4
-12   42   11 183
-10   52   39 182
 -9   86   81   2
 -8   71   63 183
 -7   60   77   3
 -6   81   80 183
 -5 106   93   2
 -1 164 149   2
  0   89   81 357
  1 121 113   2
  2 216 213 181
  4 366 346 181
  6 209 199 359
  7 206 194   1
  8   86   83 182
  9   35   41 176
 10 164 154 181
 12   41   41 183
 13   80   75   2

** K= 9 L= 2 **
-11   85   83 182
-10   32   30   5
 -8   81   71   3
 -7   63   56 184
 -6 131 116   2
 -5   41   42 186
 -4   78   77   4
 -3   68   64 184
 -2   52   57   5
 -1   77   73 184
  0 135 131   2
  2   94   92   3
  3 253 238 181
  4 227 217 179
  5 180 167 182
  6   54   39   4
  7   29   15 347
  8   40   37 175
  9 184 173 181
 10   47   41   4
 12 109 106   2

** K= 10 L= 2 **
-10   49   43 183
 -9   31   18   2
 -8   51   39 184
 -7   51   44   3
 -5   71   69   2
 -4   84   86 182
 -3   66   61   3
 -2 182 178 181
 -1   66   75   2
  0   52   48 184
  1 196 195   1
  3 149 144   2
  4 123 121 182
  5   96   90 179
  6 119   77 182
  8 129 123 181
  9   27   34 177
 10   39   22 185
 11   35   32   3

** K= 11 L= 2 **
 -9   28   25 181
 -5   32   34 181
 -4   66   64 180
 -1   54   57 360

  0   47   41 180
  1   51   55   2
  4   32   30 180
  5   30   30 183
  6   50   46   2
  7   43   37 181
  9   47   46 180

** K= 12 L= 2 **
 -8   64   54   2
 -6   53   49   2
 -5   26   20 356
 -4   70   63   2
  0 110 106   1
  1   89   84 182
  3 110 105 182
  5   52   48 183
  7   77   71 182

** K= 13 L= 2 **
 -7   71   70   2
 -6   34   24 186
 -5   80   75   2
 -4   57   50 183
 -3   74   68   3
 -2   51   45 357
 -1   35   35   5
  1   44   37   4
  4   70   67 183
  6   61   58 183
  7   74   24   5

** K= 14 L= 2 **
 -4   53   53 182
 -3   55   54 182
 -2   44   42   3
  0   54   36   2
  2   92   83   2
  3   37   39 355

** K= 1 L= 3 **
-13   37   34 183
-12   51   43   3
-11 144 133   2
 -9 226 212 181
 -8   51   44   3
 -7 687 622 181
 -6 470 477 180
 -5 383 373 181
 -4 376 379   1
 -3 479 481 360
 -2 307 301 179
 -1   65   63 356
  0 242 268 177
  1 285 225 181
  2 294 287   1
  3 219 201 181
  4   87   69   5
  5 173 162 182
  6 107 104   2
  7 113 117 182
  8   55   55   5
 11   55   47   1
 12   56   53   3
 14   47   45 179
 15   57   44 182

** K= 2 L= 3 **

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  H  /FO/ /FC/ PHI        H  /FO/ /FC/ PHI        H  /FO/ /FC/ PHI        H  /FO/ /FC/ PHI

 -15   42   35    4        9   51   67    1        4  144  133  182     ** K= 11  L=  3 **
 -14   56   48  183       10  250  240  181        5  141  170
 -13   67   72    3       11  118  102    1        6  193  193  358    -10   44   44
 -12   34   32  187       12   72   65  181        7  128  183    2     -9   84   81  182
  -7  330  312    1       14   41   34  182        9   77   70    3     -7   77   55  183
  -8   48   12  205                               10   61   49  184     -5   40   45  184
  -7  128  118  177    ** K=  5  L=  3 **         11  100   94    2     -3   53   48  183
  -6  399  404  181                               12   79   74  182      0  118  110  179
  -5  136  141    3    -15   23   23  179         13   51   52    3      3   40   36  178
  -4   58   37  190    -13   66   38    1                                4   89   85  182
  -3   30   35   17    -12   41   43  359    ** K=  8  L=  3 **          6   45   45    4
  -2  119  114  356     -6  392  366  181                               7   72   66  183
  -1  132  138  177     -5   91   77  179    -11   95   82  181          8   28   23    7
   0  137  131  357     -4  313  302  181    -10   92   87  179
   1  881  912    1     -3  344  327    1     -8   42   41    3    ** K= 12  L=  3 **
   2  170  167  183     -2   62   43  357     -7   61   63  182
   3  133  131  177     -1  349  360    1     -6  115  111    2     -9   53   50    2
   4  379  349  181      0  185  177  359     -5  139  153  181     -8   79   79  183
   5   68   56  173      2  208  194  360     -4   42   34  178     -6   42   42  183
   6  218  205  182      5  388  371    1     -3  191  184  181     -5   43   42    4
   7  103   77    3      6   74   72  182     -2  200  186    1     -3   37   38
   8  265  269  357      7   86   77    1     -1   49   44  184     -2   42   36  134
   9  100   92    3      8  121  113  181      2  139  131    2     -1   85   83    2
  12   55   41  185      9   54   36    1      3  124  127  359      3   41   32    4
  14   44   46  184     11   74   69    1      4  262  258    1      6   37   33  184
  15   29   38  177     12   32   32  182      7  114  110  359      7   32   30    4
                       14   83   83  181      9  123  118  181      8   59   61  182
** K=  3  L=  3 **                            10   44   43  178
                    ** K=  6  L=  3 **        11   45   43  183    ** K= 13  L=  3 **
 -15   61   53  182                           12   37   36    2
 -13   52   54  183    -14   82   83    2                           -2   31   35    2
  -9  144  138  182    -12  127  116    2    ** K=  9  L=  3 **     -1   76   70  181
  -8  131  160    2    -11   82   71  183                            1   99   95  181
  -6   63   79    4    -10   51   44    5    -10   32   27    1      3   44   41  181
  -5  528  528  131     -8   86   87    3     -9  106  101  180
  -4   66   79    4     -7  135  128  182     -7   63   59    0    ** K= 14  L=  3 **
  -3  595  608  131     -6  100   94  178     -4   75   74    1
  -2  146  133    3     -5   57   59  185     -2   85   81    1     -4   22   24    3
  -1  483  490  181     -4   71   70    5     -1  155  151  180     -2   43   39    2
   0  565  576  180     -3  211  209  182      0   66   61  180      1   67   61  182
   1  513  520  181     -2  214  206    2      1  296  290  180      2   33   35  127
   2  606  600    1     -1   96  102  184      2   50   44    1      3   33   35  183
   3  133  129  183      0  146  125  178      3  267  255    0
   4  498  457  180      1  402  361  181      4   61   57         ** K=  0  L=  4 **
   5  413  400  181      2   97   10   28      5  167  157    0
   6  103   78    3      3  312  297  181      6  110  107    0    -13   53   52  183
   7   36   34  355      4  331  312    1      8   65   69  180    -11  111  147  182
   8  284  273    1      5  154  143  182      9  135  129  180    -10  293  302    1
   9  103  143  182      6  220  205    2     10   36   58    1     -8  423  379    1
  10   72   55    4      7  108  109  183     11   37   35  181     -7  149  141  358
  11  107  105  182      8  169  156    2     12   51   53    1     -6  111  115    3
  12   97  100    2      9   99   99  182                           -5  282  221  182
  13   96   90  182     10  105   76    2    ** K= 10  L=  3 **     -4  133  104  177
  15   56   52  182     12   75   93    2                           -3  442  430  181
                       13   41   42  183     -9   87   80    2     -2  103   74  176
** K=  4  L=  3 **                            -6   53   55  358     -1  717  722  181
                    ** K=  7  L=  3 **        -5   59   52    3      0  281  276
 -10   81   74  181                           -4   35   40  184      1  184  178  183
  -8   58   61  182    -14   27   25  356     -3   93   74    2      2  566  546  179
  -6   92   83  182    -13  129  129    1     -2  148  149  182      3  317  325  177
  -5   28   15  174    -12   82   74  182     -1  153  151    1      4  163  150  177
  -4  290  282  181    -10   92   88  182      0  143  132  182      5  371  357  359
  -3  261  252  180     -9   90   87    3      1   44   59    3      6   74   77    1
  -2  262  263  360     -8   70   63  357      2  207  196  181      7   65   68  185
  -1  447  433    0     -7  199  198    2      3   48   36  176      8   87   75    1
   0  420  409  180     -6  104  100  183      4   91   89  359      9   77   72  182
   1  329  311    1     -4   73   77  184      5   81   72    2     10   80   79  177
   2   76   71  359     -3  170  160    2      6   48   46  183     11  123  114  182
   3  518  486    0     -2  166  158  182      7   33   39    4     12  317  302    1
   4   88   82  359     -1  215  209    2      8   55   52  183     13  237  221  360
   5   69   72    2      0   51   40  188      9   88   76    2     14  104  101
   6  163  156  181      1  213  209    2     11   46   50    2     15   46   40  183
   7  143  147    1      3  144  141    2
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** K=  1  L=  4 **          2  343  320  180          -5   28   60    3          2   52   40  156
                            3  709  673  180          -4   65   78  182          3   31   31  179
 -14   47   50  183         4  174  166    1          -3  247  243    1          5  135   68    1
 -13   31   23    6         5   27   23  301          -2   44   20  187          6   47   52  358
 -11   79   77    2         6  121  105    2          -1   34   36    5          8   74   70  182
 -10  185  180  181         7   86   73  358           2  192  177  360         10   55   66  183
  -9   99   98    2        11   39   30  184           3  129  119  179         11   49   45    3
  -8   95   89  358        12   31   27    4           4  131  119  181
  -7  454  447    1        13   38   39  183           5  101  102    1       ** K= 10  L=  4 **
  -6  535  519  360        14   46   47    2           6  179  200  181
  -5  201  176  179                                    7  113  109    1        -10   35   34    3
  -4   83   84  184      ** K=  4  L=  4 **             8   38   38  183         -9   43   44  182
  -3  320  319    1                                    9  137  127    1         -8   36   40    2
  -2   52   50  182       -15   37   29    4          10  106  102  181         -6   65   70    2
  -1  181  173  177       -14   40   30  185          12   43   45  182         -5   36   26  355
   0  202  190  357       -13   36   38    4                                    -4   63   51  178
   1  728  728    1       -12  109  102  182        ** K=  7  L=  4 **          -3   63   66  183
   2   34   38  352       -11   97   87    3                                    -2  230  235  180
   3  161  118    2       -10   38   31  354         -13   41   45    1          0   88   87    2
   4  142  134  182        -9   52   60    6         -11   64   61    1          1  209  198  360
   5   67   38  176        -7  355  344    1         -10   40   40  181          2  141  135    1
   6  109  100  183        -6  218  221  182          -8  135  130  181          3   51   44  184
   7  235  226    1        -5   94   95    3          -7  124  115    1          4   42   35    2
   8  169  157  182        -4  438  422  181          -4   35   27  184          5   34   34  357
   9   36   37    4        -3  176  172    2          -3  212  208  180          6   37   35    3
  10   37   40  185        -2  200  216  182          -2   44   37  358          7   70   69  182
  11   67   60    3        -1  329  320    1           0  111  117  181          9   48   47  182
  12   77   73  358         0  173  164  182           2   43   43  182         10   59   59    2
  13  169  180    1         2  439  415  181           3   29   16  175
  14   36   37  357         3  156  169    2           4  172  163  181       ** K= 11  L=  4 **
                           4  331  314  181           5   33   81    1
** K=  2  L=  4 **          5  274  258    2           7  232  217    1         -3   45   51  180
                           6   35   41  354           9  177  171    1         -2   64   61  181
 -14   43   36    1         9   65   60    4          10  115  109  181         -1   35   32  180
  -9  270  255  181        13  116  106    2          11   41   40    2          0   36   27  181
  -8  140  136  180        14   93   76  182          13   37   38  180          1   49   49    0
  -7  283  275    0                                                              4   74   72    0
  -6  417  414    0      ** K=  5  L=  4 **         ** K=  8  L=  4 **            5   76   72    0
  -5  149  141  360                                                              6   58   60    0
  -4   92   85  181       -14   71   67    2         -12   37   33    4          8   36   40    0
  -3  313  277    0       -13   66   65  182          -9   66   57  183
  -1   60   56  340       -12   65   69    3          -7  156  150  181       ** K= 12  L=  4 **
   0  303  337    0       -11  178  188  182          -6   61   54    4
   1  384  363  180       -10   39   39    2          -5  123  120  182         -6   39   33  184
   2  113   93    1        -9   43   36  189          -4   74   72    1         -5   47   45    3
   3   59   36  360        -8  123  118    2          -3  157  154  182         -4   47   40    3
   4  139  123  180        -7  248  229  181          -2  233  230    1         -3   66   67  352
   5  455  424  180        -5  403  379  181          -1  168  164  182          3   36   41    3
   6   30   33  180        -4  289  284    1           0  244  244    1          7   57   54    3
   7  184  170  181        -3  131  134  182           1   84   80  183          8   28   23  184
   8  106   98    1        -2  292  267    1           3  343  338  181
  10   65   59  180        -1  157  155  182           5  206  196  359       ** K= 13  L=  4 **
  11   57   54  181         0  132  133    3           6  212  194    1
  12  104   98    1         1  174  163  358           7   38   45  184         -5   67   65  182
  13   48   47  360         2   80   65  175           8   99   94    2         -3   40   36  184
  14   24   20  180         3  573  539  181           9  174  159  181          0   67   63    3
                           4  113  106    3          11   69   64  182          1   63   61  183
** K=  3  L=  4 **          5  136  127  182          12   29   28    4          2   66   67    3
                           6  133  133    2                                     4   37   35    5
 -15   34   28  183         7  452  428  181        ** K=  9  L=  4 **
 -12  114  107    1         8   99   92    3                                  ** K= 14  L=  4 **
 -10   72   77  177         9  140  132  182         -12   35   33  184
  -9   37   24  186        10   38   43    5         -11   48   42    3         -2   49   45  183
  -8   92   89  179        11  134  130  182          -8   78   74  183         -1   23   20  178
  -7   69   59  358        13   33   29  185          -7   67   64    3          0   64   78  182
  -6  173  154    1        14   59   60    2          -6   38   39  186          1   72   46    3
  -5   45   43  356                                   -5  148  141    2          2   60   67  182
  -4  348  340  180      ** K=  6  L=  4 **           -4   60   58  184
  -3  291  295  359                                   -3   39   25   10        ** K=  1  L=  5 **
  -2   50   46  176       -13   62   78    1          -2  125  119  152
  -1  174  161  181       -10   67   64  182          -1  276  261    1        -14   35   35  184
   0  358  329  180        -9  103  102  179           0  103  103  358        -12   43   37  177
   1  130  131  182        -7   87   78  179           1  362  360    1        -11   99   74    3
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H /FO/ /FC/ FHI	H /FO/ /FC/ FHI	H /FO/ /FC/ FHI	H /FO/ /FC/ FHI
-10 127 123 357	10 34 28 354	3 61 57 179	-11 .. 41 ..
-9 92 94 2	11 23 24 2	4 340 350 180	-6 .. 75 172
-8 104 111 182	13 82 81 2	5 134 137 2	-5 44 43 ..
-7 172 165 179	14 24 24 356	6 157 179 182	-4 .. 64 350
-5 50 55 4		8 205 203 181	-2 152 144 1
-4 52 61 185	** K= 4 L= 5 **	9 105 104 2	-1 47 37 357
-3 197 197 179	-15 38 32 181	11 173 172 1	0 179
-2 109 121 182	-14 33 34 2	13 60 64 2	1 145 138 181
-1 289 267 179	-13 31 23 359		5 96 85 182
1 219 211 1	-11 32 35 182	** K= 7 L= 5 **	7 93 71 183
2 411 392 360	-8 344 340 0	-13 52 46 183	8 73 68 2
3 281 265 1	-7 37 11 182	-11 53 46 184	
4 341 307 360	-6 47 45 2	-10 44 35 5	** K= 11 L= 5 **
5 91 77 177	-5 212 210 181	-8 81 77 3	-9 .. 68 ..
7 46 44 5	-4 129 122 1	-7 81 77 183	-8 50 44 183
8 38 33 185	-3 76 68 359	-6 278 268 1	-7 33 33 5
9 73 85 7	-2 264 257 180	-5 240 240 181	-6 38 29 183
10 55 47 357	-1 374 353 181	-4 87 87 3	-4 118 109 182
11 174 179 1	1 156 145 360	-3 212 204 182	-3 60 58 3
12 41 41 358	2 147 132 1	-2 219 211 2	-1 127 120 2
13 28 27 4	3 40 42 183	0 96 87 4	0 35 36 184
14 86 80 182	5 100 92 360	1 122 113 183	1 35 34 6
	6 187 182 1	2 96 88 177	3 37 31 5
** K= 2 L= 5 **	7 92 90 181	3 355 343 181	6 51 44 184
-15 36 32 184	8 35 34 2	4 115 103 3	7 67 62 3
-13 76 68 183	10 115 113 1	5 271 258 181	
-12 29 25 7		6 226 218 1	** K= 12 L= 5 **
-10 261 254 1	** K= 5 L= 5 **	7 47 40 183	-3 32 35 3
-8 168 163 2	-14 38 41 2	9 104 107 182	-3 34 34 183
-7 47 48 184	-13 33 31 182	12 39 39 4	-2 53 62 2
-6 35 77 4	-12 40 48 2		-1 55 52 183
-5 150 145 182	-11 46 41 182	** K= 8 L= 5 **	0 35 52 3
-4 125 125 3	-10 130 123 1	-13 35 33 2	2 88 79 2
-3 115 104 357	-9 111 108 359	-12 50 49 182	4 41 35 4
-2 185 187 2	-8 71 64 179	-9 32 40 178	5 40 39 358
-1 213 200 182	-7 46 46 358	-8 43 38 358	7 31 34 183
0 546 534 1	-6 62 57 178	-6 71 67 182	
1 216 218 182	-5 127 130 181	-3 57 53 178	** K= 13 L= 5 **
2 327 304 1	-4 153 153 177	-2 142 125 182	-3 35 34 1
3 109 97 184	-3 81 75 358	-1 92 95 179	-1 38 40 1
4 274 242 179	-2 121 115 1	0 67 62 183	-5 57 55 182
5 363 345 181	-1 188 175 181	1 68 63 178	5 54 35 1
6 77 72 4	1 333 299 181	2 167 150 181	
8 107 93 3	2 37 42 177	3 41 47 177	** K= 14 L= 5 **
9 129 122 182	3 115 109 357	4 105 104 181	0 27 21 358
10 185 170 2	4 175 156 1	5 282 271 1	
12 138 132 2	5 191 177 181	6 216 204 360	** K= 0 L= 6 **
	7 155 145 360	11 24 35 178	-14 77 65 183
** K= 3 L= 5 **	8 88 88 179		-12 62 60 183
-15 56 55 2	10 59 59 2	** K= 9 L= 5 **	-11 70 74 177
-14 37 34 184	11 32 35 358	-11 30 26 180	-10 155 151 182
-12 113 105 182	12 79 76 1	-10 42 41 181	-9 38 41 174
-11 58 40 176		-6 56 59 360	-8 43 50 185
-10 32 38 185	** K= 6 L= 5 **	-5 133 121 1	-7 78 83 4
-9 333 320 1	-14 25 31 184	-3 126 122 1	-6 78 53 356
-7 161 156 2	-13 77 71 2	-2 42 47 181	-5 43 45 6
-6 62 52 355	-12 72 59 183	-1 88 85 180	-4 23 9 224
-5 92 90 3	-11 61 56 3	0 243 229 180	-3 73 70 5
-4 122 125 358	-10 89 91 182	1 33 33 180	-2 358 354 181
-3 224 217 2	-9 112 112 2	2 83 81 181	-1 96 89 176
-2 339 331 181	-8 52 52 184	4 59 51 360	0 377 357 181
-1 135 124 3	-7 207 206 1	5 158 147 0	1 137 112 178
0 187 180 182	-6 227 219 181	6 81 78 181	2 285 274 181
1 624 787 1	-5 245 241 1	7 41 31 180	3 204 191 181
2 493 480 181	-4 186 179 182	8 51 50 181	4 138 134 181
3 74 75 4	-3 269 260 1	10 39 35 0	5 40 34 ..
4 243 217 182	-2 74 76 183	11 33 29 180	6 112 179 180
5 70 67 176	0 38 39 183		
7 81 75 3	1 57 53 176	** K= 10 L= 5 **	
8 103 95 183	2 81 78 184		
9 114 104 2			

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   H  /FO/ /FC/ PHI        H  /FO/ /FC/ PHI        H  /FO/ /FC/ PHI        H  /FO/ /FC/ PHI

   7  293  269    1        3   37   27  178        6   72   56  182       -7   ..   ..   ..
   8  320  304  181        5   48    6  160        4  183  138    1       -6   ..   ..   ..
   9  282  253  177        6   44   44  184        5  137  138  181       -5   ..   ..   ..
  10  406  378  181        7   49   42    3        7  138  139  360       -4  154   ..  184
  11  186  171    2       10   53   51  182        8   38   36  173       -3  117   ..  177
  12   80   75  358       11   59   54    2        9   60   69  359       -2  215  204  181
  13  169  166    1                                                      -1   61   55   ..
  14   34   35  184     ** K=  4  L=  6 **       ** K=  7  L=  6 **        0   72   70  182
                                                                          3   60   57  178
** K=  1  L=  6 **       -14   41   42    3       -13   33   33  359        5   43   50  178
                        -13   58   55  183       -12   40   41    1        6   59   53  174
 -14   39   43    3     -12  116  112    2        -9   50   51  181        7   48   41    3
 -13   57   54  183     -11   73   80  182        -8  158  146    1        9   40   43    3
 -11  110  107  182      -9   96   96  358        -7   69   71  181
 -10   57   53  177      -8  185  174    2        -6   74   69    1     ** K= 11  L=  6 **
  -9  170  170  181      -7   30   29  352        -5   31   32  181
  -8  144  137    2      -6   36   36    8        -4  100   97    1       -7   53   54    0
  -6  106   97  358      -5  108  103  183        -3   72   74  181       -6   55   52    4
  -4  216  208    1      -4  163  162    2        -2   30   29    2       -5   69   60   ..
  -3  497  486  181      -2  338  335    1        -1   69   63  182       -4   37   31   ..
  -2  167  171    2      -1  146  135  358         0  282  274    0       -2   87   87  180
  -1   55   53  355       0  249  240    1         2  209  200  180       -1  112  105  180
   0  202  193    2       1  107  104  184         3  216  210  181        1   44   40  181
   1   99  101  357       2  104   83  177         4  263  258  180        2  111  101  180
   2  380  359    1       3  234  221  182         5   40   37  359        4   31   27  181
   4  158  155  178       4  311  299    1         6   37   34  179        6   43   38    0
   6   66   60    4       5  193  181  182         7   92   92  360
   7   38   33  139       6  136  134    2         8   64   64    1     ** K= 12  L=  6 **
   8  118  111    2       7  144  128  182         9   68   73  360
   9  307  283  181       8  135  130    2        10  109  109    1       -7   42   37  182
  10  206  191  180       9   97   89  183                               -4   56   55    2
  11   41   42  184      10   81   75    3     ** K=  8  L=  6 **        -3   44   46  182
  12  118  111    2      12   30   48    4                                1   55   39  182
  13   52   85  185                             -11   97   90    2        3   41   40  182
                      ** K=  5  L=  6 **        -10   55   50  183        5   56   56  359
** K=  2  L=  6 **                               -9   49   47    3        6   67   57    2
                       -14   41   35  183        -8  170  162  181
 -13  107  103    1     -12   55   54  183        -7   70   71    2     ** K= 13  L=  6 **
 -11   57   51  180     -11   81   83    2        -6   35   31  186
 -10  324  301  180     -10   35   36  185        -3   65   57  177       -2   24   27  185
  -9   53   54  180      -8  117  107  182        -2   48   40  185        0   55   48  183
  -6  123  121  181      -7  152  150    2        -1  131  131    2        2   66   59  182
  -5  110  106  180      -6  249  240  181         0   74   70  183        3   28   32    4
  -3   43   41    1      -5   81   80    3         2  349  358  181
  -2  237  228  181      -4  348  339  181         3   85   83    3     ** K=  1  L=  7 **
  -1  112  106    1      -3   73   73    4         6   62   61    3
   0  329  320    0      -2   69   79  183         7   75   75    2      -10   85   84  182
   1  557  515    0      -1  246  243    1         8   44   38  184      -10   80   ..   ..
   2   86   74    0       0   91   76  356                               -8  128  117   ..
   3  107  102  180       3  391  379    1     ** K=  9  L=  6 **        -6  132  142   ..
   4   40   30  182       5   71   62    4                               -5   ..   92  182
   5   74   66    1       6  117  111  182       -11   24   23  185      -4  159  158    2
   7   94   84    1       7  132  128    2       -10   48   43    3      -3  375  351  181
   9   70   66  180       9   90   89  178        -9   73   64  185      -1  473  467  181
  10   41   37  181      10   91   87  182        -8   59   53    3       0  173  164    1
  11   75   77  180      11   83   84    2        -6   81   77    3       1   27   25  351
  12   35   40  178      13   66   71    2        -4   86   83  178       2  175  177    1
  13   89   88  180                              -3  104   98  182       3   44   36  187
  14   22   23  360   ** K=  6  L=  6 **         -2   58   53  176       4   36   45    4
                                                -1   33   38  186       5   38   34  185
** K=  3  L=  6 **     -12   51   53    2         0  194  189    1       6   76   72  177
                      -10   42   39    2         1  116  114  182       7  254  271  181
 -13   73   71    1     -8   38   43    2         2   48   39    6       8   73   64    3
 -10   79   78  182     -7   76   75  182         4  179  174    2      10  267  251    1
  -9  131  133  179     -6  163  153    1         5   68   60  183      12   42   43   ..
  -7  116  107    2     -5  103   97  182         6  125  118    2      13   77   76  182
  -6   87   91  182     -4  106  103    1         7   78   78  182
  -5  106   99    2     -3   88   87  182         9   75   76  182   ** K=  2  L=  7 **
  -4   40   31  183     -2   91   87  179        10   31   31    4
  -3  232  215    1     -1   96   90  339                              -14   57   66   ..
  -1  310  297    1      0  279  268    1     ** K= 10  L=  6 **       -13   35   ..   ..
   1  221  213  179      1  148  140  359                             -12   ..   78  183
   2   84   93  182      2   54   45    3      -10   38   31  183      -10   52   51  184
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H /FO/ /FC/ PHI

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-9    49    54     4
-8    94    96   183
-7    50    46   175
-6   175   166   132
-5    53    53     6
-3    46    52   174
-2   297   287   181
-1   162   146     2
 0   142   132   183
 1   190   172     2
 2    75    58   135
 3    49    40   173
 4   150   135   132
 5   181   172     2
 6   242   228   181
 7   124   120   176
 8   289   275   181
 9    76    67     3
10    76    67   183
12    56    52   183

** K=  3   L=  7 **

-13   104    98   182
-12    31    41   173
-11   120   119   182
-10    67    66     3
 -9   129   121   182
 -8   172   163     1
 -7   122   117   182
 -6    53    52     4
 -5    37    33   353
 -4    57    50     5
 -3    48    46   186
 -2   113   127     3
 -1   192   181   359
  0   171   156     2
  1    45    37   353
  2   181   187     2
  3    42    38   187
  4   135   129     2
  5    64    65   184
  6    37    33     9
  7   222   210   181
  8    74    33     3
  9   154   147   182
 10    86    79   179
 11    50    46   184

** K=  4   L=  7 **

-13    54    54   180
-12   109   105   181
-10    30    32   182
 -9   134   125     1
 -8   127   119   181
 -7    53    55     2
 -6    60    59   359
 -5    65    64     2
 -3    43    38   179
 -2   200   187   181
 -1   126   119     1
  0   294   282   181
  2    66    66   181
  4    72    67   357
  5   177   161   180
  6    36    33   353
  7    55    57   179
 10    75    73   181

** K=  5   L=  7 **

-12    51    46   181
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-10    62    53   182
 -8    43    47   357
 -7    34    33     3
 -6   275   267   181
 -5   287   275     1
 -4    77    61   359
 -3    59    58     2
 -2    82    79   182
 -1   167   152   180
  2    80    72   359
  3    83    78   179
  4   189   175   181
  5   315   302     1
  6   134   134   181
  7    75    85   179
  8    87    88   181
 11    57    61     2

** K=  6   L=  7 **

-13    49    47   183
-11    53    44   183
-10    42    41     4
 -6   154   147     2
 -5   133   129   182
 -4   135   132     2
 -3    52    43   185
 -2   207   178     1
 -1    75    69   357
  0   385   373     1
  1   147   110   359
  2   161   157     2
  3    46    40   186
  4   101   103     2
  5    35    30   187
  6   104    98   178
  7    37    41   185
  8   151   147   179
 10    54    57     3
 11    38    45   357
 12    42    46     3

** K=  7   L=  7 **

-12    65    63   182
-10    87    89   183
 -9    44    37     5
 -6   100    99   182
 -5    38    36   354
 -1   276   262     1
  0    86    75   357
  1   111   104     3
  2   230   231   181
  3    88    84   178
  4    38    31   185
  5   210   206     1
  7    76    78   178
  8    72    71   183
 10    54    46   184
 11    61    64     2

** K=  8   L=  7 **

-12    47    40     2
-11    78    27   183
-10    30    33     3
 -7    63    59   182
 -8    41    23     5
 -6   146   136     1
 -5    33    37   183
 -4    73    72     2
 -3    43    42   357
 -2   157   146     1
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 -1    55    58   305
  1   113   175   181
  2   108   108   179
  3   111   105   181
  4   206   191     1
  6   135   135     1
  7    34    26   357
  8    61    79     2
  9    96    49   182

** K=  9   L=  7 **

-11    36    38   181
 -7    73    70   181
 -5    94    94     0
 -4    33    32     1
 -3   100    90     0
  1    39    43   181
  3    44    40     0
  6    67    65   180
  8    40    48     1

** K= 10   L=  7 **

-10    46    49   182
 -9    42    41     2
 -8    65    59   182
 -7    27    21   176
 -6   112   100   181
 -3   161   153     1
 -1    45    37     4
  0    43    41   183
  1   113   102     2
  2    50    51   183
  3    62    63     2
  4    54    47   183
  6    38    36   183
  7    27    21     5
  8    43    49   183

** K= 11   L=  7 **

 -8    69    65     2
 -7    31    19   187
 -6    87    88   182
 -4    63    47     3
 -2    70    65     2
 -1    53    51   184
  0    50    48     4
  1    40    43   184
  2    52    47     2
  3    65    57   183
  5    52    53   183
  6    28    26     6

** K= 12   L=  7 **

 -6    37    30   183
 -5    23    23   176
 -4    79    72   182
 -2    58    55   182
  0    61    48   183
  2    83    71   182
  3    37    37     3
  4    34    23   185

** K= 13   L=  7 **

  0    29    11   176
  1    65    60   181

** K=  0   L=  8 **
```

```
-14    ??    49   ???
-12    ??    ??   182
-11    ??    46   182
 -9   150   147   152
 -8    61    65   ???
 -7   147   138   182
 -6   310   304   ???
 -5    62    60   304
 -4   398   379   ???
 -3   250   315   181
 -2    82    77   ???
 -1   290   269   181
  0   118   115     3
  1    67    83   357
  2   240   220     3
  3   134   136   183
  4   113   102   ???
  5   232   209   357
  6   433   398   ???
  7    94    87   183
  8   177   173   179
  9   179   195   181
 10   112   108   ???
 11    63    32   357
 12    62    33     3
 13    31    21   186

** K=  1   L=  8 **

-14    22    25   357
-13   106   109     1
 -9    99   101     2
 -8   137   132   182
 -7    58    59     3
 -6    33    28   353
 -5    81    74     3
 -4    18    73   182
 -2   252   245   181
 -1    82    47   176
  1   224   209     1
  2   343   314   181
  3   103    96   ???
  4   131   145   132
  5   232   222   ???
  6   214   199   357
  7   291   273   ???
  8   192   162   181
 12    ??    47   183

** K=  2   L=  8 **

-14    57    60     1
 -7    53    52   181
 -5    46    41   357
 -4   363   345   180
 -3   161   158   181
 -2    46    38   182
 -1    59    64   360
  1    65    64   181
  2    71    62   ???
  4   127   117   183
  5    76    68   357
  6   163   154   ???
  7   231   225   ???
  8   157   173   ???
 11    ??    ??   181
 12    67     9   176

** K=  3   L=  8 **

-14    63    57   ???
-11    84    81   182
 -9    62    57   ???
```

h	/FO/	/FC/	PHI
-7	102	95	181
-6	57	54	3
-5	144	143	181
-4	54	52	3
-3	33	43	183
-1	50	44	357
0	61	68	3
1	102	102	182
2	165	168	1
3	169	164	181
4	143	135	1
5	328	314	181
6	231	220	1
7	115	105	181
8	33	47	3
10	56	60	2
11	43	46	182
12	39	40	2

** K= 4 L= 8 **

-12	50	50	183
-10	51	53	183
-9	82	75	3
-8	82	77	183
-7	84	85	3
-6	174	164	182
-5	94	85	3
-4	174	196	181
-3	33	37	3
-2	139	130	358
0	133	126	182
1	59	49	175
4	187	171	182
5	56	51	3
8	103	101	182
11	64	62	3
12	33	32	184

** K= 5 L= 8 **

-13	32	33	183
-12	27	30	4
-11	59	62	182
-9	61	56	359
-5	133	137	182
-4	40	31	173
-3	233	240	181
-2	56	52	174
-1	126	123	182
1	34	36	186
2	85	82	3
3	47	47	185
4	79	71	3
5	133	127	359
6	114	103	3
7	45	46	184
8	134	139	179
9	33	22	354
10	65	70	3

** K= 6 L= 8 **

-13	32	33	2
-9	60	57	179
-8	89	78	359
-7	68	60	2
-5	37	28	4
-4	242	235	181
-3	134	144	180
-2	81	74	182
-1	143	141	1
1	44	41	3

H	/FO/	/FC/	PHI
4	144	144	151
5	84		
6	61	53	182
9	67	67	1

** K= 7 L= 8 **

-8	38	36	182
-7	53	47	179
-6	131	123	0
-5	67	69	179
-4	87	78	181
-3	71	74	179
-2	144	137	0
-1	340	318	
0	32	17	357
2	79	78	181
3	69	76	180
4	71	95	181
5	151	139	180
7	87	73	181
8	36	41	360
10	31	22	183

** K= 8 L= 8 **

-11	29	27	184
-10	32	28	4
-9	60	57	182
-8	49	42	3
-4	74	63	3
-2	130	142	2
2	62	62	3
3	65	71	353
4	60	48	178
7	88	76	182
8	56	53	3
9	38	40	183

** K= 9 L= 8 **

-10	30	36	182
-9	36	36	4
-8	31	35	184
-7	87	92	2
-5	71	58	3
-4	84	82	182
-2	60	57	184
-1	66	63	3
0	130	103	182
1	57	40	4
2	31	46	357
3	32	27	7
5	35	38	4
7	74	74	2

** K= 10 L= 8 **

-9	33	35	183
-8	36	37	3
-7	30	25	357
-6	97	94	1
-5	31	29	357
-4	31	47	3
-2	71	58	2
-1	40	40	183
0	138	134	1
1	38	32	182
2	73	75	2
3	125	119	181
4	47	44	2
5	48	50	182
6	89	91	1

** K= 11 L= 8 **

-7	48	47	0
-6	32	35	0
-5	99	97	0
-2	57	52	0
-1	71	71	1
3	24	18	180
4	33	31	181
6	23	28	181

** K= 12 L= 8 **

-5	21	24	3
-4	29	25	183
-3	55	49	2
-1	95	84	1
0	54	51	182
2	116	109	181

** K= 1 L= 9 **

-12	41	38	183
-11	36	34	3
-9	83	83	2
-7	175	162	1
-6	64	64	358
-5	89	94	2
-4	34	26	186
-2	79	95	182
-1	146	131	2
0	132	123	182
1	152	145	1
2	111	102	182
3	374	353	1
4	153	147	181
5	73	75	179
6	284	264	181
8	67	67	359
9	86	84	2
10	33	40	358
12	28	25	123

** K= 2 L= 9 **

-13	46	39	183
-12	39	33	3
-11	106	103	182
-10	113	103	2
-9	117	104	182
-8	119	136	2
-7	130	134	182
-6	154	144	2
-5	70	70	184
-3	127	124	182
-2	116	112	3
-1	197	190	182
0	70	59	5
1	170	139	182
2	190	186	2
3	181	170	359
4	400	333	1
5	76	77	183
7	95	90	182
8	117	112	2
9	67	64	183
10	40	41	4
11	77	75	182
12	24	33	4

** K= 3 L= 9 **

-12	35	36	183

h	/FO/	/FC/	PHI
-11	-7	41	
-8	31	44	184
-6	37	43	186
-4	68	43	359
-3	171	164	358
-2	133	129	182
-1	112	105	3
0	97	95	184
1	43	39	6
2	43	44	354
3	94	91	3
4	206	204	359
5	103	111	3
6	132	170	357
7	130	126	3
8	130	131	182
9	72	61	2
10	45	73	184

** K= 4 L= 9 **

-10	41	37	177
-8	34	33	179
-7	36	33	358
-6	57	60	179
-5	138	129	360
-1	101	97	181
2	140	140	180
3	32	44	183
5	106	106	360
6	106	102	1
10	44	50	2

** K= 5 L= 9 **

-9	33	24	183
-8	112	110	180
-6	156	147	1
-4	36	35	178
-3	91	92	181
-2	36	44	179
-1	41	31	183
0	64	73	
1	100	103	181
3	52	50	357
4	104	105	1
8	37	44	179
10	44	70	1

** K= 6 L= 9 **

-7	39	30	178
-6	43	41	183
-4	207	172	181
-3	164	164	179
-2	43	46	185
-1	117	113	355
0	67	65	355
1	74	77	183
2	35	41	185
3	170	164	2
5	100	108	2
6	76	63	182

** K= 7 L= 9 **

-9	47	41	183
-7	73	73	182
-6	35	41	2
-5	204	214	181
-4	46	45	177
-3	102	95	182

```
  H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI

 -2  106   92    2         -5  121  133    2         -1         66  183         -4   33   35  185
 -1   55   66  337         -4   43   47  336          0  103  100    2         -3   67   55  180
  1  143  135  182         -2  176  163  182          2   35   34  183         -1  155  154    1
  4   84   88    2         -1  312  300    1          3   37   47  184          0   33   38  184
  5   43   41  184          0  244  231  181          4  203  204    1          3   71   67  182
  6   95  100    2          1  223  209    1          6   79   76    2          5   66   55  182
                            2  337  337  181          7  134  130  182          8   53   71    2
** K=  8  L=  9 **          3  221  202    2          9   47   50  183
                               144  132    2                                ** K= 10  L= 10 **
 -5   84   86  181          5  142  133  182      ** K=  5  L= 10 **
      83   74    2             75   83  178                                   -7   32   28    3
 -4   38   43  182          7  106  102    2        -10  39   21  185         -4  100   91    3
 -3   72   74    2         10  131  130  182         -9   27   32    6         -3  100   91    3
 -2   38   36  338         11   25   27  178         -8   61   62  358         -1   37   39    3
 -1   75   64    2                                   -7  197  165    1          5   29   29    3
  0   70   68  182      ** K=  1  L= 10 **           -6   62   53  358
  1   50   45  176                                   -5   97   91    2      ** K= 11  L= 10 **
  2  111  114  181        -13   32   32  183         -4  111  108  182
  3   57   58  173        -12   36   39    3         -2   33   38  305         -4   38   35  180
  4   48   46  183         -7  137  138  181          0   56   46  185          0   42   44    1
  5   56   55    2         -8   31   30    3          2  101   96  182          2   22   24    1
  8   38   39  183         -7   46   46  183          3  151  146    2
  9   37   39    2         -6  121  111    2          5  147  150    1      ** K=  1  L= 11 **
                          -3   64   78  183          6  142  137  182
** K=  9  L=  9 **        -2   54   48    4          7   40   38    4        -11   92   88  181
                          -1  114  107  182          9   30   34    4         -8   65   51    2
 -9   36   27  130          1  160  160  181                                  -4   63   58    2
 -8   24   23  181          2  131  130  179      ** K=  6  L= 10 **           -3   67   65  182
 -5        49  181          3  387  360  181                                  -2   57   58    3
 -6   50   56  180          4  100   88  178         -8   91   92    1         -1  153  140  181
      36   58    0          5  114  108  359         -7   60   61  359          1   93   92  359
  2   46   46    2          7   36   32  183         -6  109  101    1          2   97   89    2
  3   44   35  180             82   76    2          -5  127  124  181          4  140  123  180
  4   42   49  181          9   74   68  182         -4  115  103  180          5   95   83    2
  6   62   61    0         11   34   36  182         -1   53   60  359          7   73   71  182
                                                        36   23  179          8   48   43    2
** K= 10  L=  9 **      ** K=  2  L= 10 **            4   40   43    2          9  102   77  181
                                                     5   46   42  182         10   30   25  177
 -7   84   81  181        -10   67   61  360          6   31   27  178
 -3   65   74  182         -7   95   92    1          7   28   31  357      ** K=  2  L= 11 **
 -2   33   33    3         -4   43   35  359
  0   26   28    4         -2   56   58  181      ** K=  7  L= 10 **         -12   44   46  182
  2   63   63    2          0  154  145  360                                -10   53   55  181
  4   47   44    3          1   41   39  179         -9   35   36  181         -7   64   55    2
  6   27   28    4          2   94   97  181         -8   37   38    1         -6   55   49  184
                            3  405  394  180         -7   33   34  359         -5   55   45    2
** K= 11  L=  9 **          4  160  154  181         -6   73   66  180         -3  145  140    2
                            5   97   93    0         -5   90   85  181         -2  187  176  181
 -6   55   58  182          7   47   49    1         -4   39   37  180         -1   46   44  181
 -4   37   34  184          9   39   63    1         -3   61   61  360          0  250  239  181
 -3   79   70    2                                    0   87   84    1          2   69   74  358
 -2   43   42  183      ** K=  3  L= 10 **            1  139  140    0          3   83   75    3
 -1   94   88    2                                    6   41   42    1          4   60   59  180
  0   74   74  182        -12   26   27  183                                    8   56   54  183
  1   70   68    2        -11   56   59    1      ** K=  8  L= 10 **            7   59   43    4
  2   50   53  183        -10   30   29  183                                   10   64   42  182
  3   65   64    2         -9   51   49    2         -8   41   42  183
  4   29   33  184         -7   72   73    2         -4   49   47  183      ** K=  3  L= 11 **
                          -5   76   74    2         -2   57   51  183
** K= 12  L=  9 **        -4  120  116  181          1  131  126    1        -12   32   36    4
                          -3   77   76    2          2   39   42  357        -10   34   33    4
 -2   61   60    2          0  106   98  359          3   40   30    3         -7   77   79  182
  1   72   70  182          1  223  214    1          4   31   25  185         -4   43   31  184
                            2   36   45  358          6   40   47  183         -3   89   84  182
** K=  0  L= 10 **          3  175  179  180          7   48   51    2         -2   89   82    2
                            4   66   39  182                                   -1  115  126  183
-13   60   62    2                                ** K=  9  L= 10 **            0  155  149  179
-12   61   61  182      ** K=  4  L= 10 **                                      1  327  309  181
-11   55   53    3                                   -8   33   21  183          2   49   39  179
-10   93   93  182         -6   90   79    2         -7   48   44  183          3  107  108  183
 -8  183  170  181         -5  117  113  182         -6   42   30    4          4  131  147    2
 -7  101   96    2         -4  150  152    2         -5   51   47  183          6   95   95    2
 -6  109   96  358         -3   77   79  183
```

H /FO/ /FC/ PHI   H /FO/ /FC/ PHI   H /FO/ /FC/ PHI   H /FO/ /FC/ PHI

```
** K= 4  L= 11 **      -9  64  63 180      8  40  39 178    ** K=  2  L= 13 **
                       -8  24  16 182
-11  42  41   1        -2  54  51   0    ** K= 4  L= 12 **   -8  40  38 183
-10  57  50 181        -1  29  27   0                       -7  71  17 178
 -9  32  26 179         2  26  27 180     -10  85  70 131    -3  71  47 178
 -8  63  63 181         3  54  49 180      -8  36  30 184    -2  71  41 183
 -7  58  52   1                            -7  45  42   3           41
 -2 120 110 360      ** K= 10  L= 11 **    -5  67  58   2           35  15   3
 -1  98  89   1                            -4  85  79 182
  0  74  83 181        -4  31  27 183      -2  85  73 183    ** K= 2  L= 13 **
  1 161 145 180        -2  40  43 182       0  82  78 182
  2 101  99 181         0  47  37 183       2  81  43 183    -10  30  23   4
  5  41  41   2         1  38  36   3       3 103 105   2     -8  33        4
  6  60  62   1         2  32  23 184       2  34  35 356     -6  39  19 182
  7  87  87 181                             5  69  69   2     -5  74  43
  8  31  30 359      ** K=  0  L= 12 **     8  66  73 182     -5  90  63 357
  9  44  36   1                                              -4  90  76   3
                      -9  88  83 182     ** K= 5  L= 12 **    -2  44  35   4
** K=  5  L= 11 **    -8  46  43   3                          0  34  33
                      -7  64  55 183      -10  27  26 177      4  93  63
-10  42  34 182       -6  73  57   2       -9  47  43 182      5  55  47 183
 -7 112 106   1       -5  44  40 185       -8  79  73   2
 -5  57  58   1       -3  68  61 357       -6  71  62   2    ** K= 3  L= 13 **
 -4  89  82 181       -2  33  15  11       -5  40  29 185
 -1  27   1 109        0  36  22   8       -4  85  77   2     -6  73  64 182
  5  63  73 184        1 179 161 359       -1  60  50 183     -5  49  40   3
  7  50  49 179        3  78  73 358        1 108 100 182     -4  44  42 358
                       5 100  86 182        2  71  65   3     -3 241 228   1
** K=  6  L= 11 **     6 137 125   2        3  83  80 182      2 147 144 181
                       7  70  63 358        5  71  78 182      4  85  45 183
-10  43  42   3        8 110 109   1        6  64  71   2      5  83  74 183
 -8  73  69   2        9  73  75 182        7  36  43 183      6  33  23 185
 -7  52  47 358                                               7  67  78   2
 -6  72  63   2      ** K=  1  L= 12 **   ** K= 6  L= 12 **
 -5 115 109 182                                              ** K= 4  L= 13 **
 -3  67  64 183      -11  23  14   6       -9  39  26   2
 -1  34  51 184      -10  46  46 182       -8  25  30 309     -7  40  39 181
  0  46  48 179       -8  77  73 182       -7  45  46   1     -5  67  57 181
  1  80  81 182       -7  35  29   4       -6  69  61 181     -4  57  34
  2  81  79   3       -6  65  60   2       -4  41  42 182     -3  44  51 360
  3 101  95 182       -3  53  46   3       -2  36  37 182     -2 154 175 181
  6  97 101   3       -1 223 209   1       -1  36  31   3     -1  45  43 181
  8  40  47   3        1  60  51   3        3  72  69 181      0  45  44
                       2  94  84 182        4  79  82 181      3  45  45 181
** K=  7  L= 11 **     3  67  64   2
                       7  87  82   2     ** K= 7  L= 12 **   ** K= 5  L= 13 **
 -9  74  74   2
 -7  40  33   3      ** K=  2  L= 12 **    -4  55  49 181     -3  47  43   1
 -6  36  35 184                            -3  45  41 180     -2  51  53 181
 -5  60  50   3      -11  20  11 182       -2  85  82 181     -1  55  55
 -4  47  42 184      -9  37  34 181        -1  52  46   1      0  42  39
 -3  73  67   3      -3  39  34 360         3  69  71   1      3  57
  0  67  66 183      -4  82  77 180         5  48  53   1      5  62  67 181
  1  69  59   3      -2 172 160   1
  2  82  84 182      -1  89  89   0       ** K= 8  L= 12 **   ** K= 6  L= 13 **
  3  31  30   5       0 307 290   0
  5 104 108   2       1 123 117 181       -6  38  29   3      -7  38  41   3
  6  43  46 183       2  67  63 180       -4  83  42   3      -5  44  57
  7  36  44   3       3  95  86 181       -3 104  96 181      -4  84  37 183
                      6  88  82 180       -1  44  46 182      -3  55   3
** K=  8  L= 11 **     9  52  60 181        0  63  61   3      -2  52  34 183
                                            2  52  52   2     -1  37  71   4
 -8  21  21   3      ** K=  3  L= 12 **     3  39  42 182           109 114 183
 -6  35  31   3                                                3  25  25   4
 -7  71  63 181      -6  36  37   2       ** K= 9  L= 12 **
 -4  64  63   3      -5 109  99 181                          ** K= 7  L= 13 **
 -2  70  67   3      -3 181 172 181        -3  37  33   4
  2  39  35   3      -1 141 132 360        -2  34  33 183     -6  33  17   4
  3  30  23 183       0 163 164   1        -1  33  18   6     -5  43  23 183
  5  37  41 182       1  45  47 182         0  32  34 184
                      2  49  43 179         1  24  29   4
** K=  9  L= 11 **     4  90  87   2         2  30  30 184
                      5  45  36 182
```

1.3.   Structure Factors for I(c)

H	/FO/	/FC/	PHI		H	/FO/	/FC/	PHI		H	/FO/	/FC/	PHI		H	/FO/	/FC/	PHI

** K= 0 L= 0 **

```
2 2436 2230 180
4  388  378   0
```

** K= 1 L= 0 **

```
0 1137 1519 180
1  758  790   0
2 1300 1274   0
3  354  343 180
4  307  307 180
6  129  146   0
```

** K= 2 L= 0 **

```
0  295  358 180
1  122   65   0
2  203  202 180
4  181  182   0
5  130  122 180
7   46   45   0
```

** K= 3 L= 0 **

```
0  437  450 180
2  212  190   0
3  101   73   0
4  231  241 180
6   65   75 180
```

** K= 4 L= 0 **

```
0  165  148   0
1  101  161 180
2  562  577 180
4  319  333   0
5   82   93   0
6   51   72 180
```

** K= 5 L= 0 **

```
0  284  308 180
1  478  467   0
2  293  243   0
3  146  135 180
4   97   95 180
7   54   54   0
```

** K= 6 L= 0 **

```
1  193  176 180
2   56   79   0
3   91   92   0
4   52   62 180
```

** K= 7 L= 0 **

```
0   43   46 180
3   71   72 180
4   41   47 180
5   50   46   0
```

** K= 8 L= 0 **

```
3   45   27   0
```

** K= 9 L= 0 **

```
1  125  106 180
3   53   53   0
```

** K= 10 L= 0 **

```
2   62   45   0
3   69   58 180
```

** K= 11 L= 0 **

```
3   35   27   0
5   37   33 180
```

** K= 12 L= 0 **

```
0   39   24 180
```

** K= 0 L= 1 **

```
-7  169  187 180
-5  899  887   0
-3 1837 1672 180
-1  430  424   0
 1  288  198   0
 3  390  370 180
 5  207  232   0
 7  166  147 180
```

** K= 1 L= 1 **

```
-7  131  140   0
-6  141  166 180
-5  368  392 180
-4  628  588   0
-3  381  363   0
-2 1995 1851 180
-1   94   39 180
 0  223  251   0
 1   63  115 180
 2  133  125 180
 3   49   34 180
 4   51   66 180
 5  204  180 180
 7   55   72   0
```

** K= 2 L= 1 **

```
-5   67   68 180
-4  219  210 180
-2  199  210 180
-1  216  249   0
 0  176  228 180
 1  149  140   0
 2   66  103   0
 3  117  109 180
 4  213  257 180
 5   91   88   0
 6  122  129 180
```

** K= 3 L= 1 **

```
-8   47   47 180
-6  117   95   0
-4  113   90 180
-3  156  192   0
-2   51  114 180
-1  235  247 180
 0  279  270 180
 1  257  280 180
 2  253  262   0
 3  426  411   0
 4  212  242 180
 6   83   71   0
```

** K= 4 L= 1 **

```
-5   79   93   0
-3  126  109 180
```

```
-2   80   74   0
-1  400  406   0
 0  147  138   0
 1  196  191 180
 2  242  241 180
 3  148  164 180
 4  246  249   0
```

** K= 5 L= 1 **

```
-7   45   49   0
-6  148  154 180
-4  246  253   0
-3   37   48   0
-2  131  117 180
-1  174  139 180
 0  167  167   0
 1  159  166   0
 3  116  123 180
 4  129  121 180
 6   78   85   0
```

** K= 6 L= 1 **

```
-6   50   54   0
-4  111   96 180
-3   82  105   0
-2   93   79   0
-1   85   95 180
 1   98  108 180
 2   48   81 180
 3  129  111   0
 5   91  120 180
 7   38   46   0
```

** K= 7 L= 1 **

```
-1   63   37 180
 1  112   76   0
 2  105   96   0
 4   61   59 180
```

** K= 8 L= 1 **

```
-4   75   69   0
 0   45   30   0
 2   49   51 180
 3   39   41   0
 4   91  100   0
 6   34   30 180
 7   29   22 180
```

** K= 9 L= 1 **

```
-6   50   53   0
-4   49   42 180
-3   62   74   0
-2   56   81   0
 2   57   71   0
 3   73   61 180
 7   29   24   0
```

** K= 10 L= 1 **

```
-3   62   64 180
-2   59   52 180
-1   57   44   0
 0   56   87   0
 1   16   33 180
 2   44   47 180
 4   39   51   0
```

** K= 11 L= 1 **

```
-2   48   41   0
 0  126   93 180
 1   37   43   0
 2   32   45   0
 3   45   39 180
 4   34   29 180
```

** K= 0 L= 2 **

```
-8  197  231 180
-6  382  309   0
-4  678  669 180
-2  134   79 180
 0   13   27 180
 2 1043 1044 180
 4   62   60   0
 6   48   46   0
 8   43   55 180
```

** K= 1 L= 2 **

```
-9   84  106   0
-8   87   80   0
-7  270  279 180
-6  128  123 180
-5  335  342   0
-4   66   47 180
-2  137  137 180
 0   47   44 180
 1  343  284   0
 2  143  186 180
 3   87   30 180
 4   91   70 180
 6   85   95 180
 7  104  120   0
```

** K= 2 L= 2 **

```
-9   36   66 180
-7  107  119   0
-6   54   71 180
-4  257  247   0
-3  168  133 180
-2  230  234 180
-1  404  471 180
 0   45   15 180
 1  178  197   0
 2  107  142   0
 3  423  425   0
 4   94   87 180
 5  181  163   0
 7  108  112 180
```

** K= 3 L= 2 **

```
-4   87   91   0
-3  301  304   0
-2  350  339   0
-1  450  462 180
 0   65   84 180
 1  144   92   0
 2  174   96 180
 3   42    1   0
 4  348  354   0
```

** K= 4 L= 2 **

```
-8   64   67 180
-7   42   55   0
-6   95   94   0
-5   92   90 180
-4  101   77 180
-3  158  146 180
```

H /FO/ /FC/ PHI

```
 -2   158   166     0
 -1   519   530     0
  0    43    68   180
  1   373   374   180
  2   189   227     0
  3    93   103   180
  4    90    70   180
  5    62    63   180
  6    54    53     0

** K=  5  L=  2 **

 -9    45    62     0
 -7    72    85   180
 -5   136   141     0
 -4   139   140     0
 -3   167   188   180
 -2   196   201   180
 -1   127   130   180
  0   128    88     0
  1   471   464     0
  2    70    50   180
  3   323   320   180
  4    55    44     0
  5    69    67     0

** K=  6  L=  2 **

 -7    43    47     0
 -5    37    42   180
 -4    51    24   180
 -3    56    42     0
 -2    77    56     0
 -1   141   136     0
  1    87    93   180
  2   143   146     0
  3    66    33     0
  4    65    59   180
  5    36    36   180
  8    36    36     0

** K=  7  L=  2 **

 -4    53    51     0
 -3    48    48     0
 -1    65    56   180
  1    95   103     0
  2    76    96     0
  4    83    83   180
  6    66    67     0

** K=  8  L=  2 **

 -4    34    40     0
 -1    36    59     0
  1    89    91   180
  4    70    73     0

** K=  9  L=  2 **

 -4    61    54   180
 -1    54    47   180
  1    58    48   180
  2    74    92     0
  3    76    57     0
  4    86    69   180

** K= 10  L=  2 **

 -6    25    15     0
 -2    64    47   180
  2    85    82   180
```

H /FO/ /FC/ PHI

```
** K= 12  L=  2 **

  3    35    25     0

** K=  0  L=  3 **

 -9   112   128   180
 -7    93    80     0
 -5   225   249     0
 -3   739   729   180
 -1  1439  1369     0
  1   125    41     0
  3   110   104   180
  5    40    27     0
  7   120   115     0

** K=  1  L=  3 **

 -7    69    87     0
 -6   103    98     0
 -5   171   156   180
 -4   153   166     0
 -3   225   191     0
 -2   312   286   180
 -1   626   667   180
  0   495   523     0
  1   698   780     0
  2   384   400     0
  3   220   224     0
  6    59    71   180
  7    68    91   180

** K=  2  L=  3 **

 -9    48    73     0
 -7   131   135   180
 -6    44    63     0
 -5   166   177     0
 -4   154   168     0
 -3   196   195   180
 -2   111   107     0
 -1   204   157     0
  0   383   485     0
  1   588   595   180
  2   232   301   180
  3   321   329     0
  4   133   150     0
  5   188   196   180
  6    73    94     0

** K=  3  L=  3 **

 -8    72    88     0
 -6   142   147   180
 -5   133   139   180
 -4    62    69     0
 -3   275   267     0
 -2   157   192     0
 -1    99    94     0
  0    52    80     0
  1   394   442   180
  2   150   136     0
  3   504   474   180
  5   169   154     0

** K=  4  L=  3 **

 -8    36    42   180
 -7    71    64     0
 -6   165   164     0
 -5    55    71   180
 -4   283   280   180
 -2   131    89     0
```

H /FO/ /FC/ PHI

```
 -1   117   118     0
  0    46    20     0
  1   125   151   180
  2   160   168   180
  3   124   134     0
  4   135   152     0

** K=  5  L=  3 **

 -6    86    82   180
 -5    70    60     0
 -4   248   258     0
 -3    36    34     0
 -2   343   370   180
  0   360   345     0
  1   117   135     0
  2    64    53   180
  3    61    44   180
  4   108   106   180
  5    56    67     0

** K=  6  L=  3 **

 -5    73    71     0
 -4   158   130   180
 -3    47    52   180
 -2   143   155     0
  1    34    18     0
  2    59    57   180
  3    65    80     0
  4    47    48   180
  5    35    18   180

** K=  7  L=  3 **

 -5    62    54   180
 -4    88    92     0
 -2    91    98   180
 -1   162   137   180
  0    72    67   180
  1   183   175     0
  3    45    30   180
  4    67    76     0
  5    74    59   180
  6    52    51   180
  7    34    45     0

** K=  8  L=  3 **

 -4    58    66   180
 -3    52    61   180
  2    50    60     0
  3    66    77   180
  4   102    91   180
  5    50    56     0

** K=  9  L=  3 **

 -6    31    34   180
 -1    60    73   180
  0    36    49   180
  2    48    41   180
  3    82    77     0

** K= 10  L=  3 **

 -1    87    66     0
  0    54    65   180
  4    30    28     0

** K= 11  L=  3 **

 -1    39    27     0
```

H /FO/ /FC/ PHI

```
  2    52    15     0

** K= 12  L=  3 **

 -3    33    22     0
 -1    43    31   180
  0    33    26   180
  2    45    35     0
  3    33    24   180

** K=  0  L=  4 **

 -8    49    69   180
 -6   271   294     0
 -4   341   348   180
 -2   186   197     0
  0   260   253     0
  2   775   743     0
  6   190   174   180

** K=  1  L=  4 **

 -9    41    31   180
 -7    39    58   180
 -6    31    81   180
 -5    93    71     0
 -4   216   211     0
 -3    94    89     0
 -2   173   212     0
 -1   664   756   180
  0   391   432   180
  1    83    72     0
  2   104   134     0
  3    71    67   180
  4   107   122     0
  6    48    35     0

** K=  2  L=  4 **

 -8    41    53   180
 -5    67    55     0
 -3    34    64   180
 -2   179   191     0
 -1    60    75   180
  0    58    95     0
  1   406   419   180
  2   247   250   180
  3    77    55   180
  4   185   166     0
  5    58    60     0
  7    97   116   180
  8    52    47     0

** K=  3  L=  4 **

 -8    34    45     0
 -6    95   103   180
 -2   163   167   180
 -1    51    38     0
  0   210   251     0
  1    51    48   180
  2    95   106     0
  3   243   252     0
  4   135   120   180
  5   100    89   180

** K=  4  L=  4 **

 -6    94    84     0
 -4   127   149   180
 -3   103   127   180
 -2   198   220     0
 -1   521   574     0
```

```
 H /FO/ /FC/ PHI        H /FO/ /FC/ PHI        H /FO/ /FC/ PHI         H /FO/ /FC/ PHI

 0  222  242 180        2   27   20 180       -8   42   42 180      ** K=  1  L=  6 **
 1   26   17 180                              -6   78   71   0
 2  135  117 180     ** K=  0  L=  5 **       -5   66   61   0       -6   39   31 180
 3  151  158 180                              -4  144  151 180       -3   58   66   0
 4   69   67 180       -9   65   89 180       -3  301  320 180       -2  159  147   0
 5  144  153   0       -7   75   73   0       -1   83   93   0       -1  361  360   0
 6   49   56   0       -3   88   62 180        0  159  159   0        0  567  603 180
                       -1  156  145 180        2   33   42 180        2  234  278   0
** K=  5  L=  4 **      1  522  586 180        4   54   40 180        4   89   68   0
                        5   83   85   0        5   74   66 180        5   75   72 180
-3   37   73   0        7   95  100 180                               6  133  146 180
-2   75   54 180                            ** K=  6  L=  5 **        7   55   52   0
-1  115  131 180     ** K=  1  L=  5 **                               8   59   64   0
 0  180  168   0                              -4   77   67   0
 1   74   88   0       -9   29   28   0       -3  100  104   0     ** K=  2  L=  6 **
 2  207  240 180       -8   60   77 180       -2   90   75 180
 4   82   96 180       -4   61   72   0       -1   47   57 180       -5   49   47   0
                       -2  201  207   0        2  121  115   0       -4  136  134   0
** K=  6  L=  4 **      -1   82   34   0        5   46   55 180       -2  116  129 180
                        0  852  869 180        7   52   44   0       -1   45   66 180
-6   39   44 180        1  260  240 180                               0  273  290 180
-4   63   57   0        2  123  114   0     ** K=  7  L=  5 **        1   78    5 180
-3  205  218 180        3  224  172   0                               2   61   75   0
-2  124  123 180        4   59   35   0       -7   28   26 180        3  128   91   0
-1   96   86   0        5  234  210 180       -5   69   77   0        4  154  128 180
 0   59   55 180        6   99   91   0       -2   42   31   0        5  215  222   0
 2   58   52   0        7   65   64   0        0   46   51   0        7   88  114 180
 3   75   48 180                               1  185  170   0        8   38   41 180
 6   70   59 180     ** K=  2  L=  5 **        3  161  167 180        9   34   42   0
 7   37   29 180                               4  115  100   0
 8   40   46   0       -4   92   97 180        5  142  121   0     ** K=  3  L=  6 **
                       -3  115  115   0        6  111  121 180
** K=  7  L=  4 **      -2   83   93   0        8   56   74   0       -5   63   53 180
                       -1  327  306 180                              -4  201  209 180
-5   51   41 180        0  257  267   0     ** K=  8  L=  5 **       -3   68   88   0
-4   44   38   0        1  665  676   0                              -2  199  191   0
-2  104  125 180        2  527  554 180       -7   26   14   0       -1  310  332   0
 1   67   75 180        3  224  246 180       -5   46   50   0        0  138  145   0
 2   34   59   0        4  184  217   0       -4   49   62   0        1  520  526 180
 4   52   56 180        5   79   89   0       -3   63   65 180        2  249  238 180
 5   50   40 180                              -2   55   38   0        3  133  130   0
 6   93   83   0     ** K=  3  L=  5 **       -1  121  118   0        5   66   73 180
 7   31    7 180                               1  103   92 180        6   64   44   0
 8   57   74 180       -9   41   32   0        3  115  106   0        7   74   71   0
                       -3  100  120   0        4  134  124 180        8   57   76 180
** K=  8  L=  4 **      -2  102   91   0        6  113  123   0
                       -1  345  346   0        7   42   58 180     ** K=  4  L=  6 **
-1   71   57 180        0  489  526 180
 3  115   97   0        1  541  580 180     ** K=  9  L=  5 **       -8   36   40   0
 4   62   43   0        2  206  229 180                              -7   37   70   0
 7   40   52   0        3  311  316   0       -3   78   71   0       -6   45   41 180
                        4  118  153   0        3   42   25 180       -5  112  104 180
** K=  9  L=  4 **      5   97  102   0        5   42   42 180       -4   42   35 180
                        6   74   81 180                              -3   36   15 180
-5   31   26 180                            ** K= 11  L=  5 **       -2   83   70   0
-4   30   42   0     ** K=  4  L=  5 **                              -1  137  126 180
-3   97   92   0                               2   31   31 180        0  274  291   0
-1   67   69 180       -8   35   30   0        3   33   44 180        1  191  212   0
 1  107   94   0       -5   75   72 180                               2   87   89 180
 2   60   60   0       -4   37   44 180     ** K= 12  L=  5 **        3  191  214 180
 3   47   45 180       -3   86  102   0                               8   42   59   0
                       -2  146  149 180       -1   51   36   0
** K= 10  L=  4 **      -1   77  104 180        0   30   34 180     ** K=  5  L=  6 **
                        0  113   95   0        2   63   56   0
-1   75   77   0        1  103  100   0                              -6   48   68   0
 0   56   41   0        2   83   89 180     ** K=  0  L=  6 **       -5  126  144   0
 1   54   58 180        3  168  151 180                              -4   72   56   0
                        4   98   99 180       -6   80   94   0       -3  144  168 180
** K= 11  L=  4 **      5   60   59   0       -2  460  437 180       -1   99  115   0
                        6   50   48   0        0   33   90 180        0   64   59   0
-1   46   44 180                               2  146  200   0        1   88   88 180
                    ** K=  5  L=  5 **         6   73   43   0        2   70   31   0
** K= 12  L=  4 **                                                   3  120  127   0
```

H	/FO/	/FC/	PHI
4	62	75	0
6	45	60	0

** K= 6 L= 6 **

H	/FO/	/FC/	PHI
-6	41	39	0
-5	46	38	180
-3	172	168	0
1	47	31	0
2	112	105	0
3	70	67	180
5	64	67	0
7	55	48	180

** K= 7 L= 6 **

H	/FO/	/FC/	PHI
-5	45	44	0
-4	95	94	0
-3	83	90	180
-2	113	92	180
-1	111	112	0
0	83	73	0
1	151	166	180
2	75	36	180
3	245	271	0
4	34	42	180
5	137	124	180
6	64	74	0
8	56	74	180

** K= 8 L= 6 **

H	/FO/	/FC/	PHI
-6	60	61	0
-4	69	59	180
-3	49	64	0
-2	50	42	0
-1	203	199	180
1	256	269	0
2	176	159	180
3	225	205	180
4	172	175	0
6	98	97	180
7	48	49	0

** K= 9 L= 6 **

H	/FO/	/FC/	PHI
-6	45	53	180
-3	69	70	180
-2	49	69	180
-1	86	70	0
0	44	29	180
1	102	88	180
2	129	121	0
4	100	87	180

** K= 10 L= 6 **

H	/FO/	/FC/	PHI
-2	34	31	0

** K= 11 L= 6 **

H	/FO/	/FC/	PHI
3	44	37	0
4	40	20	180

** K= 12 L= 6 **

H	/FO/	/FC/	PHI
-1	57	53	180
1	56	53	0

** K= 0 L= 7 **

H	/FO/	/FC/	PHI
-7	65	45	180
-5	87	91	0

H	/FO/	/FC/	PHI
-3	177	181	0
-1	107	103	180
1	55	32	0
3	235	257	0
5	220	255	180
7	159	161	0

** K= 1 L= 7 **

H	/FO/	/FC/	PHI
-8	33	20	180
-7	41	43	0
-5	52	45	180
-4	65	53	0
-3	66	69	0
-2	77	101	0
-1	162	153	180
0	430	449	180
1	58	54	0
2	154	175	0
3	34	58	0
4	33	44	180
5	146	125	0
7	68	90	180
8	61	73	180

** K= 2 L= 7 **

H	/FO/	/FC/	PHI
-3	85	81	0
-2	280	285	0
-1	167	185	180
0	69	85	180
2	392	374	180
3	137	138	0
4	360	340	0
5	94	96	180
6	179	172	180
7	54	52	0
8	75	99	0

** K= 3 L= 7 **

H	/FO/	/FC/	PHI
-8	44	40	0
-6	51	41	180
-4	52	86	0
-3	64	47	180
-2	189	227	0
-1	72	41	0
0	124	105	0
1	150	172	0
2	292	334	0
3	349	357	180
4	109	84	180
5	160	159	0
6	62	50	0
7	92	101	180
9	34	55	0

** K= 4 L= 7 **

H	/FO/	/FC/	PHI
-6	81	73	0
-5	38	23	0
-3	175	176	180
-1	195	170	0
0	73	93	0
1	48	17	0
2	31	36	0
3	228	188	0
5	216	210	180
6	118	128	0

** K= 5 L= 7 **

H	/FO/	/FC/	PHI
-3	74	56	0

H	/FO/	/FC/	PHI
-2	34	28	0
0	38	46	180
1	118	135	0
2	45	49	0
3	146	151	180
4	55	78	0
6	60	55	180

** K= 6 L= 7 **

H	/FO/	/FC/	PHI
-4	107	106	180
-2	44	30	180
1	58	52	180
2	31	33	180
4	67	43	180
6	94	100	180

** K= 7 L= 7 **

H	/FO/	/FC/	PHI
-3	56	53	180
0	224	228	180
1	46	62	0
3	141	137	180
5	190	180	0
7	98	108	180

** K= 8 L= 7 **

H	/FO/	/FC/	PHI
-6	41	45	180
-4	64	59	0
-3	87	101	180
-2	116	122	180
-1	198	196	0
0	83	59	0
1	287	297	180
2	38	40	0
3	185	178	0
4	83	90	180
5	81	78	180
6	40	53	0
7	48	46	0

** K= 9 L= 7 **

H	/FO/	/FC/	PHI
-3	105	102	0
-1	171	169	180
0	83	84	0
1	128	120	0
2	72	79	180
4	46	32	0

** K= 10 L= 7 **

H	/FO/	/FC/	PHI
-3	34	16	180
-1	48	26	0

** K= 11 L= 7 **

H	/FO/	/FC/	PHI
1	32	25	0
2	39	38	0
4	27	17	180

** K= 12 L= 7 **

H	/FO/	/FC/	PHI
-1	31	24	0
1	34	25	180

** K= 0 L= 8 **

H	/FO/	/FC/	PHI
-8	38	30	0
-6	60	60	180
-4	95	104	0
-2	69	76	180

H	/FO/	/FC/	PHI
0	310	241	180
2	415	386	0
6	160	132	180

** K= 1 L= 8 **

H	/FO/	/FC/	PHI
-5	90	88	180
-4	83	84	0
-3	122	111	0
-2	65	66	180
0	122	141	0
1	57	31	0
2	39	55	180
3	37	40	180
4	78	66	180
6	133	134	0

** K= 2 L= 8 **

H	/FO/	/FC/	PHI
-3	134	130	180
-2	203	201	0
-1	627	656	0
1	653	681	180
2	288	265	0
3	155	165	0
4	118	137	180
5	80	61	180
8	56	56	0

** K= 3 L= 8 **

H	/FO/	/FC/	PHI
-7	57	65	0
-6	53	63	0
-5	121	136	180
-4	88	91	180
-3	287	310	0
-1	500	509	180
0	297	290	0
1	291	254	0
2	349	331	180
3	110	106	180
4	313	289	0
5	59	70	0
6	84	98	180
7	59	50	180

** K= 4 L= 8 **

H	/FO/	/FC/	PHI
-5	58	57	0
-4	46	53	0
-3	107	112	180
-2	35	45	180
-1	132	128	0
0	201	234	180
1	98	81	0
2	70	81	0
3	153	173	180
4	89	82	180

** K= 5 L= 8 **

H	/FO/	/FC/	PHI
-4	104	97	180
-2	89	80	180
0	47	57	0
1	196	171	180
2	31	39	180
3	170	142	0
4	169	168	180

** K= 6 L= 8 **

H	/FO/	/FC/	PHI
-5	50	48	0
-3	76	81	180

H	/FO/	/FC/	PHI
-1	82	85	180
0	131	103	180
1	46	68	180
2	39	12	0
3	252	264	0
5	89	96	180
6	38	46	180

** K= 7 L= 8 **

H	/FO/	/FC/	PHI
-5	118	111	180
-3	153	116	0
-2	37	54	180
-1	99	104	180
0	147	140	0
1	127	143	0
2	209	219	180
3	95	92	180
4	172	180	0

** K= 8 L= 8 **

H	/FO/	/FC/	PHI
-6	28	46	0
-5	82	83	0
-4	113	116	180
-3	90	74	180
-2	195	198	0
-1	55	38	0
0	68	81	180
1	62	73	0
2	72	54	0
3	119	116	180
5	81	66	0
7	33	7	0

** K= 9 L= 8 **

H	/FO/	/FC/	PHI
-6	32	44	180
-4	80	90	0
-2	46	37	180
-1	102	91	0
1	57	64	180
3	42	43	0

** K= 11 L= 8 **

H	/FO/	/FC/	PHI
-1	45	37	180

** K= 0 L= 9 **

H	/FO/	/FC/	PHI
-3	114	94	0
1	118	108	180
5	47	39	0

** K= 1 L= 9 **

H	/FO/	/FC/	PHI
-7	58	54	180
-4	98	95	0
-3	125	139	0
-1	210	203	180
0	62	35	180
1	187	178	0
3	177	182	180
6	50	33	0

** K= 2 L= 9 **

H	/FO/	/FC/	PHI
-4	124	138	180
-2	64	62	0
-1	148	146	180
1	60	86	180
2	171	150	0
3	208	225	0

H	/FO/	/FC/	PHI
4	126	135	180
5	144	151	180
6	71	70	180

** K= 3 L= 9 **

H	/FO/	/FC/	PHI
-6	55	61	180
-5	56	57	0
-3	289	313	180
-2	101	113	0
-1	473	473	0
0	369	391	180
1	200	203	180
3	99	96	180
4	74	83	180
5	47	92	0

** K= 4 L= 9 **

H	/FO/	/FC/	PHI
-5	141	131	180
-3	172	183	0
-2	263	234	180
-1	197	208	180
0	242	224	0
1	209	209	0
2	233	220	180
3	77	96	180

** K= 5 L= 9 **

H	/FO/	/FC/	PHI
-5	65	68	0
-4	72	78	180
-3	75	66	180
-2	101	96	0
-1	138	145	180
0	123	121	180
1	148	147	0
2	129	128	0
3	68	57	0
4	72	72	180

** K= 6 L= 9 **

H	/FO/	/FC/	PHI
-4	94	90	0
-2	73	67	0
-1	90	85	0
0	106	116	180
1	104	85	180
2	61	78	0
3	67	53	0
4	87	72	0
5	78	76	180
7	64	67	0

** K= 7 L= 9 **

H	/FO/	/FC/	PHI
-3	57	53	180
-2	82	80	0
-1	192	211	0
0	46	59	180
1	206	217	180
2	75	72	0
4	93	109	0
5	49	36	0
6	78	87	180
7	53	46	180

** K= 8 L= 9 **

H	/FO/	/FC/	PHI
-5	69	73	180
-4	59	69	0
-3	101	97	0
-2	171	174	180

H	/FO/	/FC/	PHI
-1	113	109	180
0	210	206	0
1	43	53	0
2	57	64	180
4	62	53	180
5	43	61	0
6	57	63	0

** K= 9 L= 9 **

H	/FO/	/FC/	PHI
-5	30	24	0
-4	93	97	180
-2	83	95	0
0	57	60	180
5	31	30	180

** K= 10 L= 9 **

H	/FO/	/FC/	PHI
-3	48	43	180
-2	33	37	180
0	46	50	0
2	51	45	180
3	45	30	0

** K= 0 L= 10 **

H	/FO/	/FC/	PHI
-8	60	67	180
-6	91	93	0
-4	42	22	180
-2	109	80	0
0	287	276	180
2	231	228	0
4	153	166	180
6	81	80	0

** K= 1 L= 10 **

H	/FO/	/FC/	PHI
-7	33	22	180
-6	91	109	180
-4	111	130	0
-2	244	280	180
-1	79	79	180
0	426	426	0
1	124	117	0
2	406	396	180
3	176	162	180
4	79	97	0

** K= 2 L= 10 **

H	/FO/	/FC/	PHI
-5	105	109	180
-4	60	60	180
-3	169	165	0
-2	180	168	0
-1	200	204	180
0	406	402	180
2	90	97	0
3	131	130	0
4	115	113	180
5	62	81	180
6	55	59	0

** K= 3 L= 10 **

H	/FO/	/FC/	PHI
-6	54	64	0
-4	62	59	180
-2	115	116	180
-1	196	202	0
0	78	90	0
2	63	79	180
4	106	97	0
6	58	57	180
7	60	58	0

** K= 4 L= 10 **

H	/FO/	/FC/	PHI
-3	34	42	0
-5	110	115	0
-3	164	165	180
1	204	188	0
2	234	247	0
4	49	56	180
6	41	44	180

** K= 5 L= 10 **

H	/FO/	/FC/	PHI
-7	33	39	0
-4	164	155	0
-3	86	101	0
-2	81	72	180
-1	68	57	180
0	157	156	0
1	62	54	180
2	70	53	180
3	96	114	0
4	90	88	0

** K= 6 L= 10 **

H	/FO/	/FC/	PHI
-5	66	69	180
-4	52	41	180
-3	147	169	0
-2	126	122	0
-1	150	168	180
0	161	147	180
1	128	139	0
2	255	269	0
3	146	154	180
4	114	113	180

** K= 7 L= 10 **

H	/FO/	/FC/	PHI
-4	110	117	180
-3	84	78	180
-2	60	49	0
-1	115	108	0
0	91	93	0
1	208	205	180
2	211	190	180
3	171	174	0
4	116	130	0
5	53	58	180
6	67	69	180
7	35	35	180

** K= 8 L= 10 **

H	/FO/	/FC/	PHI
-6	53	46	180
-5	55	60	0
-2	45	45	0
0	89	69	180
1	62	60	0
2	41	52	180
3	78	73	180

** K= 9 L= 10 **

H	/FO/	/FC/	PHI
-5	55	60	180
-2	36	49	180
3	43	56	180

** K= 10 L= 10 **

H	/FO/	/FC/	PHI
0	34	47	180

** K= 11 L= 10 **

```
 H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI

 1   38    24  180         4  208  207    0          5   46    35    0          1  128  128  180
                           5   52    73  180                                    3  133  128    0
** K= 0  L= 11 **          6   53    50  180      ** K= 2  L= 12 **             4   35    32  180

-7   37    27  180     ** K= 6  L= 11 **         -8   44    51    0        ** K= 8  L= 12 **
-5   43    55  180                               -6   79    89  180
-3  129  125    0        -6   73    89  180      -4  135  140    0         -5   34    38    0
-1   82    62  180       -5   82    95  180      -3  118  115    0         -4   33    39  180
 3  103  110  180        -4   53    57    0      -2  149  154  180         -3   49    54  180
                         -3  137  112    0       -1   82    79  180          0   68    59    0
** K= 1  L= 11 **        -2   47    55  180        0  162  146    0          1   45    51    0
                         -1  182  181  180         1   88    94    0
-6   64    68  180         0  198  186  180         5   67    67  180     ** K= 9  L= 12 **
-5   96  107    0          1   93    86    0         7   45    59    0
-4   82    75    0          2  253  273    0                              -4   29    29    0
-3  193  205  180          4  169  173  180     ** K= 3  L= 12 **
-2  117  101  180          5   54    42  180                              ** K= 10  L= 12 **
-1  127  140    0          6   38    40    0      -6   81    82    0
 0  194  167    0                                -5   66    53    0          0   54    44    0
 1   65    49  180     ** K= 7  L= 11 **         -4  129  130  180
 2  142  131  180                                -3   93    83  180      ** K= 11  L= 12 **
 5   60    49    0       -4   41    50  180      -2  103  109    0
                         -3   64    53  180      -1   42    43  180          0   35    26  180
** K= 2  L= 11 **        -2   91    79    0        0   81    67  180          2   35    20    0
                         -1  104   93    0         1   52    51  180
-5   35    37  180         0   97    98  180                              ** K= 0  L= 13 **
-4   42    20  180         1  104   93  180     ** K= 4  L= 12 **
-3  100  116    0          2  122  103  180                              -7   31    78    0
-2   68    48    0          3  110   85    0     -7   43    43    0       -5   71    71  180
-1   62    58  180          4  113  110    0     -5   53    60  180       -3   49    35    0
 0   76    67  180          6   58    68  180     -4   69    90    0        1   81    55    0
 1  210  231    0                                 0  122  111  180
 2  233  228    0      ** K= 8  L= 11 **          1   99    97    0      ** K= 1  L= 13 **
 3   54    44  180                                3  118  101  180
 4  146  137  180        -1   37    46    0        5   74    75  180      -7   34    55  180
 7   55    53    0         0   62    69    0                              -6   42    42    0
                          4   48    39  180     ** K= 5  L= 12 **         -5   79    91    0
** K= 3  L= 11 **                                                        -3  133  150  180
                      ** K= 9  L= 11 **          -7   34    46  180       -1  210  217    0
-7   54    67    0                               -6   45    46    0        2   73    51  180
-5   80    75  180       -2   51    52  180      -5   56    50    0        3   76    74  180
-2   63    75  180        0   85    84    0      -4   76    81  180        4   35    26  180
-1  224  258    0         4   33    22    0      -3  102  110  180        6   82    79    0
 0  269  280    0                               -2   45    23  180        8   53    72  180
 1  192  169  180      ** K= 10  L= 11 **        -1  126  130    0
 2   55    50    0                                0   49    50  180     ** K= 2  L= 13 **
 3   84    75    0       -2   43    33    0        1   53    64  180
 6   53    55  180        0   39    30  180        2  122  124    0      -5   35    53  180
                         3   35    35  180        3   88    75  180      -3  107  113    0
** K= 4  L= 11 **                                 4   60    75  180      -2   42    40  180
                      ** K= 11  L= 11 **          5   62    45    0      -1  167  182  180
-5   61    61    0                                6   38    39  180        1   83    97  180
-4   38    22    0       -2   26    21    0                               2   67    67    0
-2  101  109    0        3   52    39    0     ** K= 6  L= 12 **          6   86  101  180
-1  219  212  180
 0   88    87  180     ** K= 0  L= 12 **         -7   25    16  180     ** K= 3  L= 13 **
 1   90    86    0                               -6   66    74  180
 2  101  100    0       -4   49    49  180      -4  120  120    0       -3   58    53  180
 3   44    39    0       -2   92    83    0     -3  147  154    0       -2   78    93  180
 4  120  129  180        4   36    34    0     -2  129  114  180         0   54    41    0
 6  122  133    0        6   46    55    0     -1  168  174  180         2   79    48  180
                         8   55    62  180       0   51    41    0       3   53    64  180
** K= 5  L= 11 **                                1   71    70    0       6   63    69    0
                      ** K= 1  L= 12 **          2   62    56  180
-7   36    58  180                               5  106   98    0     ** K= 4  L= 13 **
-5   58    58    0       -8   47    46  180
-4   45    42    0       -6   56    48    0     ** K= 7  L= 12 **        -3   44    35    0
-3   97    89  180       -5   36    38    0                             -2   98  101  180
-2   68    57  180       -3   66    68  180      -5   49    52  180       0   93    82    0
-1   71    66    0       -2   75    81    0     -4   57    64  180        1   48    46  180
 0  142  126    0        0   84    95    0     -2  177  161    0         2   51    56  180
 1   63    80  180        1  183  161    0     -1  116   95    0         3   97    70    0
 2  256  259  180        2  113  120  180       0  131  124  180         4   39    40    0
```

H	/FO/	/FC/	PHI
**K= 5 L= 13 **			
-5	68	78	0
-4	78	64	180
-2	78	77	0
-1	55	62	180
0	100	90	180
2	102	90	0
3	128	133	0
4	86	89	180
5	47	45	0
**K= 6 L= 13 **			
-4	126	127	0
-3	44	47	0
-2	77	79	180
-1	66	66	180
0	104	110	0
1	169	155	0
2	141	127	180
3	69	51	180
4	51	41	0
5	47	36	180
7	33	44	0
**K= 7 L= 13 **			
-5	73	74	180
-4	54	51	180
-2	118	121	0
0	77	85	180
2	45	57	0
**K= 8 L= 13 **			
-5	25	18	0
-3	34	31	180
0	41	32	0
4	52	41	0
**K= 9 L= 13 **			
-4	34	32	180
-3	28	22	0
-2	36	30	0
2	39	26	0
**K= 10 L= 13 **			
-3	26	21	180
**K= 0 L= 14 **			
-2	127	144	0
0	266	245	180
4	73	74	0
8	67	67	180
**K= 1 L= 14 **			
-2	132	140	180
0	148	161	0
2	54	58	180
3	51	44	180
6	55	62	180
8	38	42	0
**K= 2 L= 14 **			
-3	58	62	180
-2	100	90	0
-1	40	22	180

H	/FO/	/FC/	PHI
4	58	61	180
6	64	55	0
7	55	50	180
**K= 3 L= 14 **			
-4	38	24	0
1	112	137	0
4	58	81	0
**K= 4 L= 14 **			
1	69	84	0
2	50	61	0
6	41	26	180
**K= 5 L= 14 **			
-2	50	36	0
-1	121	120	0
1	117	99	180
2	67	71	180
6	32	27	180
**K= 6 L= 14 **			
-4	58	59	0
-2	59	47	180
2	134	129	0
3	100	103	180
4	50	68	180
7	43	41	180
**K= 7 L= 14 **			
-3	34	43	0
-1	40	49	180
1	64	61	180
3	68	77	0
5	38	41	180
**K= 8 L= 14 **			
0	50	34	0
6	46	37	0
**K= 9 L= 14 **			
3	51	31	0
5	34	26	180
**K= 10 L= 14 **			
-2	43	46	180
2	49	37	180
**K= 0 L= 15 **			
-5	45	33	180
-3	74	77	180
-1	220	191	0
1	117	99	180
3	74	70	180
5	131	124	0
7	126	148	180
**K= 1 L= 15 **			
-1	109	116	180
0	96	117	0
1	36	45	0
2	45	44	180
3	110	91	0

H	/FO/	/FC/	PHI
5	104	103	180
6	86	98	0
7	62	67	0
8	53	70	180
**K= 2 L= 15 **			
-5	42	46	0
-4	61	31	0
-3	41	42	180
-1	60	69	0
0	40	35	180
4	100	88	0
**K= 3 L= 15 **			
-5	43	40	180
-3	53	49	0
1	66	59	0
3	110	107	180
4	48	45	0
5	42	53	0
6	64	60	180
**K= 4 L= 15 **			
-5	38	30	0
1	144	136	180
3	100	94	0
4	76	73	180
7	45	41	180
**K= 5 L= 15 **			
-6	31	36	0
-4	60	55	180
0	62	57	0
4	54	57	180
5	41	41	180
6	59	73	0
**K= 6 L= 15 **			
-1	56	60	180
0	71	80	0
1	48	62	0
2	60	67	180
4	75	92	0
**K= 7 L= 15 **			
-2	91	90	0
0	87	96	180
**K= 8 L= 15 **			
1	45	37	0
3	39	30	180
**K= 9 L= 15 **			
0	48	36	180
**K= 10 L= 15 **			
0	31	31	180
2	39	29	0
**K= 0 L= 16 **			
-4	44	29	0
-2	109	93	180
0	218	199	0

H	/FO/	/FC/	PHI
2	131	145	180
4	258	255	0
6	162	162	180
8	44	66	0
**K= 1 L= 16 **			
-5	63	65	0
-3	98	87	180
-2	106	113	0
0	140	140	180
1	79	106	0
2	186	173	0
3	115	109	180
4	100	95	180
5	172	179	0
7	121	135	180
**K= 2 L= 16 **			
-5	43	42	180
-3	60	56	0
-1	79	80	0
1	165	158	180
3	128	139	0
4	38	52	180
5	106	104	180
6	65	61	0
7	43	52	0
8	55	63	180
**K= 3 L= 16 **			
-1	61	54	180
2	59	47	180
3	51	55	180
5	71	53	0
**K= 4 L= 16 **			
-2	46	52	0
2	138	130	180
3	83	69	0
4	94	104	0
5	85	75	180
**K= 5 L= 16 **			
1	48	50	0
2	63	67	0
3	117	123	180
5	72	69	0
**K= 6 L= 16 **			
-4	42	48	0
-2	36	31	180
-1	84	86	0
0	40	43	180
1	93	100	180
2	56	59	0
3	69	60	0
4	45	52	180
5	36	21	180
6	39	46	0
**K= 7 L= 16 **			
-3	50	58	0
-2	41	41	180
0	75	75	0
1	56	55	0
2	62	68	180

```
  H  /FO/ /FC/ PHI

  3   55   43 180
  6   29   28 180

** K=  8  L= 16 **
  3   53   49   0
  4   44   50 180

** K=  9  L= 16 **
  2   37   33 180

** K=  0  L= 17 **
  1  110   96 180
  3  156  153   0
  7   98  102 180

** K=  1  L= 17 **
 -4   80   78   0
 -2  108  115 180
  0  137  140   0
  2  311  310 180
  3   70   68   0
  4  170  158   0
  5  118  120 180
  7   74   80   0

** K=  2  L= 17 **
 -4  114  107 180
 -2  117  129   0
 -1   60   63 180
  0  209  203 180
  1  131  120   0
  2  121  109   0
  3  211  208 180
  5  150  159   0
  6   53   64 180

** K=  3  L= 17 **
 -4   37   46   0
 -3   63   65 180
 -2   47   55 180
 -1   63   51   0
  1   62   70 180
  3   78   85   0
  4   65   66 180
  5   72   71 180
  6   58   57   0
  7   54   41   0

** K=  4  L= 17 **
 -2   49   42   0
  0   61   61 180
  2   60   62   0
  6   39   38 180

** K=  5  L= 17 **
 -2   72   73 180
  0  149  150   0
  1   48   43 180
  2  121  121 180
  4   44   58   0
  5   37   45   0

** K=  6  L= 17 **
 -4   36   42 180

  H  /FO/ /FC/ PHI

 -2   75   73   0
  0   69   66 180
  1   80   66   0
  3   37   27 180
  4   36   31 180

** K=  7  L= 17 **
 -3   47   60 180
 -1   38   45   0
  3   45   48   0

** K=  8  L= 17 **
 -1   34   41 180
  0   34   30 180
  1   45   39   0
  3   42   34 180
  5   42   33   0

** K=  9  L= 17 **
 -1   23   16   0

** K=  0  L= 18 **
 -6   28   39   0
 -4   82   92 180
 -2  168  177   0
  0  191  200 180
  2   82   87 180
  4  109  121   0

** K=  1  L= 18 **
 -6   38   38 180
 -4   43   38   0
 -3  104  110 180
 -2   69   59 180
 -1  214  196   0
  0   79   76 180
  1  158  140 180
  2  195  192   0
  4  143  141 180
  5   45   48   0

** K=  2  L= 18 **
 -5   56   65 180
 -3   96   90   0
 -2  127  126 180
 -1   54   69 180
  0  221  228   0
  1   60   50 180
  2  148  140 180
  3   78   69   0
  4   78   77   0

** K=  3  L= 18 **
 -6   26   15   0
 -2   72   61   0
 -1   63   61 180
  1   91   97   0
  3   55   59 180
  4   43   32 180
  6   70   79   0

** K=  4  L= 18 **
 -4   37   44 180
 -2   75   80   0
  0   59   68 180

  H  /FO/ /FC/ PHI

  1   68   65 180
  3  109  105   0
  5   60   59 180

** K=  5  L= 18 **
 -5   44   45   0
 -3   62   67 180
 -1   41   44   0
  3   56   66 180

** K=  6  L= 18 **
 -3   33   29   0
 -2   52   62 180
  0   64   61   0
  2   46   47 180

** K=  7  L= 18 **
 -2   38   37   0
  2   32   31   0

** K=  8  L= 18 **
 -2   38   35 180
  0   47   51   0

** K=  9  L= 18 **
  0   36   20 180
  1   25   18 180
  2   31   33   0

** K=  0  L= 19 **
 -5   50   55 180
 -1   96  111   0
  1   82   98 180
  3  123  110   0
  5   51   64 180

** K=  1  L= 19 **
 -4   98  106 180
 -3  109  111   0
 -2   60   62   0
 -1  218  206 180
  0   46   53   0
  1  157  146   0
  3   44   42 180

** K=  2  L= 19 **
 -5   86   93   0
 -3  156  155 180
 -2   98  106   0
 -1  183  198   0
  0  107  117 180
  1  154  161 180
  3   58   67   0

** K=  3  L= 19 **
 -5   48   42 180
 -4   79   80 180
 -2  110  112 180
 -1   60   73 180
  0   74   73   0
  1  158  171   0
  3  146  141 180

** K=  4  L= 19 **

  H  /FO/ /FC/ PHI

 -5   50   35 180
 -4   49   52 180
 -2   52   53   0
  0   90   37 180
  1   96   94 180
  2   53   41   0
  3   37   40   0

** K=  5  L= 19 **
  5   39   26   0

** K=  6  L= 19 **
 -4   30   28 180

** K=  7  L= 19 **
  1   40   30 180

** K=  0  L= 20 **
  4  103  104   0
  6   54   62 180

** K=  1  L= 20 **
 -5   26   20 180
 -4   70   76   0
  0   55   49 180
  1   83   82 180
  2   95  101   0
  4   79   83 180
  6   47   55   0

** K=  2  L= 20 **
 -5   47   60 180
 -4   75   76 180
 -3   48   48   0
  0   86   73   0
  2  102  107 180
  4   57   55   0

** K=  3  L= 20 **
 -5   53   64   0
 -4   29   25   0
 -3   37   47 180
 -2   51   58 180
  2   46   41   0
  4   43   31 180

** K=  4  L= 20 **
 -3   44   41   0
 -1   53   57 180
  3   52   50   0

** K=  5  L= 20 **
 -4   23   19 180

** K=  6  L= 20 **
  3   35    9   0

** K=  0  L= 21 **
  1  110   96 180
  5   50   62   0

** K=  1  L= 21 **
```

H	/FO/	/FC/	PHI		H	/FO/	/FC/	PHI		H	/FO/	/FC/	PHI		H	/FO/	/FC/	PHI

H	/FO/	/FC/	PHI
-4	47	52	180
-3	47	51	0
-2	87	88	0
-1	70	68	180
1	50	37	0
2	51	55	180

** K= 2 L= 21 **

-3	54	55	180
-1	54	58	0
5	37	26	0

** K= 6 L= 21 **

3	31	13	0

** K= 0 L= 22 **

-2	46	40	0
2	55	60	180
6	46	51	0

** K= 1 L= 22 **

-1	52	55	0

** K= 2 L= 22 **

-4	32	43	180
-3	45	44	0
4	29	27	180

** K= 3 L= 22 **

-2	35	39	180
0	56	63	0
2	46	51	180
3	46	36	180

** K= 4 L= 22 **

2	58	56	0
3	37	30	0

** K= 5 L= 22 **

1	30	20	0
2	28	28	180
4	29	31	0

** K= 2 L= 23 **

-2	31	36	0
2	47	43	180

** K= 3 L= 23 **

-2	42	36	180
0	42	29	0
3	37	30	0
4	30	38	180
5	29	33	180

** K= 4 L= 23 **

-2	35	26	0
-1	45	38	180
0	32	31	180

** K= 5 L= 23 **

-1	26	30	0

** K= 0 L= 24 **

0	37	38	0
2	94	100	180
4	84	88	0

** K= 1 L= 24 **

4	46	45	180

** K= 2 L= 24 **

-1	43	34	0
0	36	38	0

** K= 3 L= 24 **

-1	39	45	180
1	47	44	0

** K= 4 L= 24 **

-1	34	36	0
1	45	33	180

** K= 0 L= 25 **

-1	51	50	0
1	61	56	180

** K= 1 L= 25 **

0	44	42	0

1.4.   Structure Factors for I(d)

```
H /FO/ /FC/ PHI        H /FO/ /FC/ PHI        H /FO/ /FC/ PHI        H /FO/ /FC/ PHI

** K= 0  L= 0 **      -13  628  625    0     ** K= 5  L= 1 **       -2 1961 1754    0
                      -11  622  631    0                             0 2661 2392  180
   2  212  229  181    -9  641  692  180     -11  656  711    0      2 5410 4642  180
   4 2721 2943  180     -7  224  255  181     -9  340  330  181      4 1941 1801    0
   8 1494 1521  180     -5  576  535    0     -7  424  439    0      8  294  324  180
  10 1113 1194  180     -3  709  695    0      1  279  249  181     12  219  244  181
  12  530  557    0     -1  518  480    0     21  259  276  181     20  294  329  360
  14 1961 1877    0      1  708  618  180                           24  274  227  180
  16  549  501  181      3 1392 1332    0     ** K= 6  L= 1 **      26  248  277  180
  18  238  171  180      5  480  510  360
  20  254  259    1      7  305  309  180     10  347  394    0     ** K= 3  L= 2 **
  24  250  273  180      9 1079 1092    0     18  315  336  180
                        13 1424 1562  180     20  356  421  180    -23  336  346  180
** K= 1  L= 0 **        15  306  313  180                          -19  201  235    0
                        17  600  558    0     ** K= 0  L= 2 **     -13  556  528    0
   1 1466 1291    0     23  495  498  180                           -9  453  408  180
   3  611  627    0                           -30  315  312    1    -7  168  152  180
   7 1183 1184  180    ** K= 2  L= 1 **       -28  311  286    0    -3  599  548  180
   9 1434 1519    0                           -22  221  191    1    -1 1287 1238    0
  11  621  609  180    -24  297  275  180     -20  201  231    0     1 1429 1349  180
  13  470  430    0    -22  231  250    0     -16  555  536    1     3  537  479    0
  17  829  865    0    -16  477  472    0     -14 2037 2011  180     7  279  279  180
  19  382  416  180    -14  239  214    0     -12  733  791  180     9  611  630    0
  21  422  363  180    -12  201  275  181     -10 3042 3072    0    11  624  626    0
  23  446  443    0    -10  450  475  180      -8 1538 1652    0    15  731  744  180
                       -6 1254 1238  180      -6  635  671    0    19  281  300  180
** K= 2  L= 0 **       -4  695  556  180       -4  809  857    0    21  513  500    0
                       -2 2649 2416  180       -2 3273 3577    0    25  259  231  180
   0 1483 1317    0      0 2756 2574    0       0  963 1096    0
   2 1744 1547  180      2 5656 4700    0       2  649  647  180    ** K= 4  L= 2 **
   4 1341 1218  180      4 1191 1095    0       4 2055 2315  180
   6  432  430    0      6  554  494  180       6 1337 1529  360   -16  254  267  180
   8  465  488  180     10  727  689  180       8 1265 1303  180   -12  590  594  180
  10  955  881  180     16 1062 1092    0      10 1422 1532    0   -10  597  555    0
  12  498  475  180     20  279  297    0      12  301  312  181    -8  255  145    1
  14 1308 1261    0     24  286  298  180      16  781  828  180    -6  435  385    0
  20  259  215  180                            18  581  595  180     2  456  399  180
  28  216  184  180    ** K= 3  L= 1 **        26  250  234  181     4 2477 2255    0
  30  266  216  180                                                  6  252  234  180
                      -19  640  615  180      ** K= 1  L= 2 **      12  597  591    0
** K= 3  L= 0 **      -15  205  132  181                           14  425  370  180
                      -13  613  599  180      -29  362  370    1    22  434  461    0
   1  270  334    0    -11  204  196  180     -23  516  474    1
   3  273  197  180     -9  434  455    0     -19  544  561    0    ** K= 5  L= 2 **
   5 1361 1310  180     -7  332  339    0     -17  761  807    0
   7  223  213    0     -5  573  582  180     -15  463  441  180   -25  205  249    0
  11  271  241  360     -3  243  259  180     -13  550  533  180   -23  215  216    0
  13  355  372    0     -1  613  685  180      -9  335  292    0   -21  336  357  180
  17  403  438  180      3 1522 1419    0      -7 1114 1219    0   -17  227  279  180
  19  286  312  180      7  486  455  360      -5  357  413  180   -11  316  284  180
  25  342  319  180      9  502  423    0      -3 2125 2216    0    -5  464  442    0
  27  301  317    1     11  233  251    0      -1 1731 1763  180     1  983  987  180
                       13  463  493    0       1  746  714  180     3  450  408    0
** K= 4  L= 0 **       17  333  336    0       3  476  415  180     5  331  370    0
                       21  330  317    0       5  460  510  180     7  306  326    0
   0  450  482  180     29  236  220    0       7 1077 1100    0     9  353  317    1
   6  354  358  360                             9  486  499  180    15  280  264  180
  10  824  851    0    ** K= 4  L= 1 **        11  492  516  180    21  629  615    0
  12  346  304  180                            13  321  315  180    23  349  375    0
  18  696  701  180    -28  226  242  180      17  295  257  180
  22  481  487    0    -26  480  455  180      23  331  326  180    ** K= 6  L= 2 **
                      -19  213  249  180      29  247  250  181
** K= 5  L= 0 **      -14  466  446    0                           -20  248  302  180
                      -10  331  333    0     ** K= 2  L= 2 **      -8  286  274  180
   3  296  303  180     -2  296  258    0                          16  305  318  180
   9  578  580  180      2  294  285    0     -24  434  492    0    18  191  151  180
  25  232  208    0      4  631  564  180     -16 1161 1134    0
                        6  331  257  180     -14  495  500  180    ** K= 7  L= 2 **
** K= 1  L= 1 **        8  422  359  180     -12  460  496  180
                       14  332  326  181     -10  345  404    0   -15  207  181  180
 -21  243  304    0     16  373  346    0      -8  503  458  180
 -19  558  543  181     18  209  203    0      -6  469  469  180    ** K= 1  L= 3 **
 -17  934  939    0     24  302  358    0      -4  333  323  180
```

H	/FO/	/FC/	PHI
-23	230	235	0
-21	666	656	0
-17	232	210	0
-15	1370	1360	0
-9	447	510	0
-7	1113	1193	0
-5	623	641	180
-3	2882	3140	0
-1	1228	1162	0
1	2209	2165	180
3	840	887	180
5	322	272	0
7	356	321	360
9	960	881	0
11	373	374	0
13	1356	1342	180
15	1232	1248	180
17	405	424	0
25	289	354	181
27	345	393	0

** K= 2 L= 3 **

H	/FO/	/FC/	PHI
-26	519	533	0
-24	300	260	0
-22	320	325	180
-20	553	531	0
-16	438	412	0
-12	192	223	0
-10	288	256	180
-8	568	511	180
-6	1446	1439	0
-4	506	479	180
-2	290	275	180
0	2374	2194	0
2	2622	2487	0
4	1810	1601	180
6	279	232	180
8	903	927	0
12	832	824	180
14	649	596	0
18	326	329	181
24	502	483	180
26	382	359	180

** K= 3 L= 3 **

H	/FO/	/FC/	PHI
-29	257	285	0
-27	369	338	1
-25	504	461	180
-23	408	403	180
-21	287	271	0
-17	293	302	0
-15	275	290	0
-13	566	525	180
-11	1125	1114	180
-7	1397	1267	0
-5	527	494	180
-3	511	541	0
1	559	531	180
3	601	486	0
7	617	589	180
9	179	197	360
11	309	285	0

** K= 4 L= 3 **

H	/FO/	/FC/	PHI
-26	271	282	180
-18	325	261	0
-12	294	283	0
-8	235	262	181
-6	542	531	0
-2	365	332	360

H	/FO/	/FC/	PHI
0	1123	1073	0
2	1468	1239	180
4	1402	1267	180
10	320	329	180
14	402	395	0
20	694	719	0

** K= 5 L= 3 **

H	/FO/	/FC/	PHI
-13	378	394	0
3	246	194	181
7	525	497	1
15	232	233	180
21	402	405	0

** K= 6 L= 3 **

H	/FO/	/FC/	PHI
-12	413	428	180
6	724	794	0
8	336	313	0
18	320	339	180

** K= 0 L= 4 **

H	/FO/	/FC/	PHI
-32	277	249	1
-28	311	311	1
-24	574	581	180
-22	351	362	180
-14	1637	1706	180
-10	519	532	0
-6	1090	1187	0
-4	134	106	358
-2	1821	2263	0
0	2549	2854	180
2	303	339	180
4	652	642	0
6	1304	1299	180
8	1123	1227	0
10	871	887	180
12	1011	1031	0
14	711	684	180
28	465	501	0

** K= 1 L= 4 **

H	/FO/	/FC/	PHI
-27	431	409	180
-19	417	393	0
-17	652	669	180
-11	179	155	180
-9	469	503	180
-5	841	962	180
-3	1010	1046	180
-1	545	562	181
1	245	279	180
3	2372	2507	0
5	1567	1680	180
7	682	680	0
9	974	990	180
11	1042	1027	180
13	329	299	181

** K= 2 L= 4 **

H	/FO/	/FC/	PHI
-24	286	294	0
-20	421	375	0
-16	419	366	180
-12	931	913	0
-8	1087	1020	180
-6	441	465	0
-4	400	318	180
-2	1903	1944	180
0	3116	3018	180
2	920	832	0

H	/FO/	/FC/	PHI
8	746	724	0
10	402	357	181
12	190	203	181

** K= 3 L= 4 **

H	/FO/	/FC/	PHI
-23	228	220	180
-17	348	291	180
-15	379	388	0
-13	336	365	0
-7	783	724	0
-5	479	530	180
-3	373	382	180
1	1205	1083	0
5	567	553	0
7	396	399	180
9	570	583	180

** K= 4 L= 4 **

H	/FO/	/FC/	PHI
-28	225	268	181
-22	350	375	180
-18	385	373	1
-16	270	279	180
-14	317	336	180
-12	1039	975	0
-6	354	332	1
-4	291	254	0
-2	717	647	180
0	558	593	0
2	2279	2215	0
4	845	842	0
6	282	257	180
8	650	597	180
12	276	273	180
18	559	511	0
20	260	277	0
22	250	247	180

** K= 5 L= 4 **

H	/FO/	/FC/	PHI
-13	438	454	0
-11	595	587	180
-7	489	519	0
-3	422	404	0
3	516	454	0
5	353	315	0
7	282	242	180
19	568	632	0

** K= 6 L= 4 **

H	/FO/	/FC/	PHI
-10	399	446	180
0	504	491	0
2	464	524	0
4	432	425	180
6	478	513	180

** K= 1 L= 5 **

H	/FO/	/FC/	PHI
-29	283	286	0
-27	466	462	180
-23	526	556	0
-21	344	360	0
-19	519	499	0
-13	787	823	0
-11	212	235	180
-7	353	323	180
-5	686	762	180
-3	266	252	180
-1	2940	3160	0
1	189	208	0
3	512	478	180

H	/FO/	/FC/	PHI
5	1363	1408	180
7	535	524	180
9	281	265	360
11	213	208	180
13	616	602	180

** K= 2 L= 5 **

H	/FO/	/FC/	PHI
-26	541	517	0
-22	285	287	180
-20	218	220	1
-14	442	491	0
-12	700	709	180
-10	454	458	180
-8	260	280	0
-4	558	521	180
-2	1543	1512	0
0	548	574	360
2	2161	2104	180
6	843	817	180
8	515	546	180
10	428	405	0
12	763	697	0
26	262	270	191
28	312	355	0

** K= 3 L= 5 **

H	/FO/	/FC/	PHI
-25	212	164	180
-21	456	445	180
-17	243	201	0
-13	424	423	180
-11	536	525	180
-7	358	387	180
-5	460	453	0
-3	398	411	180
3	225	225	180
7	333	297	180
25	246	191	1

** K= 4 L= 5 **

H	/FO/	/FC/	PHI
-22	221	258	1
-14	279	245	180
-10	731	720	0
-8	720	694	0
-6	214	226	180
-2	669	679	0
0	1288	1110	180
2	2019	1836	180
6	320	268	0
8	520	502	180
10	422	398	0

** K= 5 L= 5 **

H	/FO/	/FC/	PHI
-11	274	339	0
-9	475	477	0
-1	375	433	180
1	609	548	0
3	231	211	0
21	245	240	0

** K= 6 L= 5 **

H	/FO/	/FC/	PHI
-14	330	317	180
-8	259	262	0
2	309	331	0
4	992	1034	0
6	269	321	0
16	408	401	180

H	/FO/	/FC/	PHI

Column 1

```
** K=  7  L=  5 **

-11  213   282  180
  1  313   328  180

** K=  0  L=  6 **

-24 1289  1300  180
-18  899   949  180
-14  879   873    0
-12 1319  1511  180
-10 1076  1092  180
 -8 2006  2092    0
 -6  241   208  181
 -2  991  1121    0
  0 2349  2581    0
  2 1552  1627  180
  4  623   625  180
  6 2131  2216    0
  8  342   414  181
 10  677   628    0
 12  955   854    1
 26  333   354    0
 30  264   258  181

** K=  1  L=  6 **

-29  485   519  180
-27  234   239  180
-25  507   515    0
-19  660   657  180
-15  385   394  180
-13  506   537  180
 -9  704   703    0
 -7  578   547  180
 -5  360   395  360
 -3  985  1047    0
 -1  198   165  180
  1  675   778  180
  3 1256  1321  180
  5  802   799    0
  7  386   385  181
  9 1803  1841    0
 11  369   345    1
 27  389   359  180

** K=  2  L=  6 **

-16  238   227  180
-14 1197  1182    0
-10 1571  1543  180
 -6 1577  1544  180
 -4  515   568    0
 -2  593   534  180
  0  820   771  180
  2  829   770    0
  4  652   655  180
  8  289   272    0

** K=  3  L=  6 **

-25  201   156  180
-17  593   540    0
-15  228   236    0
-11  262   258  180
 -7  338   327  180
 -5  172   176  180
 -1  587   599    0
  1  796   794    0
  3  711   668  180
  5  894   887  180

** K=  4  L=  6 **
```

Column 2

```
-14  247   217  181
-10  536   554    0
  0  525   490    0

** K=  5  L=  6 **

-13  295   305  180
 -7  350   310    0
  5  270   229  180
  9  273   262  180
 13  257   255  180
 15  239   253    0
 17  415   420    0
 19  205   185    0

** K=  6  L=  6 **

 -2  324   342    0
  4  826   881  180

** K=  1  L=  7 **

-27  379   381  181
-23  643   623    0
-19  214   202    0
-17  198   157  180
-15 1089  1077  180
-13  272   289  180
-11 1285  1274    0
 -9  201   171    0
 -5  386   394    0
 -3 1091  1254  180
  1 1160  1167    0
  3  626   623  180
  5  487   536    0
  7  527   461  180
  9 1077  1159    0
 11  307   345    0
 25  724   745    0

** K=  2  L=  7 **

-26  191   153    0
-24  205   215  180
-22  259   264  180
-20  243   306  180
-16  381   387  180
-12  271   332    0
-10  824   848  180
 -8  827   808  180
 -6  186   155    1
 -4  351   412  180
 -2  386   384  180
  0  693   718    0
  2  477   499    0
  4  267   295  180
  6  488   418    0
  8  935   888    0
 26  453   428    0

** K=  3  L=  7 **

-27  398   416  180
-25  292   275    0
-21  413   459  181
-19  209   202  180
-17  198   195  180
-15  419   397  180
 -7 1263  1200  180
 -3  303   351  180
 -1  455   395  180
  1  308   343    0
  3  575   513  180
```

Column 3

```
  5  317   240  180
 25  356   339    1

** K=  4  L=  7 **

-12  787   764    0
-10  253   232    0
 -8  313   328  180
 -6  612   574  180
  0 1372  1281  180
 24  183   118    0

** K=  5  L=  7 **

-25  234   204    0
-23  271   261  180
-13  318   276    0
 -3  309   341  180
  1  725   701    0
  3  349   324    0
  5  455   462  180
  7  356   338  180
 15  420   429    0

** K=  6  L=  7 **

-10  281   279    0
  2  681   732    0
  4  456   506    0
  6  281   310  181

** K=  0  L=  8 **

-32  296   251  180
-26  590   602  180
-18  340   350    1
-16  267   293    0
-12  615   691  180
-10 1015  1007    0
 -8  499   435    0
 -4 1680  1755    0
 -2  952   954  180
  0 1923  2074    0
  2 2019  2199    0
  4  894   946  180
  6  748   726    0
  8 1202  1165  180
 10  575   585  180
 12  521   534  180
 26  542   555  180

** K=  1  L=  8 **

-29  266   270  180
-25  510   488    0
-23  426   422  180
-13  926  1025    0
-11  724   758    0
 -9 1156  1212  180
 -7  502   506    0
 -5  520   506    0
 -3  377   397  180
 -1 1238  1370    0
  3  456   474  180
  5 1175  1159    0
 11  243   277  180
 25  671   683  180
 27  378   375  180
 29  289   330    0

** K=  2  L=  8 **

-24  362   355    0
```

Column 4

```
-22  301   312    0
-20  264   309  180
-16  359   329    0
-10  225    26    2
 -8  780   769  180
 -6  890   920  180
 -4  969   947    0
 -2  405   378  180
  0  364   373  180
  2  469   516    0
  6  728   689    0
  8  359   305    1
 24  599   626  180

** K=  3  L=  8 **

-27  344   328    0
-25  545   567  180
-21  247   231    0
-17  322   283    0
-15  297   282  180
-13  337   339  180
-11  376   306    0
 -9  354   356  180
 -5  344   352    0
 -3  323   368  180
 -1  238   227  181
  1  211   240  180
  3  274   279  180
 25  200   196  180

** K=  4  L=  8 **

-28  208   196    1
-24  362   398  180
-16  332   304  180
-14  250   281    0
-12  328   330  181
 -6  254   278  180
 -2  467   493  180
 22  336   356    1

** K=  5  L=  8 **

-21  205   156  181
 -9  263   295    0
 -7  760   782  180
 -5  301   317    0
 -1  348   312  180
 11  428   426  180
 15  477   422    0
 17  236   260    0
 21  220   210    1

** K=  6  L=  8 **

-10  283   356    0
  2 1151  1169  180
  6  294   305    0
 12  231   257    0
 14  359   335  180
 16  362   426  180

** K=  7  L=  8 **

 -3  279   294  180

** K=  1  L=  9 **

-27  335   286  180
-23  249   305    0
-21  275   285    0
-17  368   404    0
```

```
 H  /FO/  /FC/  PHI

-13  317   304  181
-11  371   390    0
 -9  921   947    0
 -7  228   279  180
 -5  681   670    0
 -3  637   614    0
 -1  226   233    0
  3  407   415    0
  5  545   519    0
  7  501   499    0

** K=  2   L=  9 **

-24  418   388  180
-14  310   230    0
-12  299   249  180
-10  943   911  180
 -8  150   222    0
 -6  556   528    0
 -4  695   646    0
 -2  182   235  180
  0  778   759    0
  2 1611  1607    0
  6  811   803    0

** K=  3   L=  9 **

-19  399   376  181
-17  285   298  180
-15  196   270    1
-13  406   376  180
 -5  246   311    0
 -1  363   318    0
  1  362   347  180

** K=  4   L=  9 **

-20  284   312    0
-14  254   251    0
-12  385   340    0
-10  436   396  180
 -4  421   441  180
 -2  236   244  180
  0  590   578  180

** K=  5   L=  9 **

-23  320   365  180
-19  293   299    0
-15  345   399    0
 -1  399   426    0
 13  433   442    0

** K=  6   L=  9 **

-14  282   333    1
 -2  261   283    1
  0  327   343    0
 14  344   382  181

** K=  0   L= 10 **

-26  528   502  180
-24  604   563    0
-18  278   240    0
-16  227   242  180
-14  753   734  180
-12 1167  1180  180
-10 1793  1769    0
 -8 1212  1203    0
 -6 1532  1632    0
 -4  429   470  180
 -2  935  1013  180
```

```
 H  /FO/  /FC/  PHI

  2 1513  1595  180
  4  197   153  180
  6  220   233  180
  8 1303  1288  180
 26  635   630    1
 28  290   284  181

** K=  1   L= 10 **

-23  336   326    0
-15  250   208  360
 -9  358   387  180
 -7  833   772    0
 -5  235   269  180
 -3 1191  1240  180
 -1  502   531    0
  1  639   552  180
  3 1069  1122    0
  5  147   139  181
  7  413   451  180
 23  748   719  180
 27  240   232    1

** K=  2   L= 10 **

-24  568   550    0
-22  369   340    0
-20  357   379    0
-16  308   283  180
-14  498   450    0
-12  510   482  180
-10  302   249    0
 -8  230   202  180
 -6  212   221    0
 -4  647   632  180
 -2  281   297    0
  0 1066  1044    0
 22  313   284  181
 24  360   381  180

** K=  3   L= 10 **

-25  510   507  180
-21  683   670    0
-13  264   227  180
-11  498   532  180
 -7  666   649    0
 -1 1089  1147    0
  1  749   723  180
 21  325   303  180

** K=  4   L= 10 **

-24  360   406  180
-22  359   305  181
-10  667   665  180
 -6  467   462    0
 -4  308   300    0
  0  277   260  180

** K=  5   L= 10 **

 -7  280   306    0
 -5  362   334  180
  3  321   302  180
 13  448   481    0
 17  234   220  180

** K=  6   L= 10 **

 10  340   311    0
 12  253   255  180
 14  317   326  180
```

```
 H  /FO/  /FC/  PHI

** K=  1   L= 11 **

-23  376   373    0
-11  637   632    0
 -7 1173  1280    0
 -5  451   440  180
  1  479   505  180
  3  302   292    1
  5  492   437    0
 23  226   229    0
 27  227   224  181

** K=  2   L= 11 **

-22  573   544    0
-18  362   363  180
-16  322   358    0
-12 1002   967  180
-10  295   244    1
 -8 1379  1329    0
 -6  298   305  360
 -4  478   468    0
 -2  415   370    0
  0  582   568  180
  2  448   466    0
 22  299   261    0

** K=  3   L= 11 **

 -9  510   470  180
 -7  183   201    0
 -5  471   444    0
 -1  331   342  180
  1  276   276  180

** K=  4   L= 11 **

-22  477   473    0
-18  246   218    1
-12  318   339  180
 -2  419   364  180
  0  331   350  180

** K=  5   L= 11 **

 -1  282   300    0
 11  322   349    0
 13  384   393    0
 19  306   288    0

** K=  6   L= 11 **

  0  338   324    0

** K=  0   L= 12 **

-28  199   242  180
-26  287   347    0
-24  331   326  180
-22  332   363  180
-20  834   847  180
-16  615   602    0
-14  213   222  180
-12  201   249  181
-10 1049  1033    0
 -6 1585  1571  180
 -2  149   137  360
  0  824   890  180
  2 1252  1237  180
  4  241   255  180

** K=  1   L= 12 **
```

```
 H  /FO/  /FC/  PHI

-21  310   341  180
-19  352   350  180
-17  535   558    0
-15  423   413  180
 -9  558   574    0
 -7  654   642  180
 -5  781   813  180
 -3  294   296    1
 -1  902  1016  180
  3  928   910    0

** K=  2   L= 12 **

-24  373   349    0
-16  341   298  180
-12  338   376    0
-10  186   137    1
 -8  379   371  360
 -6  493   458  180
 -4  467   519  180
 24  275   312    0

** K=  3   L= 12 **

-27  229   253  180
-23  384   354    0
-11  329   323    0
 -7  370   370    0
 -3  278   300    0
  1  194   149  180

** K=  4   L= 12 **

-24  257   247    1
 -6  435   421    0
 -2  266   235    0
  0  285   272  180
 16  326   331    0

** K=  5   L= 12 **

-17  200   189  180
 -9  293   287  180
 -1  253   234    1
  5  229   235  180

** K=  6   L= 12 **

 -2  296   296    0
  2  353   343    0

** K=  1   L= 13 **

 -3  884   702  180
 -1  341   315  360
 23  365   326    1

** K=  2   L= 13 **

-26  322   271    1
-20  250   277  180
-18  238   218  180
-14  232   273    1
-12  292   278  180
 -8  210   207    0
 -4  751   715  180
  0  947   915    0
 20  338   334    0

** K=  3   L= 13 **

-21  272   203  180
-11  401   397  180
```

```
H /FO/ /FC/ PHI

-5  380  405  180
-3  319  292    0
-1  231  148  180
 1  517  513  180

** K=  4  L= 13 **

-24  359  420    0
-12  319  351    0
 -2  413  403  180
 14  404  388    0
 18  297  318  181

** K=  5  L= 13 **

-21  224  252    0
 -7  254  283    0
  1  358  342    0
  5  217  219  181
 11  287  263    0
 13  266  265    1

** K=  6  L= 13 **

-10  216  227    1
 -4  243  258    0
 -2  338  342    0

** K=  0  L= 14 **

 20  491  473    0

** K=  1  L= 14 **

-23  703  665  180
-19  257  243    0
-11  319  283  181
 -9  316  289  180
 -7  250  291    0
 -3  768  798    0
 -1  252  300  180
  1  507  500    0

** K=  2  L= 14 **

-26  215  224    0
 22  279  261  180

** K=  4  L= 14 **

-16  294  245  180
-14  304  302    0
 -2  345  357  180
 14  260  259    0

** K=  5  L= 14 **

 -7  276  306  180
 -5  404  390    0
 -1  358  347  180
 13  434  413    0

** K=  6  L= 14 **

-10  283  316    0
 -8  290  299    0
  2  301  293  180

** K=  1  L= 15 **

-21  377  398  180
 -9  200  179  360
 -1  586  606  180
```

```
H /FO/ /FC/ PHI

  1  322  322    0

** K=  2  L= 15 **

 18  267  275    1
 20  297  324    0

** K=  3  L= 15 **

 15  213  188  181

** K=  4  L= 15 **

-12  291  267    0
 -8  674  703  180
  0  439  435  180

** K=  5  L= 15 **

-13  246  204  180
-11  294  291  181
 -3  215  188    1
 -1  333  304  180
  1  308  298  180
 11  271  279    0

** K=  6  L= 15 **

 -4  322  349    0

** K=  0  L= 16 **

-26  211  272  180
 18  881  645    0
 20  722  729  181

** K=  1  L= 16 **

-11  294  311    0
 -7  345  337  180
 -5  543  524    0
 -3  692  631  180
 -1  537  563    0
  1  271  270    0
 17  333  344  180

** K=  2  L= 16 **

 20  386  347  181

** K=  3  L= 16 **

-21  340  322    0
 13  412  407  180
 17  331  322    0

** K=  4  L= 16 **

 -2  769  744  180
 12  280  288  180

** K=  5  L= 16 **

-11  415  422  180
 -1  349  358  180
  5  336  336    0
 11  216  219    0

** K=  6  L= 16 **

-10  310  348    0
 -2  265  290  180
```

```
H /FO/ /FC/ PHI

** K=  1  L= 17 **

-21  396  352  180
-17  355  338    0

** K=  2  L= 17 **

 18  195  193    0
 20  224  252    0

** K=  3  L= 17 **

-19  253  226    0

** K=  4  L= 17 **

-12  278  291    0
-10  295  284  180
 -8  402  347  180
 -2  310  311  180
  8  239  268    1
 12  234  228  180

** K=  5  L= 17 **

 -3  229  215  180
  5  252  261    1

** K=  6  L= 17 **

 -6  222  270    0
 -2  295  311  180

** K=  0  L= 18 **

-24  215  209    1
 16  315  297    0
 18  266  277  180

** K=  1  L= 18 **

 -9  328  318  180
 -7  359  378  180
 -1  307  302    0
 17  399  396  181

** K=  2  L= 18 **

 14  615  611    0
 18  469  493  181

** K=  4  L= 18 **

-16  211  236    0
-10  217  152  180
 -8  251  308  180
 -4  351  361  180
 -2  337  333    0
  4  248  328  180

** K=  5  L= 18 **

  3  303  293    0

** K=  1  L= 19 **

-19  242  248  180
 -7  321  305  180
 15  391  367    0

** K=  2  L= 19 **

-24  197  210  180
```

```
H /FO/ /FC/ PHI

-20  242  234    0
 10  195  172  180

** K=  4  L= 19 **

-10  423  431  180
 -2  321  360    0

** K=  0  L= 20 **

 14  267  264  181

** K=  1  L= 20 **

 -9  440  414  180
 -7  398  392    0
 -3  303  289    0
 -1  485  497  180
  1  530  560  180

** K=  2  L= 20 **

  8  237  211  181
 12  245  258    0

** K=  4  L= 20 **

-10  228  220  180
 -2  344  338    0
  2  621  614  180

** K=  1  L= 21 **

 -9  592  571  180
  1  233  274  180

** K=  0  L= 22 **

  6  701  722  180
 14  323  305  180

** K=  1  L= 22 **

-13  231  170    0
-11  330  352  180
 -7  255  285    0
 -3  305  299  180

** K=  2  L= 22 **

  2  362  403    0
  4  314  324    0

** K=  3  L= 22 **

  1  446  453    0
  3  212  155  180
  5  296  320  180

** K=  4  L= 22 **

  4  355  374  180

** K=  1  L= 23 **

  1  366  329  180
  7  260  246    1

** K=  2  L= 23 **

-10  331  374    0
  4  357  358    0
```

```
 H /FO/ /FC/ PHI        H /FO/ /FC/ FHI        H /FO/ /FC/ PHI        H /FO/ /FC/ PHI

** K=  4  L= 23 **

  -8  199  212 180

** K=  0  L= 24 **

 -12  284  322   1
 -10  274  243 180
  -8  428  418 180
   0  661  642   0
   4  468  476 180
   6  266  263 180

** K=  1  L= 24 **

  -9  252  227   0
   3  236  222 181
   5  234  242   0

** K=  2  L= 24 **

 -10  241  247 180
  -6  280  322   0

** K=  2  L= 25 **

 -10  193  186   0
   2  206  240   0

** K=  3  L= 25 **

  -7  272  254   0

** K=  0  L= 26 **

  -4  205  218 180
```

APPENDIX 2

Dielectrics

2.1. Basic Definitions

Any medium subjected to a steady external electric field E may show a finite amount of charge transport by either electrons or ions resulting in a current i, but the magnitude of the resulting direct current (dc) conductivity, $\sigma_O = i/E_O$, may vary in very wide limits. In cases where σ_O is very small in comparison to any polarisation displacement currents the medium may be regarded as an insulator, in which dielectric phenomena are important. In the opposite case where σ_O dominates, the medium is a conductor of electricity. The term dielectric refers to the presence of relaxation in a predominantly insulating medium, which may show a finite amount of dc conductivity.

The application on an external field, E, to a dielectric medium placed between two electrodes induces two component charges. The first Q_O, which would be present even in the absence of the material medium and which is due to the free space between the electrodes, is given by

$$Q_O = \varepsilon_O E \qquad\qquad 2.1(A)$$

where ε_O is the permittivity of free space (8.854×10^{-12} F m^{-1}). The second, Q_S, which appears on the surface of the material, arises from the re-arrangement of internal charges of the dielectric medium. The total charge appearing on the electrodes, D, given by

$$D = Q_O + Q_S \qquad\qquad 2.2(A)$$

is termed the "dielectric induction" or the "dielectric displacement".
The surface charge per unit area normal to the plane of the electrodes is
termed the "dielectric polarisation" (P).

There are several distinct physical mechanisms of polarisation
which are characterised by very different response rates:

(1)   At the atomic level the application of an external field to
a dielectric medium shifts the centres of the electron clouds with
respect to the centres of the positive nuclei. This effect produces
induced dipoles and "electronic polarisation" is said to occur. This
type of polarisation is found in all materials and occurs very rapidly
with typical response times of the order of 10^{-15} seconds.

(2)   There are many materials which contain permanent dipoles in
the absence of an electric field. The permanent dipoles, which arise
from the asymmetric charge distribution between the unlike partners of a
molecule develop "orientational (or dipole) polarisation" in the presence
of the applied field, E.

(3)   In ionic materials, the external field displaces the ions
with respect to each other and induces a second type of polarisation,
"ionic polarisation", which has a response time of the order of
10^{-13} seconds.

In addition to the bound charges, some mobile charges (electrons or
ions) are also found in dielectrics. Although "free carrier conduction"
is uncommon, electronic carriers may move by hopping between localised
sites, in which case their effective mobility becomes low and they then
make a distinctive contribution to dielectric dispersion.

For a linear system polarisation, P, is proportional to the applied field E,

$$P = \varepsilon_o \chi E \qquad\qquad 2.3(A)$$

or

$$D = \varepsilon_o E + P \qquad\qquad 2.4(A)$$

where χ is called the "dielectric susceptibility" and is defined by

$$\chi = P/\varepsilon_o E = Q_s/Q_o \qquad\qquad 2.5(A)$$

The dielectric induction per unit field is called the "dielectric permittivity", and from equations 2.3(A) and 2.4(A) it can be written

$$D/E = \varepsilon = \varepsilon_o (1 + \chi) \qquad\qquad 2.6(A)$$

here ε consists of the free space contribution and that due to the charges in the medium. Re-writing equation 2.6(A)

$$D/\varepsilon_o E = \varepsilon/\varepsilon_o = \varepsilon_r = 1 + \chi \qquad\qquad 2.7(A)$$

where ε_r is defined as the "relative permittivity" or the "dielectric constant" of the material.

2.2. Time Dependent Dielectric Behaviour

The variation of the dielectric response corresponding to a time varying electric field $E(t)$ can be described in a manner similar to the static field response of equation 2.4(A)

$$D(t) = \epsilon_o E(t) + P(t) \qquad 2.8(A)$$

where $P(t)$ is a time dependent polarisation. The polarisation can be related to a response function $f(t)$ by the equation:

$$P(t) = \epsilon_o (E\Delta t)f(t) \qquad 2.9(A)$$

where E is the applied field strength for a time interval Δt. The term $E\Delta t$ is referred to as a delta function excitation.

The response function has two important properties

$$(i) \quad f(t) = 0 \quad \text{for } t < 0 \qquad 2.10(A)$$

i.e. there can be no response before the application of an exciting force.

$$(ii) \quad f(t) = 0 \quad \text{for } t \longrightarrow \infty \qquad 2.11(A)$$

i.e. response should vanish as the time tends to infinity because there can be no permanent polarisation as a result of a delta excitation. If it is assumed[106] that (a) the dielectric system is linear, (b) the response to individual excitations can be added to evaluate the total response and (c) the time dependent $E(t)$ is a summation of a series of

delta function excitations each of strength E(t)dt then at any time t

$$P(t) = \varepsilon_o \int_o^\infty f(\tau)E(t - \tau)d\tau \qquad\qquad 2.12(A)$$

In practice the time domain study of dielectrics is based on step

function excitation $E(t) = E_o 1(t)$ which has the following properties:

$$E(t) = 0 \qquad \text{for } t < 0 \qquad\qquad 2.13(A)$$

$$E(t) = E_o \quad \text{for } t > 0 \qquad\qquad 2.14(A)$$

In which case equation 2.9(A) becomes

$$P(t) = \varepsilon_o E_o \int_o^t f(t)d\tau \qquad\qquad 2.15(A)$$

giving the dielectric induction as

$$D(t) = \varepsilon_o E_o \left\{ 1(t) + \int_o^t f(\tau)\,d\tau \right\} \qquad\qquad 2.16(A)$$

Differentiating w.r.t. time now gives the charging current

$$i_c = dD(t)/dt$$
$$= \varepsilon_o E_o \left\{ \delta(t) + f(t) \right\} \qquad\qquad 2.17(A)$$

The delta function describing the instantaneous reaction to the step

function represents the response of free space which is equivalent to the

volume of the dielectric material. The response function f(t) describes

the polarisation arising from the material medium which is not instantaneous.

If the dielectric system has any dc conductivity σ_o, this should also be taken into account while considering the charging current, although it does not contribute to the polarisation. At finite times the dc current has a steady value and therefore the charging current can be written as

$$i_c(t) = \varepsilon_o E_o \left\{ \delta(t) + f(t) \right\} + \sigma_o E_o \qquad 2.18(A)$$

The polarisation after an infinite charging time under a steady electric field E_o is given by

$$P(\infty) = \varepsilon_o E_o \int_0^\infty f(t)dt \qquad 2.19(A)$$

which means that the integral of the function $f(t)$ must be finite otherwise the steady state polarisation will not be finite. Using equation 2.3(A) which defines the polarisation, equation 2.9(A) can be written in the form

$$P(\infty) = \varepsilon_o \chi(0) E_o \qquad 2.20(A)$$

where $\chi(0)$ relates to the static (zero frequency) susceptibility. If, after achieving the steady state polarisation, the field is removed abruptly, then the depolarisation (discharging) current results from the return of the partially oriented polarising species to their initial equilibrium orientations or positions which they have in the absence of a field. The depolarisation current[107] does not include the direct

current (because there is no driving force) and therefore it offers a
more convenient form of measuring f(t) in comparison to the charging
current.

2.3. Frequency Dependent Dielectric Behaviour

The dielectric behaviour as a function of frequency is known as
the frequency domain response. It is linked to the time domain response
through Fourier transformations by the relation

$$\mathcal{F}\{\chi(t)\} = \mathcal{K}(\omega)$$

$$= (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{+\infty} \mathcal{K}(t)\exp(-i\omega t)dt \qquad \text{2.21(A)}$$

where $\mathcal{K}(t)$ is a time dependent function and $\mathcal{K}(w)$ is its frequency
dependent transform which provides all the information concerning the
amplitude, phase, and frequency of the sinusoidal waves which make up the
time dependent signal. It can be shown that the Fourier transform of the
convolution integral of equation 2.12(A) gives[107],

$$P(\omega) = \varepsilon_{0}\chi(\omega)\,\xi\,(\omega) \qquad \text{2.22(A)}$$

where $P(\omega)$ and $\xi(\omega)$ are the Fourier transforms of the time dependent
polarisation and the field respectively. The function $\chi(w)$ is called the
frequency dependent susceptibility and is a Fourier transform of the
response function f(t). This function is defined by

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$$

$$= \int_{0}^{\infty} f(t)\exp(-i\omega t)dt \qquad 2.23(A)$$

$$\text{or} \quad \chi'(\omega) = \int_{0}^{\infty} f(t) \cos \omega t \, dt \qquad 2.24(A)$$

$$\chi''(\omega) = \int_{0}^{\infty} f(t) \sin \omega t \, dt \qquad 2.25(A)$$

The real component $\chi'(\omega)$ is an even function of frequency and gives the amplitude of polarisation in phase with the harmonic driving frequency. On the other hand the imaginary component $\chi''(\omega)$ is an odd function of frequency and is in quadrature with the field. It should be noted that one half (t < 0) of the integral limits is being ignored, in describing the real and imaginary parts of the complex susceptibility, because f(t) = 0 for t < 0 for the step field. For zero frequency equations 2.24(A) and 2.25(A) can be expressed as

$$\chi'(0) = \int_{0}^{\infty} f(t)dt \qquad 2.26(A)$$

which is the static values of susceptibility, and

$$\chi''(0) = 0 \qquad 2.27(A)$$

Consequently the real part has a finite value at zero frequency and the imaginary part becomes zero as the frequency vanishes.

The real part of the complex susceptibility contributes to that

component of the frequency dependent displacement current which is in quadrative with the driving field, and therefore does not give rise to power loss. In contrast, the imaginary part $\chi''(\omega)$ appears as the component of the displacement current which is in phase with the driving field, and therefore does contribute to the power loss. Because of this behaviour the imaginary component of the dielectric susceptibility $\chi''(\omega)$ is known as the "dielectric loss". Correspondingly the frequency dependent complex capacitance and hence the complex relative permittivity can be described by

$$C(\omega) = C'(\omega) - iC''(\omega) \qquad\qquad 2.28(A)$$
$$= C'(\omega) - iG(\omega)/\omega$$

where $G(\omega)$ is the frequency dependent conductance and

$$\varepsilon_r(\omega) = \varepsilon_r'(\omega) - i\varepsilon_r''(\omega) \qquad\qquad 2.29(A)$$

If A is the area and d is the thickness of the sample then

$$C(\omega) = \varepsilon_o\varepsilon_r(\omega)A/d \qquad\qquad 2.30(A)$$

Therefore the parameters which describe the complex dielectric behaviour can be described by the relationships:

$$\chi'(\omega) = \{ \varepsilon_r'(\omega) - 1 \} \ \alpha \ C'(\omega) \qquad\qquad 2.31(A)$$
$$C''(\omega) = G(\omega)/\omega \ \ \alpha \ \ \varepsilon_r''(\omega) \ \ \alpha \ \ \chi''(\omega) \qquad\qquad 2.32(A)$$

2.4. Time Dependence of Relaxation

The application of a time dependent electric field to a dielectric medium disturbs its equilibrium. The time dependent response of the medium is then described by a relationship equivalent to the one given in equation 2.3(A) for a time independent response. The process of recovery of the equilibrium within the system after the removal of the perturbing field is called "relaxation". The first model which was proposed by Debye[108] to describe the relaxation processes deals with non-interacting permanent dipoles embedded in a viscous medium. In the absence of an exciting field, thermal motions randomise the dipole which compose the system. Debye's classical model of relaxation starts from the rate equation for the polarisation[109,110] of a single dipole floating in a viscous medium, i.e.

$$\frac{dp(t)}{dt} = - \frac{P(t)}{\tau} \qquad\qquad 2.33(A)$$

where τ is a viscosity dependent relaxation time. The solution of equation 2.33(A) can be described in terms of an exponential decay function $\exp(-t/\tau)$ as

$$
\begin{aligned}
P(t) &= P_o \exp(-t/\tau) \\
&= \chi(0)E \exp(-t/\tau) \qquad\qquad 2.34(A)
\end{aligned}
$$

which can be transformed to the frequency domain using equation 2.21(A). thus

$$\chi(\omega) = \chi(0) (1 + i\omega\tau)^{-1}$$
$$= \chi'(\omega) - i\chi''(\omega) \qquad \qquad 2.35(A)$$

which affords

$$\chi'(\omega) = \chi(0) (1 + \omega^2\tau^2)^{-1} \qquad \qquad 2.36(A)$$
$$\chi''(\omega) = \chi(0) (1 + \omega^2\tau^2)^{-1}\omega\tau \qquad \qquad 2.37(A)$$

where $\chi(0)$ is the magnitude of the real part of the susceptibility at zero frequency.

The dielectric loss curve for the Debye system is symmetric in the logarithmic frequency plot about the loss peak frequency ω_p. The half-height width of the loss peak covers 1.144 decades and the loss curve slope is ±1 on either side of the peak on a log/log scale. The dielectric process is usually activated with an energy ω, in which case the loss peak frequency moves towards high frequencies with temperature such that

$$\omega = 1/\tau = \omega_o \exp(-\omega/kT) \qquad \qquad 2.38(A)$$

here ω_o is a pre-exponential frequency factor. The ratio of the imaginary to the real part of the susceptibility for the Debye model is given by:

$$\chi''(\omega)/\chi'(\omega) = \omega\tau \qquad \qquad 2.39(A)$$

However, evidence for the Debye response is very rare in solids[107,111].

In many materials where polarisation and conduction is caused by hopping charge carriers a peak in the loss cannot be readily observed, due to the onset of dc conduction[107]. It was proposed by Jonscher[112] that the loss due to conduction by the hopping charges obeys a "universal" power law of the type:

$$\chi''(\omega) \; \alpha \; \omega^{n-1} \qquad\qquad 2.40(A)$$

which corresponds to a frequency dependent ac conductivity

$$\sigma(\omega) \; \alpha \; \omega^{n-1} \; \text{with} \; 0 < n < 1 \qquad\qquad 2.41(A)$$

over several decades of frequency. Sometimes n approaches unity implying an almost frequency independent loss[107].

It can be proved[107] that the ratio of the imaginary to the real part of the susceptibility for the power law response of equation 2.40(A) does not depend on frequency, i.e.

$$\chi''(\omega)/\chi'(\omega) \; = \cot n \; \pi/2$$
$$= \tan (n-1)\pi/2 \; = \; \text{constant} \qquad 2.42(A)$$

which means the ratio of the energy lost to the energy stored, per cycle, is independent of frequency, a marked contrast to the Debye mechanism for which it is equal to $\omega\tau$.

Power law behaviour has been observed in dipolar materials as well. The dielectric response of dipolar systems which have non-Debye loss peaks has been described[107,110,111] by power laws of the form

$$\chi'(\omega) \; \alpha \; \chi''(\omega) \; \alpha \; \omega^{-1(n-1)} \; ; \; \omega \gg \omega_p \qquad\qquad 2.43(A)$$

$$\chi''(\omega) \; \alpha \; \{ \; \chi(0) - \chi'(\omega) \; \} \; \alpha \; \omega^m; \; \omega \ll \omega_p \qquad\qquad 2.44(A)$$

having $0 < m < 1$, $0 < n < 1$. The frequency corresponding to the maximum loss is given by ω_p, see figure 2.1(A).

2.5. Low Frequency Dispersion

The frequency dependence of conductivity in low conductivity materials can be expressed in the form

$$\sigma_{(\omega)} \; = \; \sigma_o + \sigma_{ac(\omega)} \qquad\qquad 2.45(A)$$

where σ_o is the frequency independent d.c conductivity. The ac conductivity, $\sigma_{ac(\omega)}$, which is due to the in-phase response of current can be expressed as the dielectric loss and can usually be described by the relationship[112].

$$\sigma_{ac(\omega)} \; \alpha \; \omega\chi''(\omega) \; \alpha \; \omega^n \qquad\qquad 2.46(A)$$

In many materials at low frequencies $\sigma_{ac(\omega)}$ becomes nearly frequency independent yet it cannot be described as a dc conductivity. This slowly varying $\sigma_{ac(\omega)}$ introduces a completely different response which was identified by Jonscher[113] as low frequency dispersion (LFD) or quasi-dc conductivity.
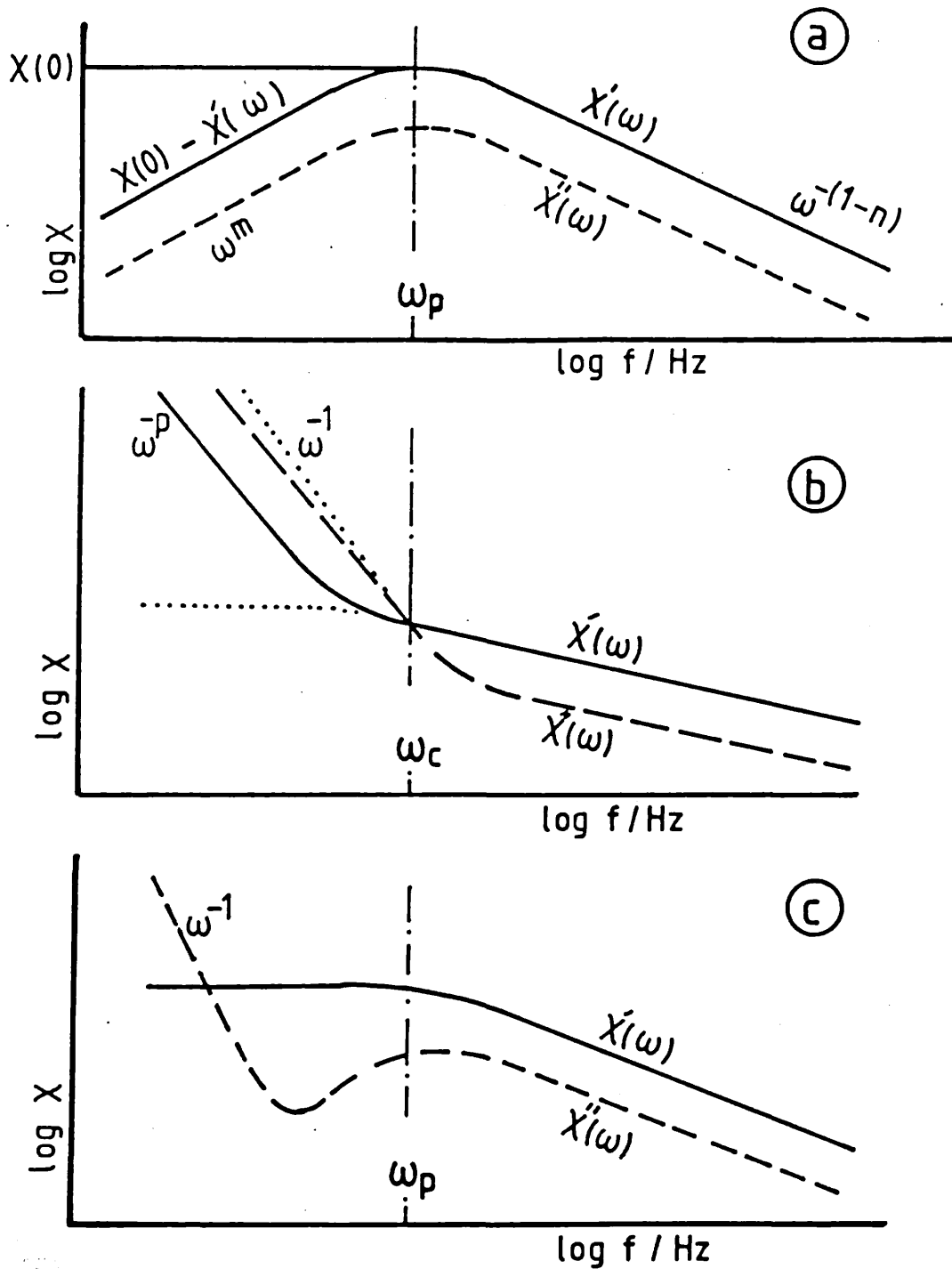
Figure 2.1(A)

Schematic diagrams to show the power law for

a) non-Debye dipolar response below and above ω_p

b) carrier dominated response with two power laws below and above ω_c. For lower frequencies ($\omega < \omega_c$) the full lines represent the LFD and the dotted lines show the dc case

c) two components of susceptibility in the presence of dc and a loss peak.

It has been observed[107] that the response of dipolar materials for $\omega > \omega_p$ and the response of the charge carrier systems for $\omega > \omega_c$ obeys the same form of power law. However in the case of carrier dominated systems the dielectric response is represented by two power laws and the frequency ω_c defines the transition frequency where one form of power law gives way to the other. This behaviour is shown schematically in figure 2.1(A)b and mathematically can be written

$$\chi''(\omega) \; \alpha \; \omega^{-(1-n)} \quad \text{for} \; \omega > \omega_c$$

$$2.47(A)$$

$$\chi'(\omega) \; \alpha \; \omega^{-p} \quad \text{for} \; \omega < \omega_c$$

The value of the exponent $(1-n)$ for the high frequency process has been observed to be less than the exponent p which refers to the low frequency process. In fact both the $(n-1)$ law (for $\omega > \omega_c$) and the -p law (for $\omega < \omega_c$) are special cases of the "universal response, and they characterise two processes which exist together at the same time.

The phenomena of LFD or quasi-dc conduction has been observed in a large variety of materials in which a polarisation process is dominated by hopping charge carriers of either electronic or ionic nature, e.g. at a liquid electrolyte-electrode interface[114], in a solid nickel suspension[115], for wetted proteins[113], and with stearic acid[116].

It is important to realise that LFD or quasi-dc conductivity is completely different from dc conductivity since $\chi'(\omega)$ remains constant under dc conditions and the imaginary part has the frequency dependence of ω^{-1} at low frequencies[113]. On the other hand in the case of LFD both the real and the imaginary parts of the dielectric susceptibility behave in a Kramers-Kronig compatible fashion with the same power law exponent and their ratio is constant. It has been observed that this behaviour is general to materials which contain high concentrations[113] of low mobility charge carriers. It has been proposed that movement of charge carriers over "limited" paths can give rise to LFD, in contrast to dc conduction in which case charges move from one electrode to the other[114].

2.6. Dielectrics of Semiconductors (DSS)

In addition to the dielectric effects observed in insulating materials it is also possible to study delayed electronic transitions between deep levels in the forbidden gap as well as between deep levels and free bands in semiconductors. The former normally involve "horizontal" thermally assisted transitions in the volume of the sample with relatively small changes in energy, the latter are termed "vertical" transitions with energy changes of the order of half the band gap and take place mainly in interfacial space charge regions and at the interfaces between semiconductors and metals. These various transitions have well recognisable spectral "signatures". Figure 2.2(A) shows schematically the various electronic processes giving rise to dielectric effects in semi-conducting and semi-insulating materials. The conduction
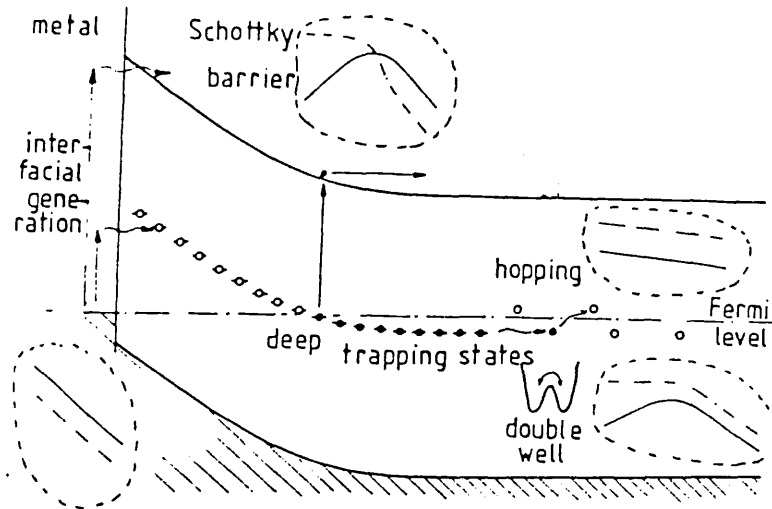
Figure 2.2(A)

and valence bands are shown with a Schottky barrier near the metal

contact and a set of deep trapping states is shown in the vicinity of the

Fermi level. The vertical arrow shows the release of an electron from a

deep trap near the crossing-over position with the Fermi level, the

resulting free electron is then driven into the neutral semiconductor.

Hopping transitions are indicated between filled and empty states near

the Fermi level. A potential double well is shown representing a

localised defect around which an electron or an ion may execute hopping

transitions of a dipole-like nature. Various interfacial generation

processes are indicated. Inserts within dotted contours show the expected

characteristic frequency "signatures" of the real (chain-dotted lines)

and imaginary (continuous lines) components of the complex

susceptibility, plotted logarithmically against the logarithm of

frequency.

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