THE CHEMISTRY OF SEDIMENT FORMATION DURING THE STORAGE OF DIESEL FUEL

by

JOANNA F PEDLEY

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The Bourne Laboratory
Royal Holloway and Bedford New College
Egham Hill
Egham
Surrey TW20 0EX.

TO MY PARENTS

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ABSTRACT

This thesis describes the identification of chemical species responsible for sediment formation during storage of an unstable diesel fuel.

It is currently not possible to reliably predict the storage stability characteristics of diesel fuels, ie. to distinguish between stable diesel fuels, which remain chemically and physically unchanged during storage, and unstable fuels, which deteriorate under the same conditions to produce insoluble sediment. This study was carried out in order to assist with the development of chemical tests to predict diesel fuel storage stability characteristics.

An unstable diesel fuel was stored under ambient conditions for two years. The sediment produced during this period was collected and analysed by TLC, IR, MS, pyrolysis/MS and pyrolysis/GC/MS. Alkyl derivatives of indole were found to be important constituents of the sediment. The diesel fuel itself was analysed using LC, GC, TLC and MS. Alkylindoles and compounds, confirmed by synthesis to be alkyl derivatives of indolylphenalene and bis(indolyl)phenalene, were detected in the fuel. It has been shown that indolylphenalenes and bis(indolyl)phenalenes are converted by acid into material whose analytical characteristics are almost identical to those of a major constituent of sediment. Phenalenone and alkylphenalenones have also been detected in the fuel. These compounds are thought to arise in fuel from autooxidation of the corresponding phenalenes. The observed increase in concentration of indolylphenalenes and bis(indolyl)phenalenes during fuel storage was attributed to reaction of alkylindoles with phenalenone and alkylphenalenones. Addition of phenalene and 2-methylindole to an otherwise stable fuel, followed by storage for 6 months at 25°C, resulted in the formation of phenalenone, 2-methylindolylphenalene, bis(2-methlyindolyl)phenalene and sediment, with analytical characteristics consistent with those of sediment formed during storage of the unstable fuel. It is concluded that sediment formation in the unstable fuel was caused by acid promoted reactions of alkylindoles with phenalenones.

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CHAPTER ONE

GENERAL INTRODUCTION

1.1 Background

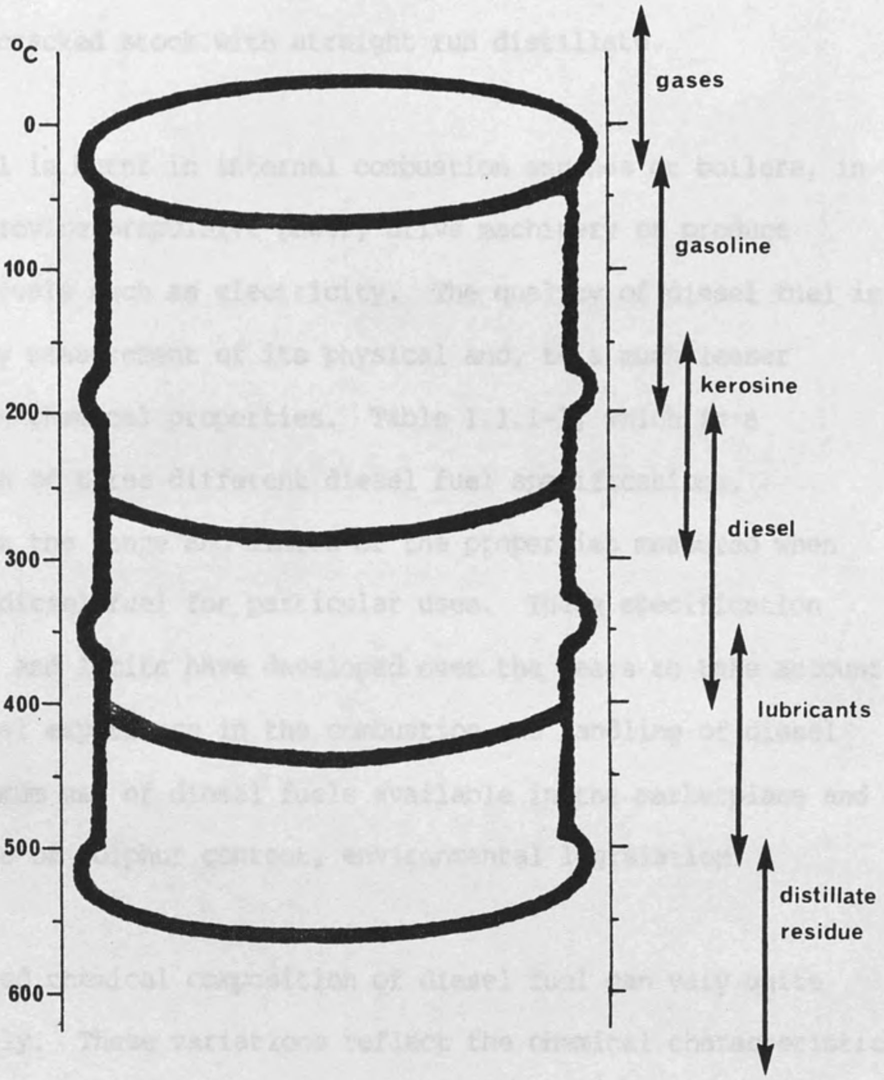
1.1.1 Introduction

The history of the modern petroleum industry is thought to date back to 1859 when "Colonel" Edwin Drake accidentally discovered oil whilst sinking a well in search of brine, near Titusville, in Pennsylvania, USA. Today the industrialised world relies heavily on petroleum and petroleum-derived products, to such an extent that the economies of many nations are vulnerable to even modest fluctuations in the price of crude oil.

Petroleum consists predominantly of a complex mixture of hydrocarbons, ranging in volatility from light gases to solids, as indicated in figure 1.1.1-1. The term diesel fuel is usually used to describe the petroleum distillate fraction which boils between approximately 180°C and 380°C. Synonymous terms include light gas oil, DERV (diesel engine road vehicle), heating oil and middle distillate fuel.

Diesel fuel is produced from crude oil directly by fractional distillation or indirectly by thermal cracking, catalytic cracking or hydrocracking of involatile crude oil components. Details of these and other refining techniques are widely available elsewhere eg.[1].

Figure 1.1.1-1 Typical composition and boiling range of crude petroleum.



Diesel fuel produced simply by distillation of crude oil is usually referred to as "straight run distillate" whilst fuel produced by catalytic cracking is sometimes described as "light cycle gas oil" and fuel produced by thermal cracking, "visbroken gas oil". Diesel fuel normally consists of either 100% straight run distillate or blends of cracked stock with straight run distillate.

Diesel fuel is burnt in internal combustion engines or boilers, in order to provide propulsive power, drive machinery or produce secondary fuels such as electricity. The quality of diesel fuel is assessed by measurement of its physical and, to a much lesser extent, its chemical properties. Table 1.1.1-1, which is a compilation of three different diesel fuel specifications, illustrates the range and limits of the properties measured when selecting diesel fuel for particular uses. These specification parameters and limits have developed over the years to take account of practical experience in the combustion and handling of diesel fuel, optimum use of diesel fuels available in the marketplace and in the case of sulphur content, environmental legislation.

The detailed chemical composition of diesel fuel can vary quite considerably. These variations reflect the chemical characteristics of crude oil originating from different areas of the world and the nature and extent of refinery processing used to produce diesel fuel from crude oil. Relatively few attempts have been made to correlate the detailed chemical composition of diesel fuel with the specification parameters listed in table 1.1.1-1.

Table 1.1.1-1 Specifications for diesel fuel quality control

Diesel fuel property	Method *	BS2869 Class A1 (intended use - automotive diesel fuel)	BS2869 Class D (intended use - domestic and industrial boilers)	DEF STAN 91-4/5 F-76 (intended use - high and medium speed compression ignition engines, gas turbines,certain helicopters and steam raising plant in HM Ships)
Appearance	Visual examination.	NS †	NS	Bright and free from solid matter + separated water at normal ambient temperatures
Colour	IP196, ASTM D1500	NS	NS	3.5 max
Density at 15°C kg/l	BS4714, IP160, ASTM D1298	NS	NS	0.820 min 0.880 max
Distillation % recovered @ 350°C	BS2000 Part 123, IP123, ASTM D86	85 min	85 min	85 min
Flash point	BS2000 Part 34, IP34, ASTM D93	56 min	NS	61 min
Viscosity, kinematic @ 40°C mm²/s	BS2000 Part 71, IP71, ASTM D445	2.5 min 5.0 max	NS	1.7 min 4.3 max
Pour point °C	BS2000 Part 15, IP15, ASTM D97	NS	NS	-6 max
Cloud point °C	BS2000 Part 219, IP219, ASTM D2500	NS	NS	-4 max
Acidity inorganic	BS2000 Part 182, IP182	NS	NS	Nil
Total acid number mgKOH/g	BS2000 Part 182, IP182	NS	NS	0.3 max
Sulphur content % mass	BS200 Part 16, IP61, ASTM D129	0.3 max	0.5 max	1.0 max
Ash content % mass	BS4450, IP4, ASTM D482	0.01 max	0.01 max	0.01 max
Carbon residue on 10% distribution residue % mass	BS4451, IP14, ASTM D524	0.2 max	0.2 max	0.2 max
Filter blocking tendency ml	DEF STAN 91-4/5 Annex A	NS	NS	NS
Detection of copper corrosion at 100°C	BS2000 Part 154, IP154, ASTM D130	Class 1 max	Class 1 max	Class 1 max
Cetane number	IP41, ASTM D613	50 min	NS	47 min
Storage stability, total sediment mg/l	DEF STAN 05-50, Method 40	NS	NS	10.0 max
Water reaction decrease in water volume ml	DEF STAN 91-4/5 Annex B	NS	NS	2 max
water phase	DEF STAN 91-4/5 Annex B	NS	NS	free from emulsion
Water content %(v/v)	BS4385	0.05 max	0.05 max	NS
Sediment %(m/m)	BS4382	0.01 max	0.01 max	NS
Cold filter plugging point °C Summer	BS6188	-4max	-4 max	NS
Winter	BS6188	-12 max	-12 max	NS

* IP = Institute of Petroleum
ASTM = American Society for Testing of Material
BS = British Standard

† not specified

Over many years the quality of diesel fuel has remained fairly consistent and therefore there has been little need to change specifications and investigate alternative and possibly more discriminating methods of assessment. However, since the "oil crises" of 1973 and 1979, there has been growing pressure to optimise the use of petroleum reserves in general. At the same time the demand for heavy distillate and residual fuel products has decreased, whilst the demand for the more volatile petroleum products has increased. In recent years, therefore, the petroleum industry has made more use of upgrading processes, such as catalytic and thermal cracking, in order to maximise production of middle and light distillate fuels. These changes in refinery practice are increasingly affecting the general quality of diesel fuel. An explanation of the nature of these quality changes and how they arise from recent developments in refinery processing is given in a report by the British Technical Council of the Motor and Petroleum Industries[2].

The work described in this thesis is concerned with developing a chemical understanding of one particular property of diesel fuel, that of "storage stability".

1.1.2 **Storage stability of diesel fuel**

The storage stability of diesel fuel refers to its resistance to physical and chemical change during storage, in particular its tendency to darken in colour and to produce involatile material (gum) and/or insoluble material (sediment).

A clear distinction should be drawn between storage stability and thermal stability. Storage stability refers to the resistance of fuel to degradation under ambient conditions of temperature over time periods ranging from a few weeks to several years, whilst thermal stability refers to the resistance of fuel to degradation when exposed to temperatures in excess of approximatley 140°C, for time periods of a few minutes or less. Thermal degradation of fuel can result in the formation of gums and lacquers on hot engine surfaces such as fuel injectors. Good thermal stability is particularly important for aviation fuel since, prior to combustion, it is frequently used in heat exchangers as a coolant for aircraft engine lubricating oil.

Diesel fuel storage stability characteristics can vary enormously. Stable diesel fuels have been reported to remain virtually unchanged over storage periods of up to six years[3], whilst at the other extreme, unstable diesel fuels can show evidence of degradation after only a few weeks in storage[4]. If the time period between refinery production and final use is short, then fuel storage stability characteristics are of little or no consequence. This rapid turn-over situation usually applies to diesel fuel which is used in road vehicles (DERV). In contrast, diesel fuel which is used in heating systems, emergency generators or diesel fuel used by the military, may potentially remain in storage for months or even years before use. Consequently in these situations it is necessary to take account of fuel storage stability characteristics. The importance of storage stability as a parameter of diesel fuel quality depends to a large extent on the tolerance of particular engine and fuel systems towards diesel fuel which has degraded during storage. For example where a high degree of fuel cleanliness is required, such as a gas turbine engine, use of degraded diesel fuel containing significant quantities of sediment (> 2mg dm^{-3}, particle size <1μm to 20μm) can lead to problems of excessively rapid fuel system filter blockage. However the same fuel could probably be used with impunity in a system tolerant of a lower standard of fuel cleanliness, such as a medium or low speed compression ignition engine.

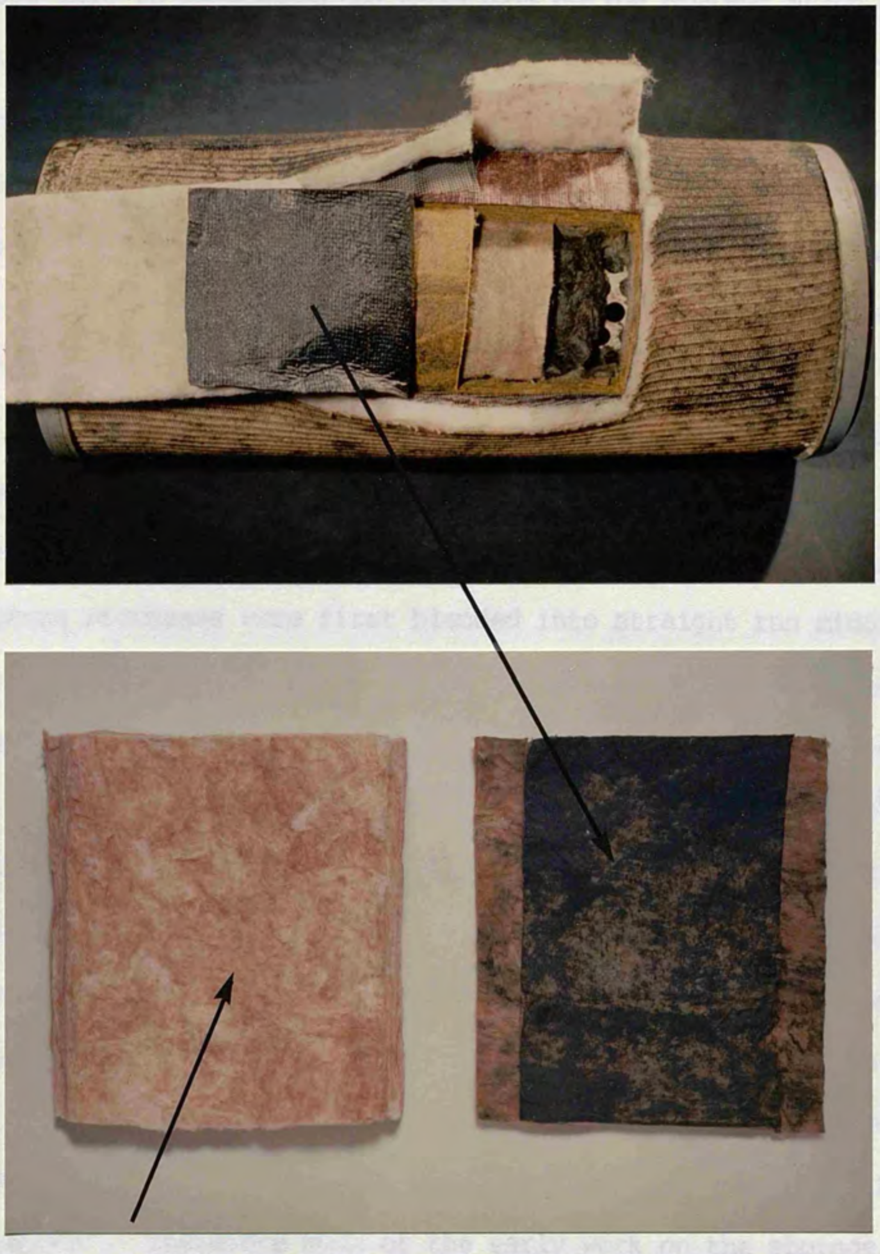
The problems of filter blockage caused by sediment produced during the storage of unstable diesel fuel have been highlighted in recent years by the experience of the Royal Navy[5].

The majority of HM ships burn diesel fuel in aero-derived gas turbine propulsion units. The diesel fuel, which is also used in high and medium speed diesel engines and in steam raising plant, is purchased to the requirements of DEF STAN 91-4/5, details of which are given in table 1.1.1-1. The operation of gas turbines in a marine environment can lead to severe corrosion of turbine blades arising from high temperature reactions involving sodium ions and oxides of sulphur. In order to minimise this type of corrosion it is essential to ensure that sea salt is rigorously excluded from both the fuel and air intake systems. The main source of salt in the fuel system is contamination of fuel by sea water. Therefore a series of filters are used to ensure that fuel reaching the gas turbines is clean, dry and essentially free of sodium ions. These filters include coalescer elements which are specifically designed to remove undissolved water from fuel, thereby ensuring that the sodium ion level reaching the gas turbine via the fuel system does not exceed 0.3ppm. However it has been found that excessively rapid blockage of coalescer elements, in some cases after only a few hours use, is caused by organic sediment which forms during storage of unstable diesel fuel. Figure 1.1.1-2 shows a photograph of a blocked coalescer element which has been sectioned to illustrate the accumulation of fuel derived sediment in the glass fibre layer of the element.

Clearly, where a high standard of fuel cleanliness is required and where it is necessary to store diesel fuel for periods in excess of a few weeks before use, it is essential to be able to predict fuel storage stability characteristics. A number of tests, largely based upon thermally accelerated aging, have been developed over the years for this purpose, including one which is currently used by the Royal Navy in its purchasing specification for diesel fuel, DEF STAN 91-4/5, detailed in table 1.1.1-1. However predictions of fuel stability based on the results of this test have been found to be unreliable[4].

In order to successfully predict the storage stability characteristics of diesel fuel, a clear understanding of the chemical processes leading to sediment formation during storage of unstable diesel fuel is required. The purpose of the work described in this thesis is to contribute to the understanding of this phenomenon.

Figure 1.1.1-2 A blocked coalescer element, sectioned to show the accumulation of sediment in the glass fibre layer.



1.2 Literature review

1.2.1 Introduction

It has been known for many years that hydrocarbon fuels are susceptible to autooxidation reactions during storage which result in the formation of soluble and insoluble materials of higher molecular weight and boiling point than the original fuel. Hydrocarbon fuels produced directly by distillation of crude oil, usually referred to as "straight run fuels", are generally more resistant to oxidative attack than fuels produced by distillation of cracked crude oil components[6]. Consequently the storage stability characteristics of middle distillate fuels (including diesel fuels) were of little concern until about 1946 when significant proportions of fuel produced by thermal and catalytic cracking processes were first blended into straight run middle distillate fuels. It was assumed that the involatile and insoluble materials formed during storage of middle distillate fuels were of the same type as those which were known to occur in gasoline[6]. However additives used to control the autooxidation of gasoline were found to be ineffective when used in middle distillate fuels[7]. Elemental analysis of middle distillate fuel sediments showed that they contained higher concentrations of sulphur and nitrogen than the fuels from which they were derived[8-11]. This is illustrated by the data in table 1.2.1-1 taken from Thompson, Chenicek, Druge and Symon[8]. Therefore much of the early work on the storage stability of middle distillate fuels was directed towards studying the role of sulphur and nitrogen compounds in the formation of fuel sediments.

Table 1.2.1-1 Elemental composition of fuels and sediments[8]

catalytically cracked stock	fuels		sediment	
	sulphur %	nitrogen %	sulphur %	nitrogen %
1	1.28	0.01	3.38	3.58
2	0.96	0.02	1.72	0.80

1.2.2 **Role of sulphur compounds**

Thompson, Druge and Chenicek[9] investigated the effect of sulphur compounds on the stability of fuel oils after reports of sludge formation in fuels consisting of blends of straight run and cracked components derived from crude oils containing high levels of sulphur. They found that the sulphur content of the precipitated sludge was more than five times higher than that of the fuel. Therefore selected sulphur compounds were added to fuel oils which were then stored at 37°C. The effect of these sulphur compounds on fuel stability was measured by the amount of soluble and insoluble gum (sediment) formed during storage. The results indicated that thiophenes, aliphatic sulphides and aliphatic mercaptans had little effect on stablity whereas disulphides, polysulphides and particularly thiophenol were found to promote sediment formation. Removal of mercaptans (including thiophenols) present in fuel oil by extraction with caustic methanol gave a product of enhanced stability.

Offenhauer, Brennan and Miller[10] likewise found that catalytically cracked fuel could be stabilised by extraction with caustic methanol. They also noted that when aromatic thiols, which had been removed by caustic methanol extraction, were added back to the stabilised fuel, the instability of the fuel was restored to its original level. It was stated by these authors that the aromatic thiol content of a catalytically cracked fuel dropped to zero during storage of the fuel for three weeks at 43°C and that sediment only began to form after the thiol content of the fuel had dropped below its original level. However the paper contains no experimental data to support this statement. It was shown by this group that addition of diaryldisulphides to fuel, which had been extracted with caustic methanol to remove aromatic thiols, did not cause sediment formation. On the basis of this observation, it was concluded that diarydisulphides were not intermediates in sediment formation involving aromatic thiols. Sulphonic acids (precise nature not given), in the presence of oxygen, were found to strongly promote colour and sediment formation. Other acids, including dichloroethanoic and trichloroethanoic acids, showed the same effect. Treatment of fuel sediments with warm alkali followed by neutralisation of the aqueous extract using a cation exchange resin and analysis by infrared spectroscopy, indicated that the sediments contained sulphonic acids. It was suggested that sulphonic acids were formed by oxidation of aromatic thiols present in fuel. This conclusion was based on an experiment in which thiols, inherently present in a catalytically cracked fuel, were removed and replaced by 2-naphthalene thiol. The presence of 2-naphthalenesulphonic acid in the sediment formed during storage of the fuel, was demonstrated by isolation and characterisation of its sulphonamide, thus indicating that the thiol had oxidised to sulphonic acid and become incorporated into the fuel sediment.

Sauer, Weed and Headington[11] provided further evidence that the sulphur in sediments produced by unstable middle distillate fuels originates from aromatic thiols. A blend of caustic treated straight run/catalytically cracked fuel was doped with p-toluenethiol labelled with radioactive ^{35}S. Analysis of the sediment produced during storage of this fuel indicated that its sulphur content could almost completely be attributed to the thiol which had been added to the fuel. However the chemical nature of the sulphur contained in the sediment was not established.

1.2.3 Role of nitrogen compounds

The origin of the nitrogen found in fuel sediments was considered by Thompson, Chenicek, Druge and Symon[8] in 1951. They carried out a number of experiments in which a variety of nitrogen compounds were added to fuels and their effect on stability assessed by the amount of sediment formed during storage. They found that pyridines and quinolines had little effect on fuel stability, an observation which was later confirmed by Offenhauer, Brennan and Miller[10]. It was established that instability could not be correlated with the presence or absence of pyrrole derivatives in fuels. However deliberate addition of pyrrole derivatives, in particular 2,5-dimethylpyrrole, was found to promote sediment formation during fuel storage at 43°C. The sediment produced had a nitrogen content of 11.1% (14.8% in 2,5-dimethylpyrrole), whereas the nitrogen content of naturally occurring fuel sediment is usually between 1.5 and 2.8%[11]. This suggests the experiment did not reproduce the reactions which occur in inherently unstable fuels. These workers also observed that unstable fuels, containing pyrrolic nitrogen compounds, could be stabilised by treatment with caustic methanol. It was noted that a mixture, containing the caustic methanol extract of an unstable fuel and a fuel free of pyrrole derivatives, was relatively stable. Subsequent addition of indole to this mixture resulted in the formation of significant amounts of sediment. This may indicate that instability arises from the interaction of pyrrole derivatives with acidic compounds present in fuels. However since the sediment produced in these experiments was not characterised, it is impossible to conclude whether or not this interaction contributes to the formation of sediment during storage of unstable fuels.

1.2.4 **Sediment analysis and mechanisms**

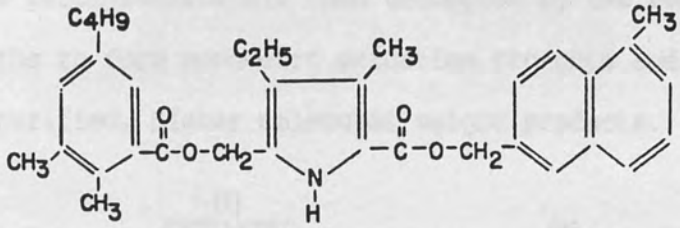
Offenhauer, Brennan and Miller[10] reported that sediment from a catalytically cracked middle distillate fuel was soluble in chloroform and acetone/methanol but insoluble in paraffinic solvents. It decomposed on heating (experimental details not given) without melting at temperatures above 175°C. The distillate from the decomposition products was found to give a positive test for pyrrolic nitrogen using Ehrlich´s reagent[12]. These observations, together with the results this group discussed earlier, led them to state that "the sediment is believed to be composed of sulphonic acids formed through oxidation of the aromatic thiols plus the basic condensate formed by the action of oxygen and acids on the pyrroles and indoles". However it is not clear from the paper exactly what is meant by this statement. No evidence is presented to substantiate the suggestion or to explain how basic material forms from reaction of pyrroles and indoles with oxygen and acids. The authors themselves noted that even assuming that all the nitrogen and sulphur in the sediment was derived from pyrroles, indoles and thiols, these species could only account for about half the weight of the sediment and that the nature of the rest of the sediment was not known.

Sediments formed during ambient storage of blends of straight run and catalytically cracked fuels were also analysed by Sauer, Weed and Headington[11]. A summary of their chemical analysis results for a variety of sediments are given in table 1.2.4-1.

Table 1.2.4-1 Summary of sediment chemical analysis data[11]

Analysis	Range of values
Carbon	60-78%
Hydrogen	6.0-7.5%
Nitrogen	1.5-2.8%
Sulphur	0.9-3.6%
Oxygen	7.4-17.5%
Relative molecular mass	500

The high carbon to hydrogen ratios showed that the sediments contained unsaturated ring structures. It was thought that the oxygen content of the sediment originated from functional groups formed by air oxidation of fuel components rather than incorporation of indigenous oxygen containing species present in the fuel, such as phenols and carboxylic acids. Chemical and infrared analysis suggested that the oxygen was present as ester-type linkages. A variety of aromatic compounds were produced by decomposition of sediment in the high temperature inlet of a mass spectrometer. These included naphthalenes (11%), decalins (7%), pyrroles (8%), indoles (11%), carbazoles (9%), pyridines (13%) and quinolines (17%). On the basis of this, it was suggested that a typical sediment molecule might have the structure indicated diagramatically below.



CALCULATED ANALYSIS

CARBON	78.1 %
HYDROGEN	7.1 %
OXYGEN	11.6 %
NITROGEN	2.5 %
SAPONIFICATION NO.	202
CARBON/HYDROGEN RATIO	10.0
MOLECULAR WEIGHT	553

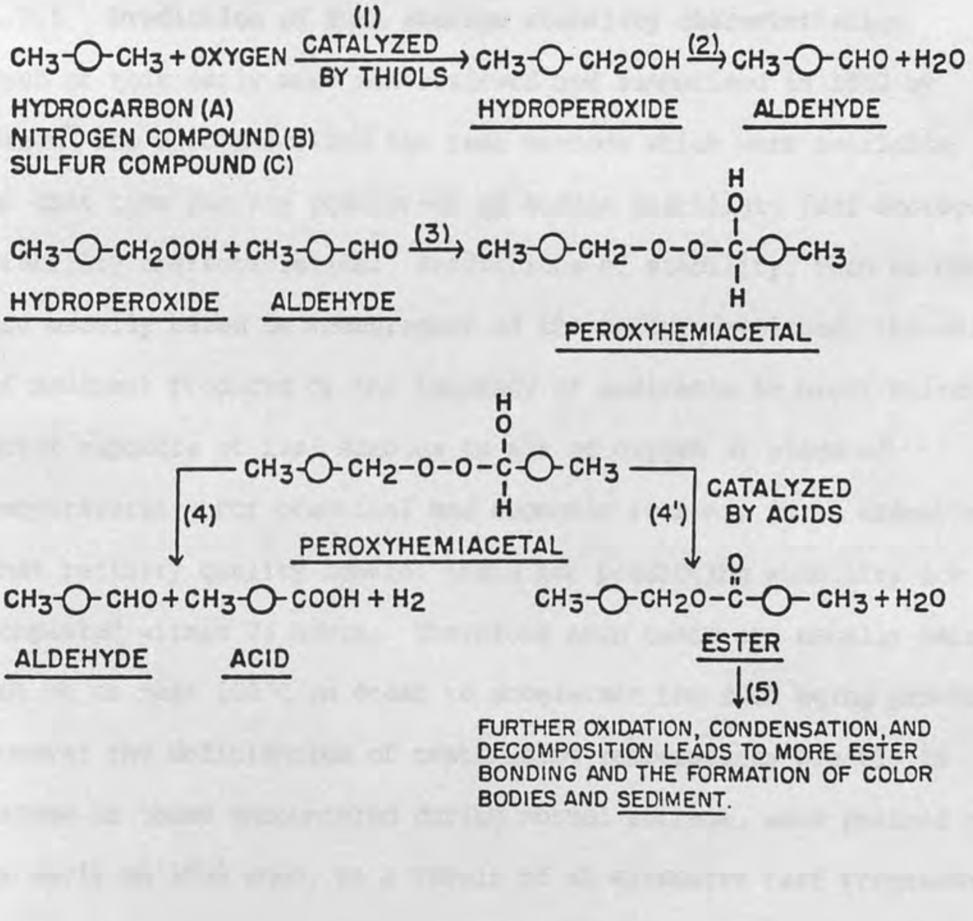
The following mechanism was proposed by Sauer, Weed and Headington[11] for the formation of sediments of this type:

Step 1 The sidechain oxidation of reactive hydrocarbons, nitrogen and sulphur containing compounds, present primarily in the catalytically cracked component, is catalysed by thiols to form hydroperoxides.

Step 2 Some of the hydroperoxides decompose with the elimination of water to form aldehydes (according to mechanism proposed by Durham, Wurster and Mosher[13])

Step 3 The aldehydes then react with other hydroperoxides to form peroxyhemiacetals[13].

Step 4 The peroxyhemiacetals then decompose by two reaction paths to form monomeric oxidation products and condensed, esterified, higher molecular weight products.



Oswald[14] proposed that co-oxidation of olefins and mercaptans to produce hydroperoxide intermediates was to a large extent responsible for subsequent colour, gum and sediment formation in untreated cracked petroleum distillates. In later work, Oswald and Noel[15] studied the effects of storing various combinations of hydrocarbons, mercaptans, hydroperoxides, pyrroles and the products of mercaptan and olefin co-oxidation reactions, in pure hydrocarbon solvents. Formation of oxidised pyrrole polymers, often termed "pyrrole black deposits", was suggested to occur by reaction of pyrroles with hydroperoxides. It was also suggested that since hydroperoxides can decompose to form aldehydes and ketones, these secondary products of autooxidation may also react with pyrrolic nitrogen compounds to produce sediments and coloured species.

1.2.5 **Prediction of fuel storage stability characteristics**

Much of this early work was reviewed and summarised in 1962 by Nixon[6] who also described the test methods which were available at that time for the prediction of middle distillate fuel storage stability characteristics. Predictions of stability, then as now, are usually based on measurement of the colour developed, the weight of sediment produced or the tendency of sediments to block filters, after exposure of fuel samples to air or oxygen at elevated temperatures. For practical and economic reasons, it is essential that refinery quality control tests for predicting stability are completed within 24 hours. Therefore such tests are usually carried out at or near 100°C in order to accelerate the fuel aging process. However the deficiencies of tests using temperatures greatly in excess of those encountered during normal storage, were pointed out as early as 1958 when, as a result of an extensive test programme, it was reported that no combination of available data would permit consistent prediction of the storage stability of diesel/distillate fuels or their blends[16].

Since that time numerous studies have been carried out in an attempt to correlate the actual storage stability characteristics of middle distillate fuels with the results of accelerated test procedures. In 1965 Ritchie[3] reported the results of a six year storage test of six fuels of differing stability. The outcome of this work was a recommendation that aging of fuels at 50°C for 4 weeks or at 100°C for 16 hours could be used to predict the amount of sediment which would form during ambient storage for periods of 12-18 months. In 1973 LePera and Sonnenburg[17] summarised developments in the prediction of distillate fuels storage stability. The lack of reliable test procedures was reiterated at this time, following many reports of problems caused by gums and sediments formed during fuel storage, such as the malfunctioning of injectors and the blockage of fuel filters. Extensive studies were carried out in the late 1970´s and early 1980´s in which the effects of storage conditions on the results of accelerated tests were considered. Variations in test parameters such as storage time, storage media, temperature and oxygen availability were investigated[18-21]. The only agreed conclusion of these studies was that storage of middle distillate fuels at 43°C for 13 weeks correlated well with storage at ambient temperatures for 1 year. However such a method is of course of no practical use for quality control of refinery products.

1.2.6 Storage stability of "syn-fuels"

Concern about diminishing world petroleum reserves, prompted by the "oil crises" of 1973 and 1979, led to the initiation of many research programmes to study the production and properties of liquid fuels from non-petroleum sources. The stability characteristics of middle distillate "syn-fuels" produced from coal[22-26] and oil shale[27-31] have been investigated. The chemical compositions of such fuels are significantly different from equivalent present day petroleum based products. In particular, the concentration of nitrogen containing compounds in shale-derived fuels is usually many times higher than in petroleum fuels. Frankenfeld and Taylor[29] found that sediments formed during low temperature storage of crude or partially refined shale liquids with nitrogen contents of 0.5-2.0% were very similar to the sediments formed by the addition of 2,5-dimethylpyrrole to model hydrocarbon systems. Elemental, mass spectrometric and infrared analysis of such sediments indicated that they were formed by oxidative condensation of pyrrole derivatives present in the fuel without the participation of other reactive hydrocarbons. However it was noted that where shale liquids were severely hydrotreated in order to reduce the level of nitrogen containing compounds, the nature of the sediments formed during storage was somewhat different, suggesting that in those cases sediments were produced by a different mechanism. This work shows the need to compare sediments produced during actual fuel storage with those produced during the storage of simplified model systems. Few workers have adopted this approach. The main agreed conclusion of work carried out on the stability of middle distillate "syn-fuels" was that addition of 2,5-dimethylpyrrole alone or in combination with thiophenol promotes the formation of sediment under a variety of storage conditions.

1.2.7 Recent work

Two publications describing analysis of sediments by mass spectrometry provide further evidence that the chemistry which results in sediment formation in shale-derived middle distillate fuels doped with pyrroles is not related to the chemistry which gives rise to sediments during normal storage of unstable petroleum-derived middle distillate fuels.

Malhotra and St John[32] stored four fuels at 80°C for 4-7 weeks. Three of the fuels were blends of 40% catalytically cracked fuel in straight run petroleum diesel fuel. The remaining fuel was a shale-derived diesel fuel doped with 2,5-dimethylpyrrole (450ppm N). The sediments from these fuels were analysed by pyrolysis/field ionisation mass spectrometry. The spectrum of the shale/pyrrole sediment corresponded to ions of m/z 50-300 which were attributed to pyrrole and its alkyl homologues, together with oxidised derivatives of these species and coupling products of the dopant, 2,5-dimethylpyrrole. The spectra of sediments from the petroluem diesel fuels were similar to one another but quite different to the spectrum of the shale/pyrrole sediment. Ions were observed up to m/z 600, with ion-current intensities showing distinct periodicity, indicative of dimeric, trimeric and tetrameric coupling products. The most abundant ions in the spectra were at m/z 131, 145 and 159. It was suggested that these ions could be assigned to dihydroquinolines or methylindoles. The authors noted that the nitrogen content of the sediment was too low for it to be composed entirely of methylindoles. Although it was not stated in the paper, presumably the same arguement would apply if the ions were actually attributable to dihydroquinolines. Qualitative comparison of the spectrum of this sediment with a pyrolysis/field ionisation mass spectrum of the coupling product formed in a reaction of tetrahydroquinoline with dihydroxynaphthalene led these authors to suggest that "methylindoles are probably coupling with phenolic and other acidic components in the fuel to form the sediments". No further evidence was given to support this rather speculative suggestion which therefore must be open to question.

Wright, Kalinoski, Udseth and Smith[33] used supercritical fluid extraction (SFE) followed by mass spectrometry (MS) to analyse sediments from petroleum diesel fuel which had been stored at 80°C for 14 days. The spectra of material obtained at the maximum extraction pressure, 415 atmospheres, indicated ions attributable to alkylindoles and alkylcarbazoles, together with a series of homologous ions centred at m/z 353, 468, 524 and 796. The presence of less abundant ions forming a second homologous series between m/z 440 and 600, 6 Daltons lighter than the major series, was noted. Since naturally occurring porphyrins show similar fragmentation characteristics under chemical ionisation conditions it was suggested that there may be structural similarities between porphyrins and fuel sediments. SFE/MS analysis of sediments from similar storage tests of shale-derived diesel fuel doped with various pyrrolic nitrogen compounds indicated that they were composed of oxidation products of alkylpyrroles, since ions attributable to alkylpyrrole-aldehydes and alkylpyrrole-CH_2OH together with oxidised dimers and trimers of the alkylpyrrole additives were observed. These spectra showed none of the structural features evident in the spectra of the sediment from petroleum-derived diesel fuel.

Infrared spectroscopy has been used by Power[34] to investigate the reasons for the continued failure of the tests currently used to predict the storage stability of middle distillate fuels. The spectra of sediments formed during ambient aging of blends of catalytically cracked and straight run diesel fuel contained strong absorptions attributable to skeletal aromatic C=C stretching vibrations of aromatic ethers ($1610cm^{-1}$) and to C-O stretching vibrations of aromatic ethers ($1300-1050cm^{-1}$), together with C-H stretching vibrations ($3000-2800cm^{-1}$) and broad hydrogen bonded O-H or N-H streching vibrations ($3250cm^{-1}$). By comparison, absorptions attributable to carbonyl vibrations ($1700cm^{-1}$) were of relatively low intensity. Spectra of sediments formed during accelerated aging of the same fuels showed similar features, but the extent of oxidation at carbon atoms and the proportion of oxygenated aromatics was lower than for sediments produced during ambient fuel storage, shown by comparison of the relative intensities of C-H to aromatic C=C(-O) and aromatic C-O absorptions. These results confirm that the products of accelerated aging are not the same as those of ambient aging. The poor predictions of high temperature aging tests are therefore not surprising. Power[34] suggested, on the basis of infrared data, that sediments formed during ambient storage might contain aromatic nuclei extensively crosslinked by ether bridges formed by phenolic oxidative coupling reactions. However he claimed that other polymerisation mechanisms may be important since spectra similar to those described above have been obtained for a phenol-dihydroxynaphthalene-formaldehyde copolymer, synthesised as a model for coal structures.

In a related piece of work, Hazlett and Power[35] extracted an unstable catalytically cracked fuel with aqueous sodium hydroxide and then added the organic part of the extract (after acidification and re-extraction into dichloromethane) to stable straight run and hydrotreated catalytically cracked fuels. These were stored at 65°C and 80°C for periods which were thought to be equivalent to two years at ambient temperatures. It was shown that the caustic extract consisted predominantly of alkyl phenols, naphthols and phenyl phenols. Small amounts of aromatic thiols were also detected in the extract, but their estimated concentration of 14 ppm was considered too low to be of significance. Analysis by infrared spectroscopy again pointed to phenolic oxidative coupling during fuel aging being responsible for the increased amounts of deposits formed in the test fuels.

Hazlett, Power, Kelso and Solly[36] have studied the effect of acids and bases on the stability of middle distillate fuels. Blends of catalytically cracked and straight run diesel fuel were used in storage tests carried out at 65°C and 80°C. The influence of four acids, decanoic, furoic (isomer unspecified), chloroethanoic and dodecylbenzenesulphonic acid (isomer unspecified), on the formation of sediment was found to depend on their acid strength as indicated by ionisation constants measured in aqueous solution. Thus decanoic acid exerted the least effect and dodecylbenzenesulphonic acid the greatest effect. The authors noted that although the extent of ionisation of these acids in fuel would be less than in water, their results indicated that acid strength in aqueous solution was a useful guide to their relative strengths in fuel. The carboxylic acids were thought to act catalytically, as a function of their effective hydrogen ion concentration, since no chlorine was detected in sediments produced using chloroethanoic acid as a promoter. However it was suggested that the sulphonic acid contributed directly to sediment formation as well as acting catalytically since the sulphur content of sediments promoted by this acid was enhanced. Thiophenol, although a very weak acid in aqueous systems, was found to be an effective promoter of sediment formation. This was explained by suggesting that a small proportion of the thiophenol was converted to benzenesulphonic acid during the test period. A proprietary stability additive containing a tertiary amine was found to reduce the amount of sediment formed in the storage tests. The mechanism of its action was thought to be by modification of the acidity of the medium rather than inhibition of free radical reactions or suppression of the catalytic activity of metals present in the fuels.

Detailed analyses of diesel fuels and blended components, before and after aging, have been carried out by Bahn, Green, Brinkman and Carley[38,37] in an attempt to detect differences which could be related to their storage stability characteristics. Five fuels covering a range of stabilities were stored at 65°C. It was concluded that oxidation of hydrocarbons in fuel to polar intermediates, for example the formation of ketones from partially hydrogenated or methylene bridged aromatic hydrocarbons, may be a major pathway for sediment formation and darkening of diesel fuels. Polar compounds originally present in fuel, such as hydroxyaromatics and aromatic amines, and those formed by oxidation reactions were lost from the fuel during aging, presumably by becoming incorporated into sediments. The most reactive compounds in a given class were usually those with highest relative molecular mass and greatest aromatic character. An exception to this was that indoles were found to be more active than carbazoles in fuel instability.

1.2.8 **Summary**

Several different reaction mechanisms have been suggested in the literature to account for the formation of sediments during the storage of unstable middle distillate fuels. However it is extremely difficult to compare results of middle distillate fuel stability studies since the chemical compositions of these fuels vary depending on the crude source and the refinery techniques used in processing. In addition, many authors do not draw clear distinctions between results obtained at temperatures below approximately 50°C which are relevant to storage stability and results obtained at higher temperatures which are relevant to accelerated testing or thermal stability measurements. Nonetheless there are four very basic conclusions which are common to almost all the studies carried out:

(i) unstable fuels can be stabilised by extraction with strong alkali.

(ii) of the sulphur compounds present in fuel, aromatic thiols and sulphonic acids are the most detrimental to stability.

(iii) of the nitrogen compounds present in fuel, pyrroles and indoles, are the most detrimental to stability.

(iv) the reactions which lead to sediment formation during fuel storage at ambient temperatures cannot simply be accelerated by raising the temperature.

The most informative results in the literature are those in which the chemical composition of fuel sediments has been investigated. Using this approach Frankenfeld and Taylor[28] have shown that some of the reactions which give rise to sediment formation in shale liquids containing high levels of nitrogen can be simulated in model systems containing 2,5-dimethylpyrrole. However it is also clear that such model systems do not produce sediments similar to those obtained from unstable petroleum derived middle distillate fuels. A proven model simulation of these latter sediments has not yet been reported in the literature.

1.3 Project Introduction

The aim of this study was to identify chemical processes involved in sediment formation during storage of petroleum derived diesel fuel. An understanding of these processes could be applied both to the development of tests to predict storage stability and to the development of additives to improve diesel fuel stability.

Most previous work has been based on studying the effect of spiking pure compounds, suspected of contributing to sediment formation, into either model fuel systems or otherwise stable fuels. Clearly, to validate experiments of this type, it is essential to demonstrate that the reactions taking place in artificial systems truly represent the reactions which occur during storage of "naturally" unstable fuel. However few workers have reported corroborating results of this type to support their use of model systems to investigate fuel storage stability.

Bahn, Brinkman, Green and Carley[38] recently described studies based on an alternative approach. They analysed fuels in detail before and after aging in an attempt to identify compounds involved in fuel degradation reactions. However, despite noting changes in the concentration of certain fuel components during fuel storage, they concluded that the effectiveness of the approach was limited by the magnitude and complexity of analysis required to detect small changes in the concentration of minor diesel fuel components.

The present study differed from those reported previously since it included a detailed analysis of sediment formed during storage of unstable diesel fuel. This analysis was carried out for two reasons. First, with a knowledge of the chemical composition of the reaction products (sediment), it ought to be possible to deduce the identity of the reactants (fuel components). Therefore, subsequent fuel analysis could be targeted for detection and monitoring of specific compounds, implicated in fuel instability by their presence in sediment. Second, the analytical data characterising the fuel sediment forms a reference point against which products of model systems can be assessed, thereby ensuring that model systems do actually simulate fuel instability.

In order to minimise analytical complications caused by variations in the detailed composition of diesel fuels, the results described here relate only to the storage stability of unstable diesel fuel produced from a single UK oil refinery.

The three stage approach used in this study can be summarised as follows:

(i) analysis of sediment produced during the storage of an unstable diesel fuel in order to identify compounds which participate in reactions leading to sediment formation;

(ii) analysis of the same unstable diesel fuel, both undegraded and degraded, to detect and monitor compounds identified in stage (i);

(iii) synthesis of "sediment" using model systems followed by analysis and comparison of these with actual fuel sediments

A systematic approach of this type has not previously been described in the literature.

CHAPTER TWO

RESULTS AND DISCUSSION

2.1 Sediment Analysis

2.1.1 Introduction

The aim of this analysis was to identify compounds which contribute to the formation of sediment during storage of an unstable diesel fuel and, in addition, to determine the analytical characteristics of fuel sediment for subsequent comparison with sediment formed in model systems.

2.1.2 Origin of sediment

The sediment analysed in this study was produced during storage of an unstable fuel purchased directly from a UK refinery. The fuel consisted of a 1:9 blend of catalytically cracked (CC) fuel blended with straight run (SR) distillate fuel originating from the North Sea. Properties of the fuel and its unblended components are given in table 2.1.2-1.

Table 2.1.2-1 Properties of the diesel fuel and its unblended CC and SR components

Property	Fuel blend (1:9 CC:SR)	CC	SR
Colour	<1	2.0	<0.5
Density @ 15°C	0.8635	0.9398	0.8550
Distillation IBP (°C)	220	245	207
50% recovery (°C)	294	298	301
90% recovery (°C)	330	350	342
End (°C)	352	362	357
Residue/recovery (%)	0.5/99	3.0/99	1.0/99
Total acidity (mg KOH/g)	0.08	0.01	0.09
Total nitrogen content (ppm)	169	834	95
Basic nitrogen content (ppm)	49	54	48
Total sulphur content (%)	0.28	0.82	0.22
Hydrogen content (%)		10.34	13.03
Aromatic content (%)		69.30	30.75

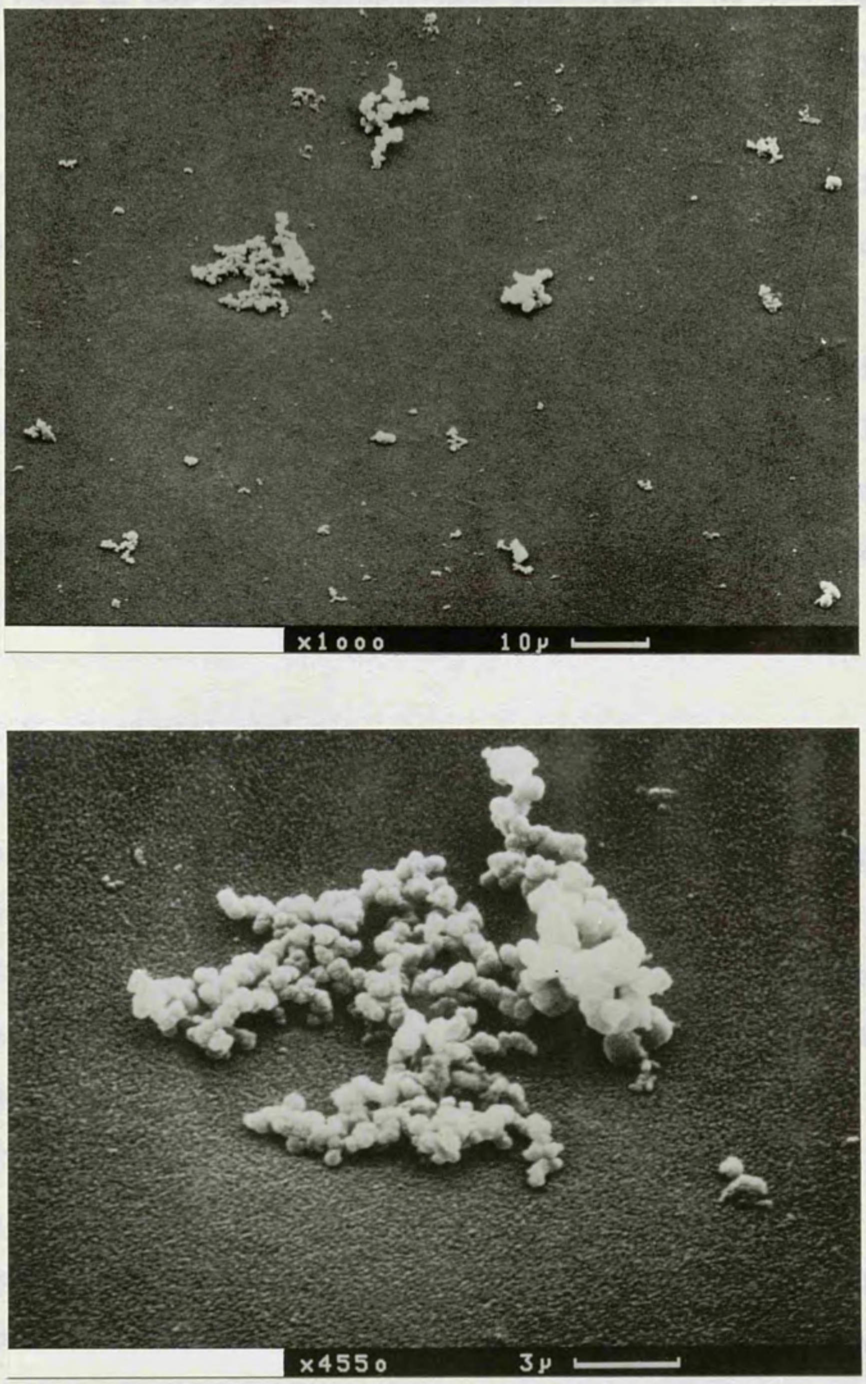
Two thousand gallons of the blended fuel were stored in vented, unlined steel tanks for thirteen months at ambient temperatures. On receipt from the refinery, the fuel was water white in colour and contained no insoluble sediments. The degradation of this fuel was monitored as part of a series of fuel storage stability trials carried out at RAE (Cobham). The fuel began to darken in colour after only six weeks in storage and significant amounts of sediment (> 2mg dm^{-3}) were detected after eight weeks. At the end of the 13 month storage period it was estimated that the total amount of sediment produced by the fuel was in excess of 50mg dm^{-3}. Detailed results of these trials have been published elsewhere[4].

2.1.3 Appearance and physical properties

Sediment particles, collected by filtration of the fuel, were viewed under an electron microscope. Photographs of the electron microscope image are shown in figure 2.1.3-1. Individual sediment particles are less than 1μm in diameter, but they agglomerate to form irregularly shaped "clumps" of up to 20μm in size.

The sediment, a dark coloured powder, was washed with hexane to remove entrained diesel fuel. The solubility characteristics of the sediment were found to be the same as those reported by Offenhauer, Brennan and Miller[10], ie. soluble in chloroform, dichloromethane and acetone/methanol, partially soluble in toluene and insoluble in paraffinic solvents. On heating the sediment decomposed without melting. This observation is also consistent with reports in the literature[10,11]

Figure 2.1.3-1 Sediment particles viewed using a scanning electron microscope



2.1.4 **Soxhlet extraction**

Soxhlet extraction of the sediment, using hexane as solvent, resulted in a weight loss of 15-20%. Concentration of the extract followed by gas chromatography/mass spectrometry (GC/MS) analysis showed it to be composed almost entirely of bicyclic, polycyclic and heterocyclic aromatic compounds with only very low levels of the major fuel components, namely alkanes and alkyl benzenes. This suggested that highly aromatic species were selectively adsorbed from the fuel onto the sediment. Wright, Kalinoski, Udseth and Smith[33] reported that up to 25% of a sediment, produced during storage of diesel fuel at 80°C, was soluble in supercritical pentane. They analysed the pentane extract by mass spectrometry and found that it contained compounds of relative molecular mass up to 400 Daltons. However these compounds were not identified.

2.1.5 **Elemental analysis**

A sample of the sediment, following Soxhlet extraction, was dissolved in dichloromethane and filtered to remove any inorganic contaminants (eg. rust). The solvent was then removed from the filtrate and the sediment was dried. Analysis of the sediment for organic elements showed that it contained 78.6% carbon, 5.9% hydrogen, 3.4% nitrogen, 0.7% sulphur and 11.4% oxygen (by difference). This corresponds to an empirical formula of $C_{27.3}H_{24.6}NS_{0.08}O_3$, normalised to one nitrogen atom.
These figures compare well with published data for other sediments formed during storage of petroleum-derived diesel fuels. The high ratio of carbon to hydrogen in the sediment suggested the presence of unsaturated or possibly aromatic structures. The involvement of nitrogen, and to a lesser extent sulphur compounds in diesel fuel

degradation, indicated by concentration of these elements from the fuel into the sediment, is well known. In this case, the original nitrogen content of the fuel was 169ppm (49ppm basic nitrogen) and the sulphur content was 2800ppm. The concentration factor for the incorporation of nitrogen compounds appeared to be higher than that of sulphur compounds. However this may be misleading since the most abundant sulphur compounds in diesel fuel are thiophene derivatives which are generally thought to be unimportant in sediment forming reactions[9,39]. The figure for the oxygen content of the sediment cannot be taken as absolute since it was not determined directly, but calculated by difference. The trace metal content of the sediment was determined by flameless atomic absorption spectrophotometry. Iron, copper and nickel were found to be present at concentrations of 0.13% w/w, 0.04% w/w and 0.005% w/v respectively. Vanadium could not be detected in the sediment (detection limit 0.000002% w/v).

2.1.6 **Thin layer chromatography**

The sediment was separated into five fractions of differing polarity by normal phase thin layer chromatography (TLC) (mobile phase 10% methanol in dichloromethane). Figure 2.1.6-1 shows the results of this separation.

Figure 2.1.6-1 TLC separation of the sediment

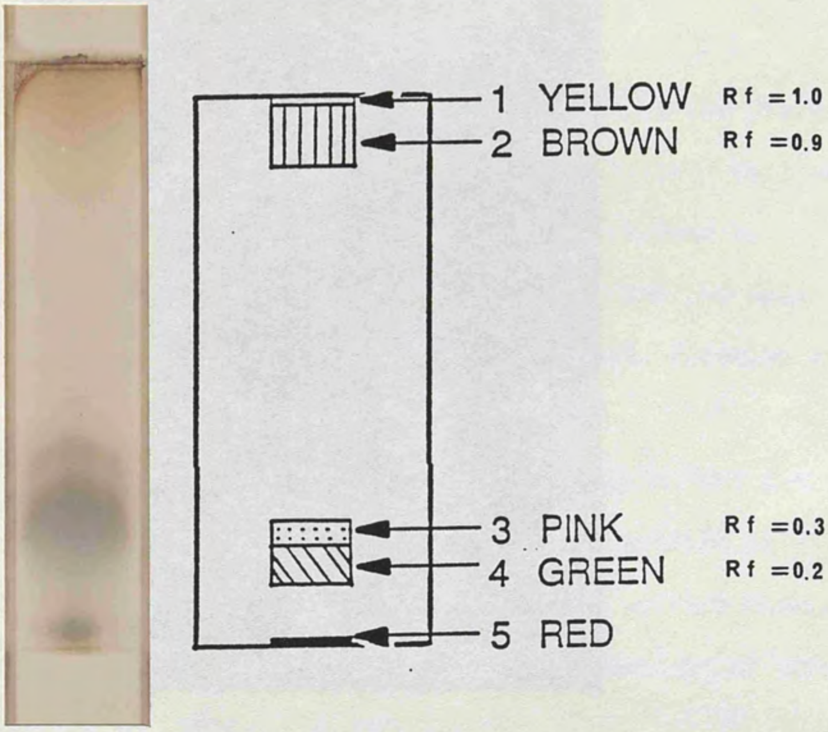
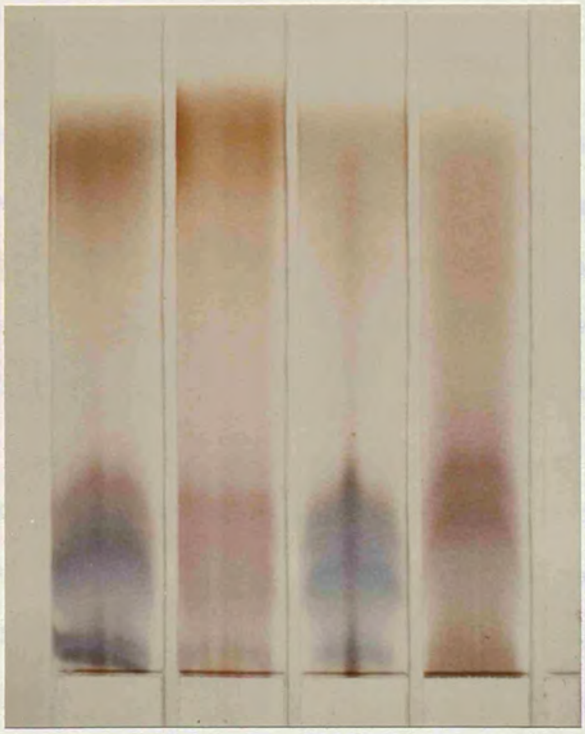


Figure 2.1.6-2 TLC separations of sediments produced during storage of other unstable diesel fuels



Fraction 1 (Rf 1.0) was unretained in the methanol/dichloromethane solvent system. However using toluene as the mobile phase, its Rf decreased to 0.2 and the more polar components of the sediment were then completely retained at the baseline. Fraction 2 (Rf 0.9) consisted of an ill-defined band which was brown in colour. The more polar fractions, 3 (Rf 0.3) and 4 (Rf 0.2) were pink and green/blue in colour respectively.

The photograph of the separation, figure 2.1.6-1, shows the presence of an additional green/blue band just above the baseline. This was in fact an artefact of the separation. It was established by re-chromatographing this material, that it actually had the same retention characteristics as the main green/blue band, fraction 4.

Sediments produced during storage of other diesel fuels were also analysed using this TLC system. They were found to consist of similar mixtures of highly coloured materials. The colours observed include brown, pink, mauve and green. The TLC separations of some of these sediments are shown in Figure 2.1.6-2.

The use of several TLC visualisation techniques, including irradiation with ultra-violet light and spraying with sulphuric acid, indicated that the sediment produced during storage of the CC/SR diesel fuel blend, had only been separated into the five coloured fraction listed in figure 2.1.6-1. However it was noted that fraction 1 changed colour on spraying with a 5% solution of concentrated hydrochloric acid in methanol. The colour change, from yellow to green/blue occurred instantaneously. A similar, though much slower colour change of fraction 1 was observed when the TLC plate was simply left exposed to the laboratory atmosphere for several hours. The Rf of the green/blue acid derived product of fraction 1, in the 10% methanol/dichloromethane solvent system, was found to be 0.2, ie. the same as sediment fraction 4. Acid treatment had no immediate effect on any of the other sediment fractions.

A larger scale liquid chromatography separation of the sediment was carried out in order to prepare a sufficient quantity of each fraction for further analysis. Gravimetric assessment of the fractions collected during this separation indicated that fraction 1 accounted for about 10%, fraction 2 about 25% and fractions 3 and 4 together, about 50% by weight of the sediment. Fraction 5 was irreversibly adsorbed on the stationary phase. This, together with other losses amounted to 15% by weight of sediment applied to the column.

The organic element analysis of fractions 1, 2 and, 3 and 4 combined are given in table 2.1.6-1. The elemental ratios of nitrogen to carbon and sulphur to carbon for the whole sediment and its fractions are given in table 2.1.6-2.

Table 2.1.6-1 Elemental composition of sediment fractions

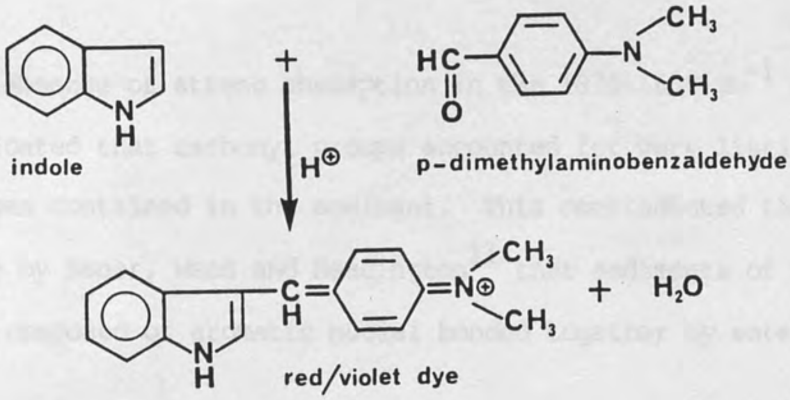
Fraction no.	carbon (%)	hydrogen (%)	nitrogen (%)	sulphur (%)
1	83.6	6.7	4.9	<0.05
2	78.9	5.8	3.4	0.6
3+4	73.5	5.9	3.0	0.5

Table 2.1.6-2 Elemental nitrogen to carbon ratios and sulphur to carbon ratios for the sediment and its fractions

Sample	nitrogen:carbon	sulphur:carbon
Unseparated sediment	1 : 27	1 : 328
Fraction 1	1 : 20	insignificant
Fraction 2	1 : 24	1 : 329
Fraction 3+4	1 : 29	1 : 307

This data showed that the nitrogen content of the sediment was distributed fairly evenly between the fractions, although the highest concentration, relative to carbon, was in fraction 1. The concentration of sulphur was very low in all the fractions, particularly fraction 2.

Fraction 1 was found to give a positive reaction (immediate development of a pink colouration) with Ehrlich´s reagent, commonly used to detect pyrrolic nitrogen compounds which are unsubstituted in the α and/or β positions on the heterocyclic ring[40,41]. The test involves reaction of p-dimethylaminobenzaldehyde (1% w/v solution in methanol-HCl) with, for example, indole to form a coloured salt as indicated in eq. 2.1.6-1[41].



eq. 2.1.6-1

The positive result of this test indicated that pyrrole derivatives accounted for at least some of the nitrogen in fraction 1. The other sediment fractions did not react with Ehrlich´s reagent.

Further analysis of the sediment fractions is described in the following sections.

2.1.7 Infrared spectroscopy

The infrared spectrum (IR) of the sediment, which is shown in figure 2.1.7-1, contained many overlapping absorption bands making detailed structural assignments difficult. However the aromatic nature of the sediment was clearly evident from the characteristic absorptions at 3075, 1625 and 900-750 cm^{-1}. Hydroxyl functional groups probably contributed to the broad absorption centred at 3275 cm^{-1}, which overlapped with another absorption at 3400 cm^{-1}. This spectrum showed a marked similarity to a spectrum of sediment produced during the ambient storage of a diesel fuel, published by Power[34].

The absence of strong absorption in the 1870-1650 cm^{-1} region indicated that carbonyl groups accounted for very little of the oxygen contained in the sediment. This contradicted the suggestion made by Sauer, Weed and Headington[11] that sediments of this type are composed of aromatic nuclei bonded together by ester linkages.

The infrared spectra of sediment fractions 2, 3 and 4 were found to be very similar to the spectrum of the unseparated sediment. However the spectrum of fraction 1, shown in figure 2.1.7-2, contained a prominent absorption at 3400 cm^{-1}. It was noted in section 2.1.6, that fraction 1 gave a positive reaction with Ehrlich´s reagent for partially substituted or unsubstituted pyrrolic nitrogen compounds (eg. pyrrole and indole but not carbazole). The N-H stretching vibration in pyrroles usually occurs in the range 3500-3430 cm^{-1}. The same vibration in indoles is normally observed between 3480 and 3020 cm^{-1}.

Figure 2.1.7.1 Infrared spectrum of the sediment

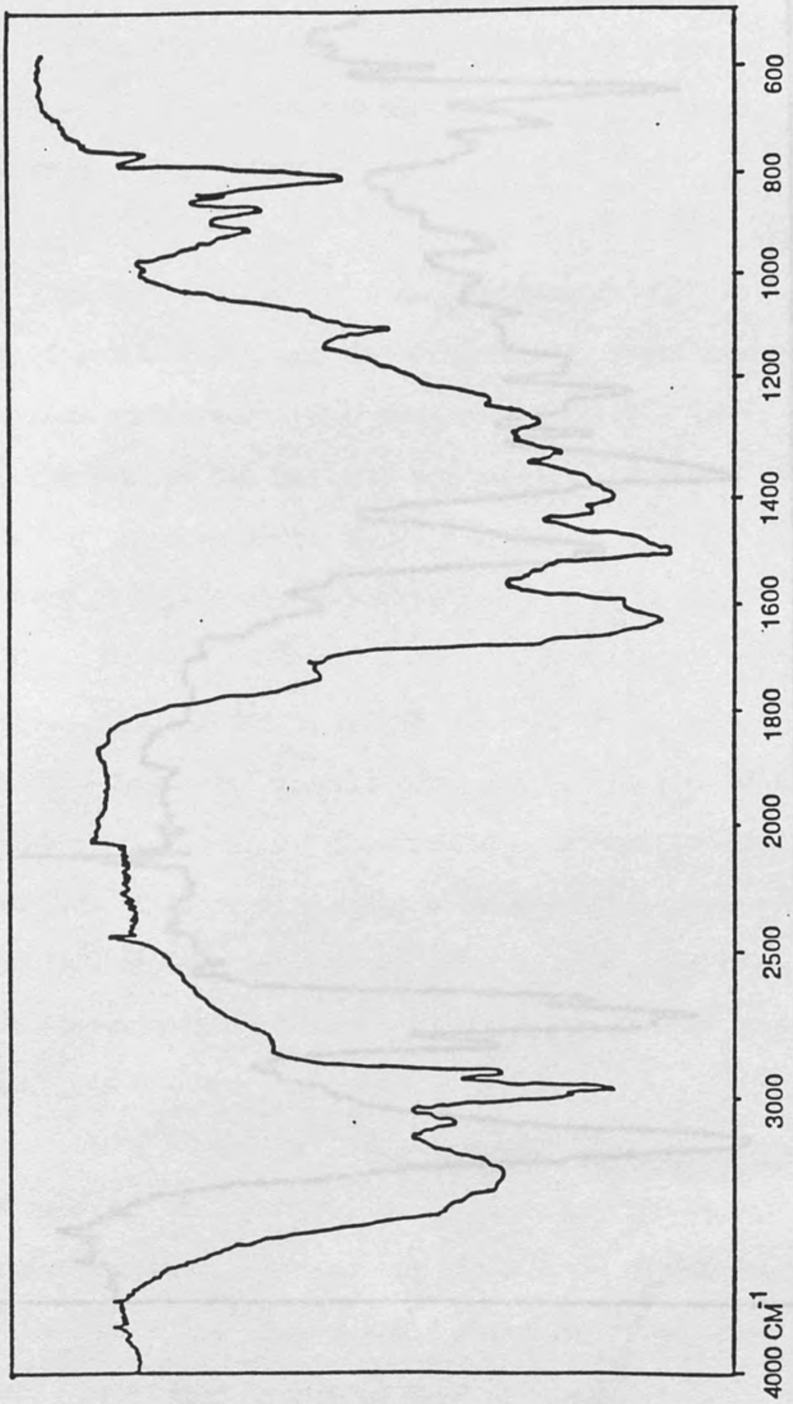
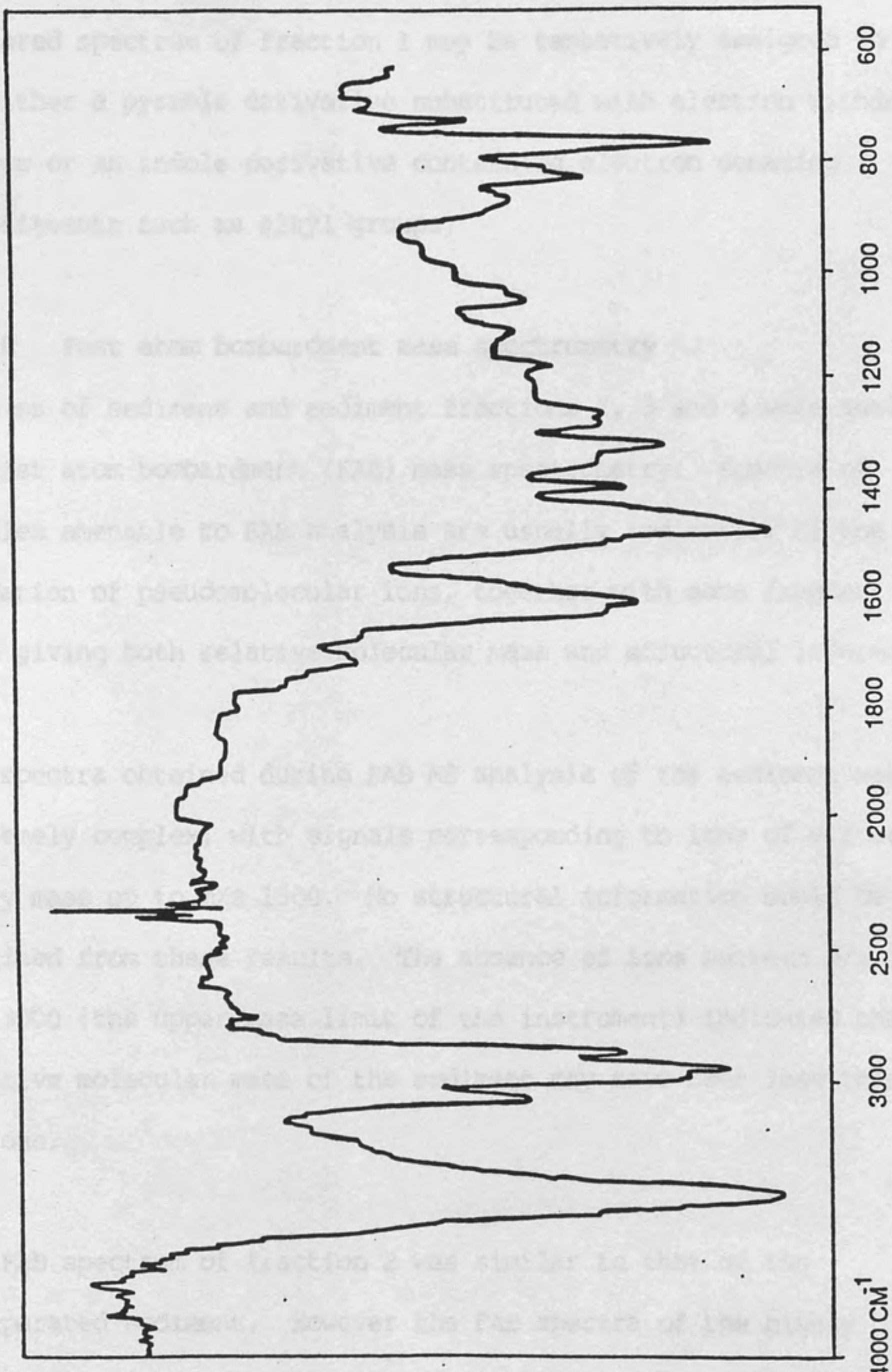


Figure 2.1.7-2 Infrared spectrum of sediment fraction 1



Substitution of both pyrroles and indoles with electron withdrawing groups tends to lower the absorption frequency whereas substitution with electron donating groups tends to raise the absorption frequency[42]. Therefore the absorption at 3400 cm^{-1} in the infrared spectrum of fraction 1 may be tentatively assigned to that of either a pyrrole derivative substituted with electron withdrawing groups or an indole derivative containing electron donating substituents such as alkyl groups.

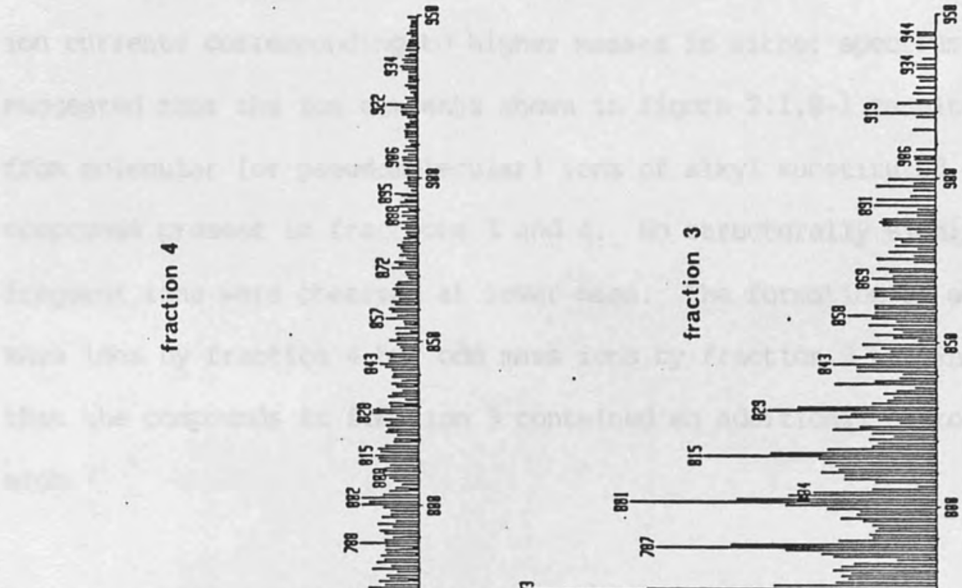
2.1.8 **Fast atom bombardment mass spectrometry**

Samples of sediment and sediment fractions 2, 3 and 4 were analysed by fast atom bombardment (FAB) mass spectrometry. Spectra of samples amenable to FAB analysis are usually indicative of the formation of pseudomolecular ions, together with some fragment ions, thus giving both relative molecular mass and structural information.

The spectra obtained during FAB MS analysis of the sediment were extremely complex, with signals corresponding to ions of virtually every mass up to m/z 1500. No structural information could be obtained from these results. The absence of ions between m/z 1500 and 3000 (the upper mass limit of the instrument) indicated that the relative molecular mass of the sediment may have been less than 1500 Daltons.

The FAB spectrum of fraction 2 was similar to that of the unseparated sediment. However the FAB spectra of the highly coloured sediment fractions 3 and 4 showed some very distinctive features. These spectra are shown in figure 2.1.8-1.

Figure 2.1.8-1 FAB MS spectra of sediment fractions 3 and 4



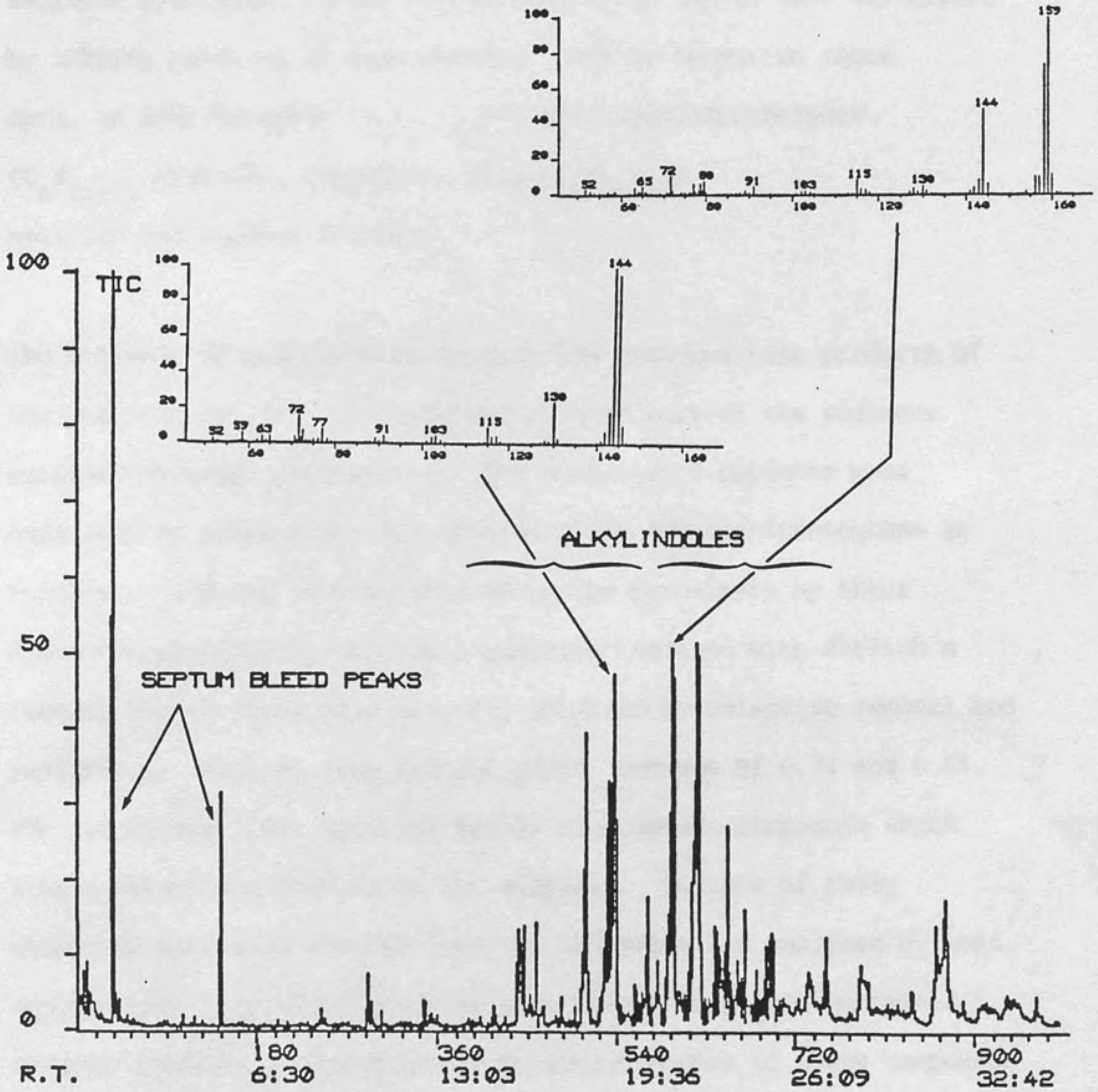
Fraction 3 produced a distinct homologous series of ions with the most abundant ion at m/z 773. Fraction 4 produced a group of ions consisting of at least two homologous series at lower mass. The spacing of 14 Daltons between the most abundant ions in these spectra is characteristic of alkyl homologous series. The lack of ion currents corresponding to higher masses in either spectrum suggested that the ion currents shown in figure 2.1.8-1 resulted from molecular (or pseudomolecular) ions of alkyl substituted compounds present in fractions 3 and 4. No structurally significant fragment ions were observed at lower mass. The formation of even mass ions by fraction 4 but odd mass ions by fraction 3 may indicate that the compounds in fraction 3 contained an additional nitrogen atom.

2.1.9 **Pyrolysis/gas chromatography/mass spectrometry**

The aim of the pyrolysis experiments described in this and the following section was to obtain qualitative information about the identity or composition of the sediment.

The total ion chromatogram showing the separation of sediment pyrolysis products is illustrated in figure 2.1.9-1. It is clear from the chromatogram that a significant proportion of the pyrolysis products were not resolved during the GC analysis. It was not possible to interpret the composite mass spectra of co-eluting species which were recorded in the latter part of the chromatogram. However the largest peaks in the chromatogram, were identified as corresponding to alkylindoles ($C_nH_{2n-9}N$ n=9-12). Mass spectra of two of these are shown in figure 2.1.9-1.

Figure 2.1.9-1 GC/MS total ion chromatogram of sediment pyrolysis products
(GC temperature programme, 2 min. @ $35^{\circ}C$, $35-250^{\circ}C$ @ $8^{\circ}C$/min., 5 min. @ $250^{\circ}C$)



The mass spectra of 11 alkylindoles have been reported by Beynon and Williams[44]. Powers[45] has reported mass spectra of the 7 isomers of methylindole. It is clear from their work that there are only very small differences between the spectra of isomeric alkylindoles. Consequently it was not possible to definitively assign the substitution patterns of the alkylindoles produced by sediment pyrolysis. Other minor pyrolysis products were identified by library matching of mass spectra[43] and GC retention index data, as alkylbenzenes (C_nH_{2n-6} n=7-10), alkylnaphthalenes (C_nH_{2n-12} n=10-12), alkylcarbazoles ($C_nH_{2n-15}N$ n=12-14) and sulphur dioxide.

The presence of alkylindoles amongst the decomposition products of the sediment was further confirmed by pyrolysis of the sediment outside the mass spectrometer. The condensable products were separated by preparative TLC (mobile phase 40% dichloromethane in toluene). Indoles were identified in the pyrolysate by their characteristic Rf values, their positive reaction with Ehrlich's reagent and by their mass spectra, obtained by selective removal and analysis of material from the TLC plate between Rf 0.74 and 0.86. The pyrolysate also contained highly fluorescent compounds which eluted behind the indoles in TLC analysis. Samples of these compounds were also removed from the TLC plate and analysed by mass spectrometry. It was found that each fluorescent band contained several compounds. The relative molecular masses of these compounds and their fluorescence colours are listed in table 2.1.9-1. The compounds are grouped into homologous series.

Table 2.1.9-1 Relative molecular masses and fluorescence colours of sediment pyrolysis products

TLC Rf	Relative molecular mass	Fluorescence colour
0.80 0.74	131, 145, 159, 173 (alkylindoles)	
0.35	230, 244, 258	pale green
0.33	184, 198, 212, 226 182, 196, 210 208, 222	mauve
0.28	180, 194, 208, 222, 236 182, 196 184, 198, 212, 226	orange
0.25	208, 222, 236	orange
0.16	180, 194, 208, 222 210, 224	green

It was not possible to identify the compounds eluting between Rf 0.35 and Rf 0.16 from these TLC and low resolution MS results.

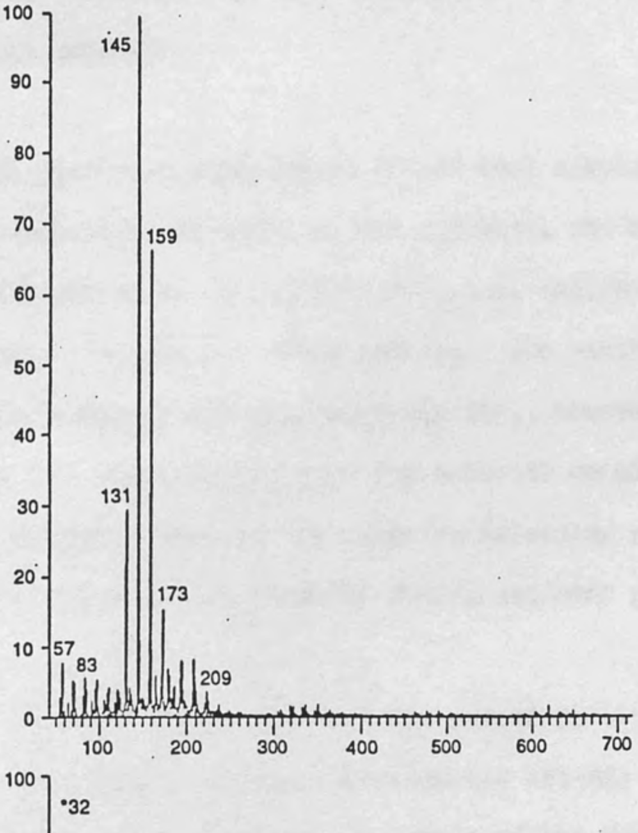
However the presence of intense even mass molecular ions, with little fragmentation other than the formation of M-15 ions, suggested that the compounds contained alkylated hydrocarbon aromatic structures (no nitrogen or an even number of nitrogens). The fact that they were more strongly retained in normal phase TLC than indoles, indicated that they contained a polar, possibly oxygenated, functional group.

2.1.10 **Pyrolysis/mass spectrometry**

This analysis was carried out to find out whether pyrolysis of the sediment produced fragments of higher relative molecular mass than those already observed using pyrolysis/GC/MS. The GC stage in pyrolysis/GC/MS analysis provided the advantage of separation but limited the analysis to relatively volatile pyrolysis products.

Pyrolysis of the sediment directly in the source of the mass spectrometer again showed that the major pyrolytic products were alkylindoles. The spectra did not contain any evidence of the aromatic hydrocarbons observed in the py/GC/MS experiments. However low abundancies of ions of much higher m/z value were observed. These results are illustrated in figure 2.1.10-1. The distribution of the high mass ions into distinct mass clusters, within which ions are separated by 14 Daltons (characteristic of alkyl homologous series) suggested that the sediment consisted of a structured polymeric material. The optimum conditions for the production of these high mass ions were found to be high source temperature (350°C) to minimise condensation and low electron energy to suppress mass spectral fragmentation.

Figure 2.1.10-1 Mass spectra showing alkylindoles and higher relative molecular mass material produced by pyrolysis of the sediment



The fractions of the sediment, prepared by liquid chromatography (ch. 2.1.6) were analysed by pyrolysis/MS. All the fractions produced alkylated indoles on pyrolysis. The spectra contained no other distinctive features and were very similar to the spectrum of the unseparated sediment.

Although these pyrolysis experiments showed that alkylindoles were the major decomposition products of the sediment, the elemental analysis data given in ch. 2.1.5 and ch. 2.1.6, indicated that it could not consist entirely of these species. The ratio of carbon to nitrogen in the sediment was approximately 28:1, whereas a ratio of approximately 10:1 would be required for material consisting simply of an indole polymer (based on the relative molecular mass distribution of alkylindoles produced during sediment pyrolysis).

Malhotra and St.John[32] have described the use of pyrolysis followed by field ionisation mass spectrometry (FI-MS) for the analysis of diesel fuel sediments. A sample of the fuel sediment, which was the subject of this study, was sent to this group for analysis. The pyrolysis/FI-mass spectrum which they obtained is shown in figure 2.1.10-2. This compared well with the spectrum obtained using the pyrolysis/MS system described earlier and shown in figure 2.1.10-1. Both spectra contained ions of the same relative molecular mass, although there are differences in their relative abundancies. This may have been due to the differing pyrolysis conditions and ionisation techniques used in the respective analyses. Examples of pyrolysis/FI-MS spectra of sediments formed in other unstable diesel fuels, reproduced from the work of Malhotra and St.John[32], are shown in figure 2.1.10-3.

Figure 2.1.10-2 Pyrolysis/FI-mass spectrum of the sediment

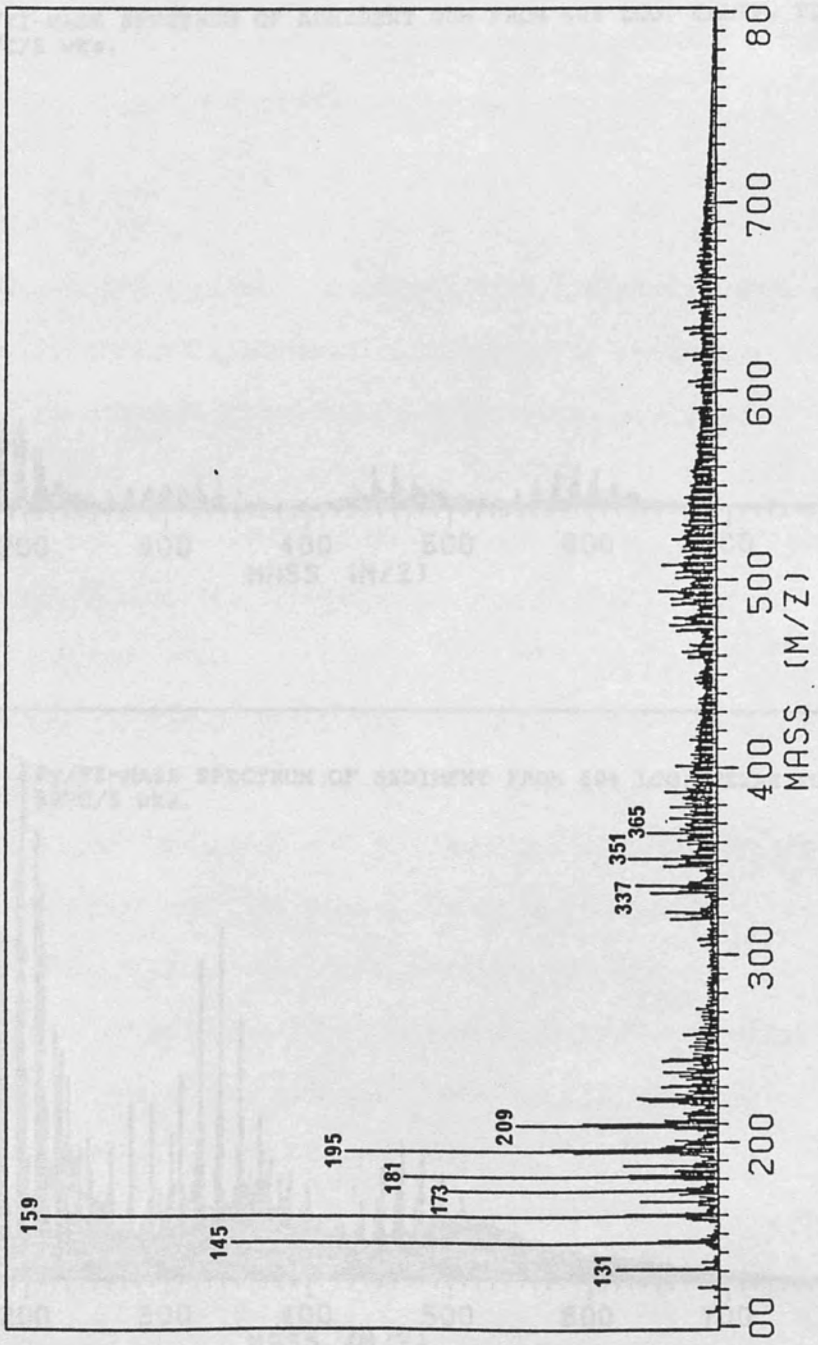
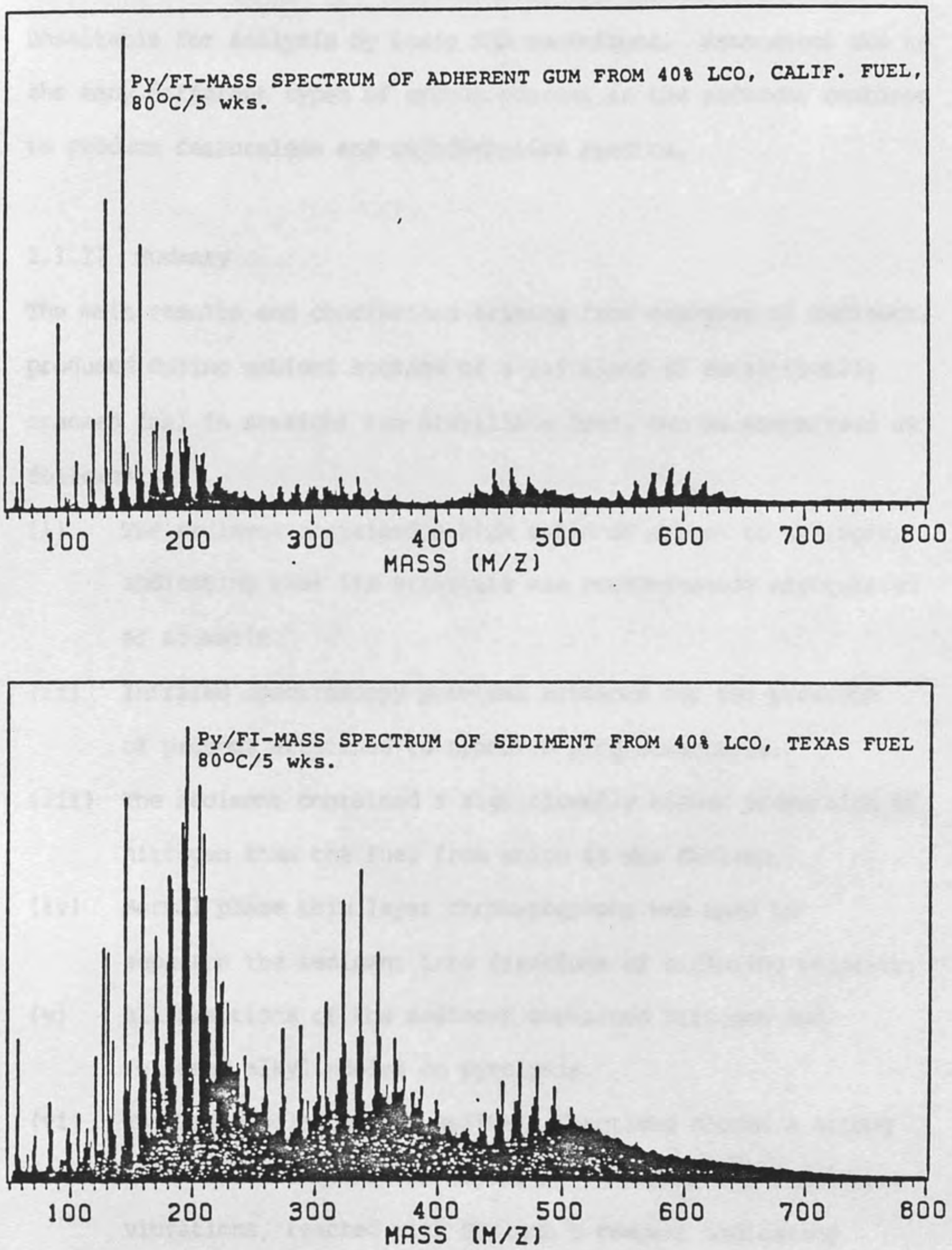


Figure 2.1.10-3 Pyrolysis/FI-mass spectra of sediment and adherent gum originating from other unstable diesel fuels[32]



2.1.11 **Proton nuclear magnetic resonance spectroscopy**

Deuterochloroform solution spectra did not yield any useful structural information about the nature of the sediment or its component fractions. The complexity of the sediment made it unsuitable for analysis by basic NMR techniques. Resonances due to the many different types of proton present in the sediment combined to produce featureless and uninformative spectra.

2.1.12 **Summary**

The main results and conclusions arising from analysis of sediment, produced during ambient storage of a 1:9 blend of catalytically cracked fuel in straight run distillate fuel, can be summarised as follows:

(i) The sediment contained a high ratio of carbon to hydrogen, indicating that its structure was predominantly unsaturated or aromatic.

(ii) Infrared spectroscopy provided evidence for the presence of protons attatched to aromatic ring structures.

(iii) The sediment contained a significantly higher proportion of nitrogen than the fuel from which it was derived.

(iv) Normal phase thin layer chromatography was used to separate the sediment into fractions of differing polarity.

(v) All fractions of the sediment contained nitrogen and released alkylindoles on pyrolysis.

(vi) The least polar of the sediment fractions showed a strong infrared absorbance corresponding to indole N-H stretching vibrations, reacted with Ehrlich´s reagent indicating that it contained at least one proton α or β to the pyrrolic nitrogen group and reacted with acids to produce a green/blue material with the same TLC and IR characteristics as the more polar components of the sediment.

(vii) Infrared spectroscopy showed that, contrary to suggestions in the literature, ester linkages did not contribute significantly to the structure of the sediment.

(viii) Fast atom bombardment mass spectrometry indicated that the relative molecular mass of the sediment itself and particularly its more polar components was less than 1500 Daltons.

(ix) Although alkylated indoles appeared to be the major decomposition products of the sediment, it did not consist simply of an indole polymer, analogous to the oxidised polymeric pyrrole sediments found in shale-derived liquids[28], since the atomic ratio of C:N in the sediment was found to be approximately 28:1 compared with a value of 10:1 expected for a polymerised indole material (based on the relative molecular mass distribution of indoles produced during pyrolysis)

(x) The production of sulphur dioxide and aromatic hydrocarbons in pyrolysis/GC/MS experiments and polar aromatic hydrocarbons in pyrolysis/TLC/MS experiments indicated that these species, along with alkylated indoles, contributed to the structure of the sediment.

The analytical data presented in this chapter did not lead directly to the assignment of the structure of the diesel fuel sediment. However the results did provide a basis for further study, since they gave an indication of the compounds in diesel fuel which combine together to form sediment.

2.2 Fuel Analysis

2.2.1 Introduction

The unstable diesel fuel was analysed in order to detect and identify fuel components involved in reactions leading to sediment formation. The following sections describe;

(i) the detection and identification of alkylindoles in the unstable diesel fuel

(ii) a storage test using nitrogen compounds selectively extracted from the unstable fuel

(iii) the identification of fuel species, other than alkylindoles, which contributed to sediment formation.

2.2.2 Analysis of diesel fuel using gas chromatography

The unstable diesel fuel consisted of a 1:9 blend of catalytically cracked (CC) fuel and straight run (SR) fuel of North Sea origin. Some physical and chemical properties of the fuel and its unblended components were shown earlier in table 2.1.2-1. Unblended samples of the SR fuel and CC fuel were analysed using high resolution capillary gas chromatography in order to survey their general chemical composition and in particular to examine the distribution of nitrogen containing compounds in the two fuels.

A flame ionisation detector (FID) was used for universal detection. A thermionic ionisation nitrogen/phosphorus detector (NPD) and a flame photometric detector (FPD) were used for selective detection of nitrogen and sulphur containing compounds respectively. Williams, Bartle, Mills and Andrews[46] have recently described capillary GC analysis of aromatic fractions of diesel fuels using simultaneous parallel triple detection. They used two two-way effluent splitters so that flame ionisation, nitrogen/phoshporus and sulphur selective detectors could be used concurrently. In the experiments described here, although all three detectors were fitted on the same gas chromatograph, the analyses were carried out by transferring the column to each detector in turn. The GC operating conditions were kept constant for all the analyses described in this section to allow direct comparison of results.

Figure 2.2.2-1 shows the FID, NPD and FPD chromatograms obtained from capillary GC analysis of the SR fuel. Table 2.2.2-1 lists the identification of the chromatographic peaks highlighted in figure 2.2.2-1. Compounds were identified using an unpublished library of retention index and mass spectral data collated at RAE, Cobham. The major constituents of this fuel, shown in the FID trace were found to be n-alkanes, ranging from C_8H_{18} to $C_{25}H_{52}$. The chromatographic peaks numbered 11 and 13 corresponded to the isoprenoid compounds, pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) respectively. These are well known examples of "biological marker compounds" which are derived from marine organisms and characteristically occur in fossil fuels such as petroleum[47]. The n-alkanes, together with lower concentrations of branched and cycolalkanes, made up almost 70% by weight of the fuel and accounted for all the resolved, plus some unresolved peaks in the FID chromatogram.

Figure 2.2.2-1 GC analysis of SR fuel with FID (top), NPD (middle) and FPD (bottom) detection.

Peak identification given in table 2.2.2-1.

(GC temperature programme, 1 min. @ 50°C, 50-270°C @ 6°C/min., 3 min. @ 270°C)

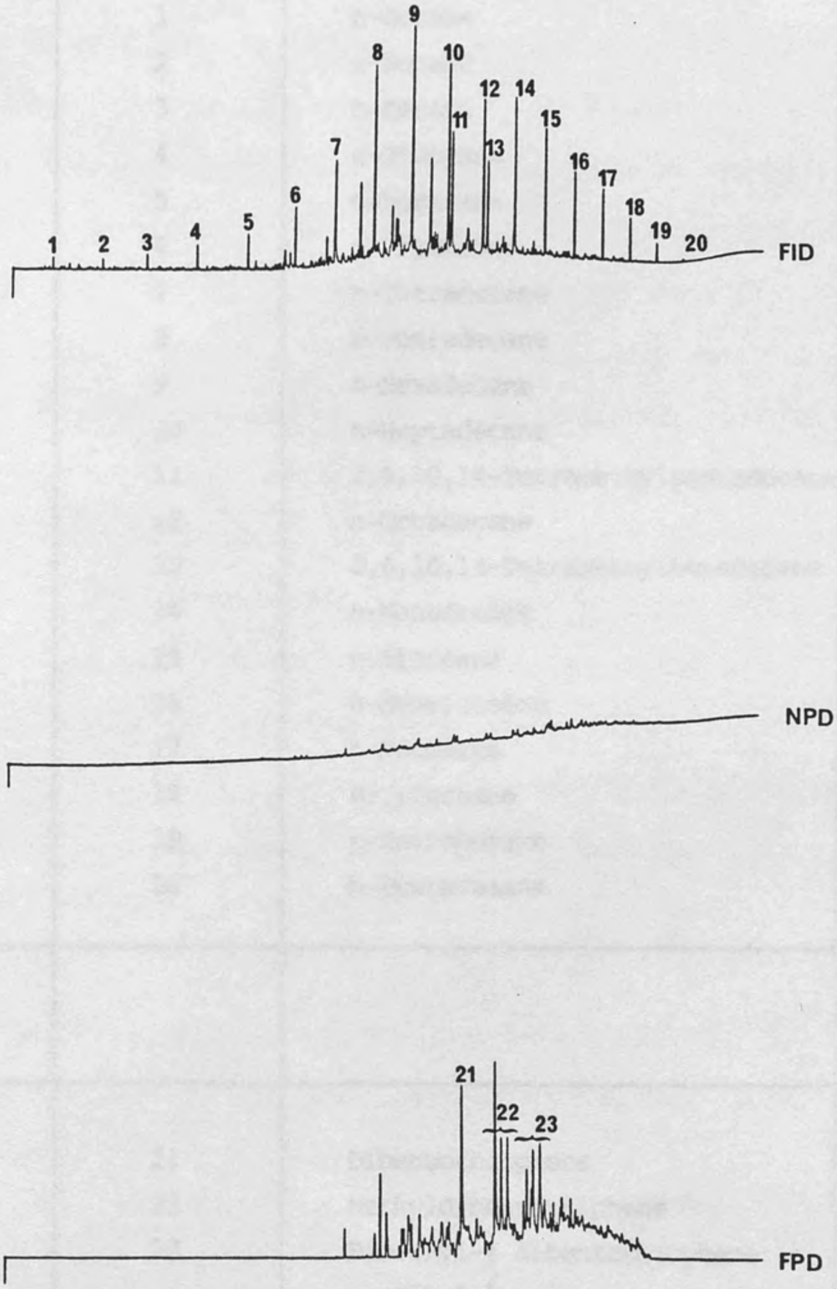


Table 2.2.2-1 Identification of compounds detected in GC analysis of SR fuel (see figure 2.2.2-1)

Detector	Peak number	Identification
FID	1	n-Octane
	2	n-Nonane
	3	n-Decane
	4	n-Undecane
	5	n-Dodecane
	6	n-Tridecane
	7	n-Tetradecane
	8	n-Pentadecane
	9	n-Hexadecane
	10	n-Heptadecane
	11	2,6,10,14-Tetramethylpentadecane
	12	n-Octadecane
	13	2,6,10,14-Tetramethylhexadecane
	14	n-Nonadecane
	15	n-Eicosane
	16	n-Heneicosane
	17	n-Docosane
	18	n-Tricosane
	19	n-Tetracosane
	20	n-Pentacosane
NPD		
FPD	21	Dibenzothiophene
	22	Methyldibenzothiphene
	23	Dimethyl-} dibenzothiophene Ethyl-}

Aromatic compounds, alkylbenzenes, alkylnaphthalenes and higher aromatics accounted for 30.75% by weight of the fuel (table 2.1.2-1), but individual compounds of this type were not resolved into discrete peaks in the FID chromatogram. The total concentration of nitrogen in the straight run fuel was low, only 95ppm. This was clearly reflected by the weak response of the NPD detector to this fuel, as shown in figure 2.2.2-1. Titration measurements indicated that about 50% of the nitrogen in this fuel was associated with basic nitrogen compounds such as aromatic amines and pyridine derivatives. The distribution of sulphur compounds in this fuel is illustrated by the FPD chromatogram shown in figure 2.2.2-1. Dibenzothiophene and its alkyl homologues were the only compounds in this chromatogram which were positively identified. Wenzel and Aiken[48] were one of the first groups to describe the use of GC with FPD detection to study the distribution of thiophenic sulphur compounds in petroleum fuels. Their analyses differed from those reported here, in that other sulphur compounds, such as sulphides, disulphides and mercaptans, were removed from the fuel prior to GC analysis, by passing the fuel over an alumina catalyst at 500°C to decompose non-thiophenic sulphur compounds to hydrogen sulphide.

Figure 2.2.2-2 illustrates the results of a similar FID, NPD and FPD GC analysis of the CC fuel, with chromatographic peak identifications given in table 2.2.2-2.

Figure 2.2.2-2 GC analysis of CC fuel with FID (top), NPD (middle) and FPD (bottom) detection. Peak identification given in table 2.2.2-2. (GC temperature programme, 1 min. @ 50°C, 50-270°C @ 6°C/min., 3 min. @ 270°C)

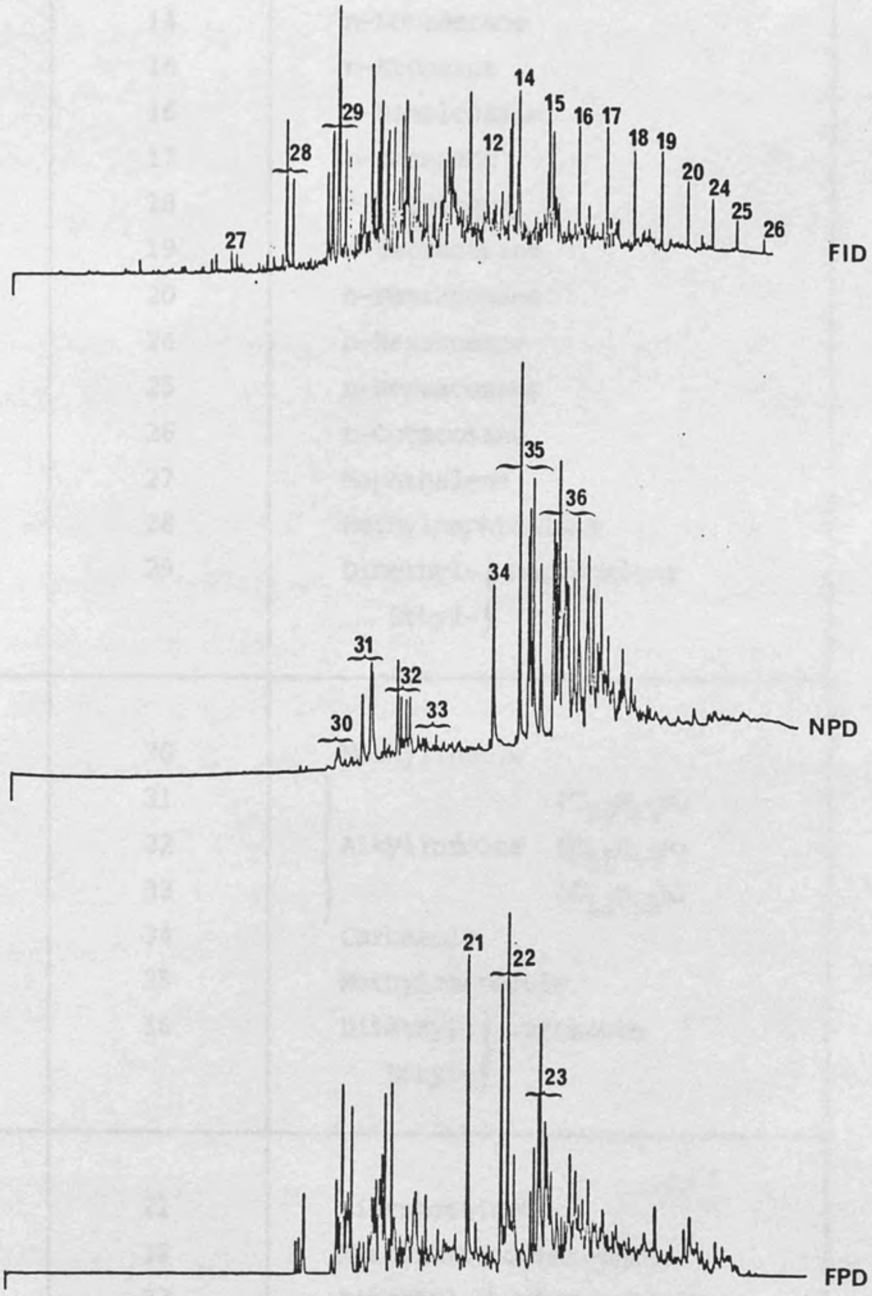


Table 2.2.2-2 Identification of compounds detected in GC analysis of CC fuel (see figure 2.2.2-2)

Detector	Peak number	Identification
FID	12	n-Octadecane
	14	n-Nonadecane
	15	n-Eicosane
	16	n-Heneicosane
	17	n-Docasane
	18	n-Tricosane
	19	n-Tetracosane
	20	n-Pentacosane
	24	n-Hexacosane
	25	n-Heptacosane
	26	n-Octacosane
	27	Naphthalene
	28	Methylnaphthalene
	29	Dimethyl- naphthalene Ethyl-
NPD	30	Methylindole
	31	Alkylindoles ($C_{10}H_{11}N$)
	32	($C_{11}H_{13}N$)
	33	($C_{12}H_{15}N$)
	34	Carbazole
	35	Methylcarbazole
	36	Dimethyl- carbazole Ethyl-
FPD	21	Dibenzothiophene
	22	Methyldibenzothiophene
	23	Dimethyl- dibenzothiophene Ethyl-

The FID trace was much more complicated than that of the SR fuel. Only the higher molecular weight unbranched alkanes were discernible as discrete, well separated peaks in the chromatogram. The complex mixture of compounds which eluted in the middle part of the chromatogram consisted predominantly of isomeric alkylnaphthalenes (C_nH_{2n-12} n=11-13). Reference to table 2.1.2-1 shows that the nitrogen content of this fuel was almost nine times higher than that of the SR fuel. The most intense peaks in the NPD chromatogram of the CC fuel were found to be attributable to alkylindoles, carbazole and alkylcarbazoles, as listed in table 2.2.2-2. Titration measurements showed that basic nitrogen compounds, such as aromatic amines and pyridine derivatives, accounted for only about 6% by weight of the nitrogen content of the fuel. No GC peaks were assigned to compounds of this type. The FPD chromatogram shows that the CC fuel contained a complex mixture of sulphur compounds. Dibenzothiophene and alkyl homologues of dibenzothiphene, previously identified in the SR fuel, were also detected in this fuel. However the isomeric distributions of alkyldibenzothiophenes in the two fuels were quite different as shown by comparison of the two FPD chromatograms in figures 2.2.2-1 and 2.2.2-2.

These results, not surprisingly, showed that there were significant differences in the detailed composition of the SR and CC fuels. The nitrogen content of the CC fuel was much higher than that of the SR fuel, and it was found to be predominantly attributable to alkylindoles and alkylcarbazoles. The presence of alkylindoles in the CC fuel was particularly significant, since it had already been shown (ch. 2.1) that these compounds formed part of the structure of sediment produced during storage of a SR/CC fuel blend. In order to establish whether or not alkylindoles were also present in the SR fuel and to study their distribution in the CC fuel in more detail, a simple liquid chromatography procedure was developed to extract and concentrate these compounds from diesel fuel.

2.2.3 **Extraction of alkylindoles from diesel fuel using liquid chromatography**

A fraction of the CC fuel containing alkylindoles was prepared using the extraction scheme illustrated in figure 2.2.3-1. The first fuel fraction collected in this extraction procedure, fraction 1, was analysed by GC with FID, NPD and FPD detection. The results of this analysis are shown in figure 2.2.3-2. Comparison of these chromatograms with those of the whole CC fuel, illustrated in figure 2.2.2-2, showed that fraction 1 contained all the major fuel components, alkanes and alkylnaphthalenes, together with all the sulphur compounds previously detected using the FPD detector. However the absence of peaks in the NPD chromatogram clearly illustrated that the nitrogen compounds, including alkylindoles, had been retained on the LC column and therefore separated from the bulk of the fuel. Fraction 2, eluted with a 1:1 mixture of hexane and dichloromethane, was collected in $20cm^3$ portions. These were analysed by normal phase TLC (mobile phase 40% toluene in hexane). The eluent portions which contained compounds with Rf values characteristic of alkylindoles and alkylcarbazoles (0.43 -0.57 in this system) and which also gave a positive reaction with Ehrlich´s reagent (specific for pyrroles and indoles, though not 2,3 disubstituted derivatives) were combined and concentrated to form fraction 3. This was analysed by GC with FID, NPD and FPD detection and the results are shown in figure 2.2.3-3.

Figure 2.2.3-1 Extraction procedure used to prepare CC fuel fractions 1, 2 and 3.

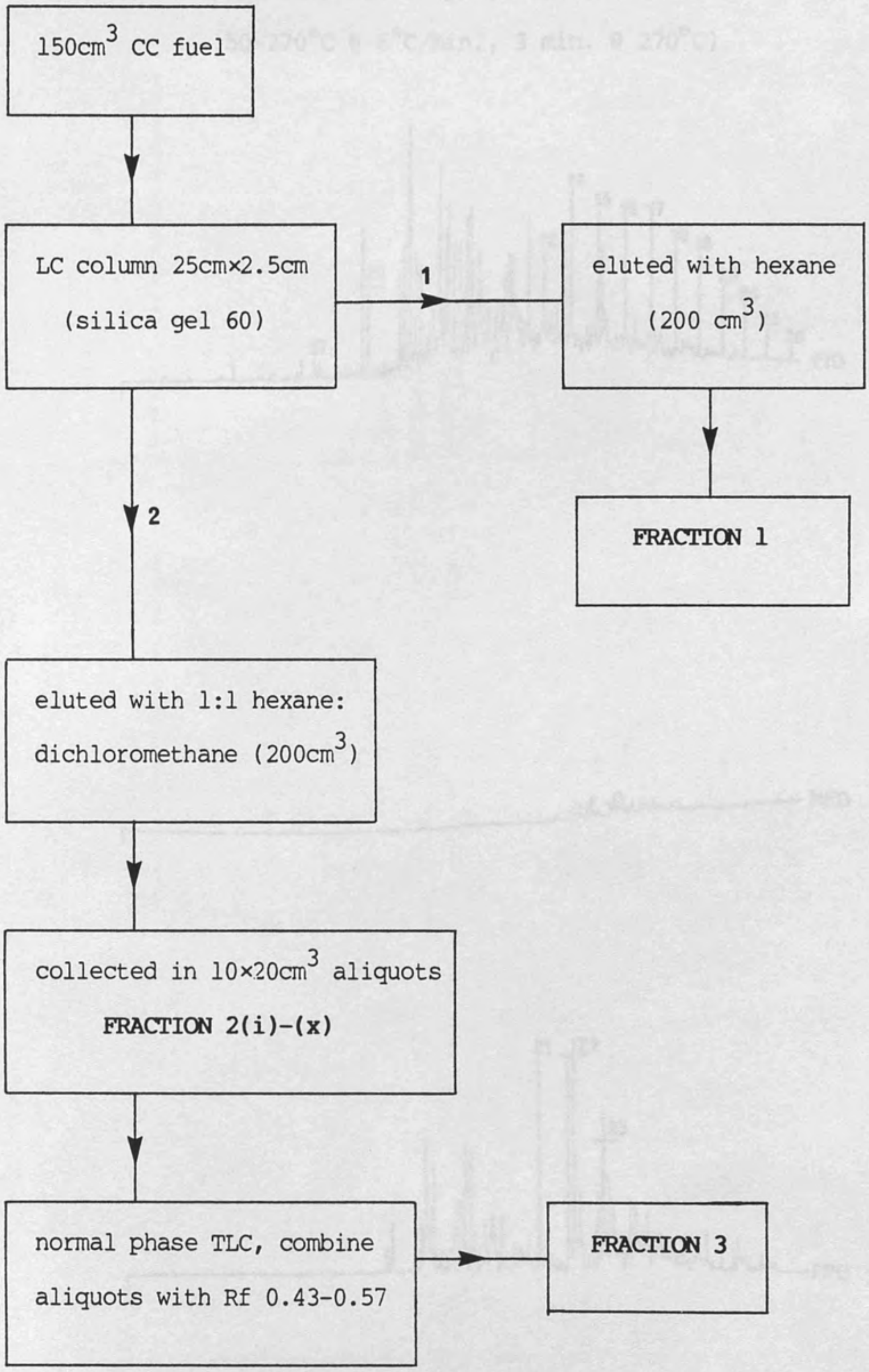


Figure 2.2.3-2 GC analysis of CC fuel fraction 1 with FID (top), NPD (middle) and FPD (bottom) detection. Peak identification given in table 2.2.2-2. (GC temperature programme, 1 min. @ 50°C, 50-270°C @ 6°C/min., 3 min. @ 270°C)

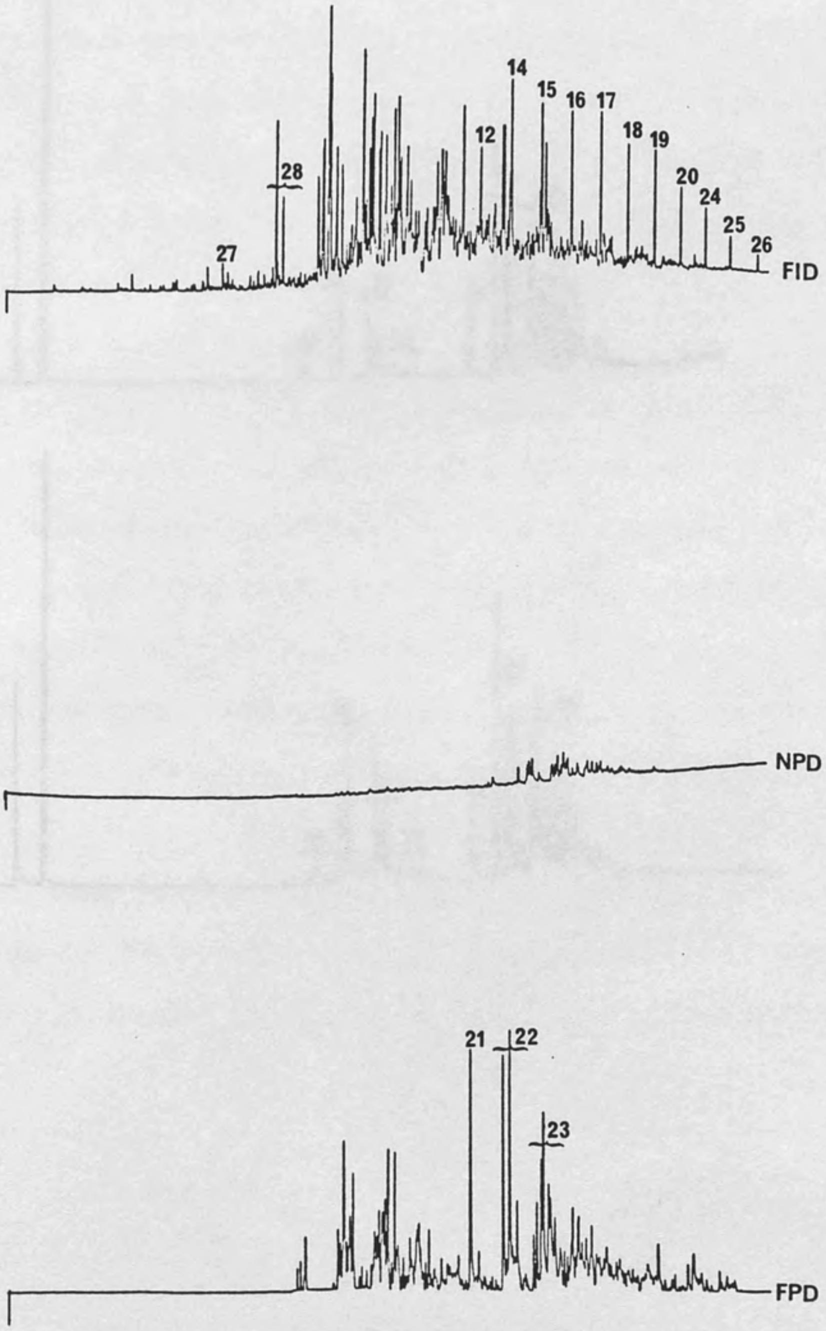
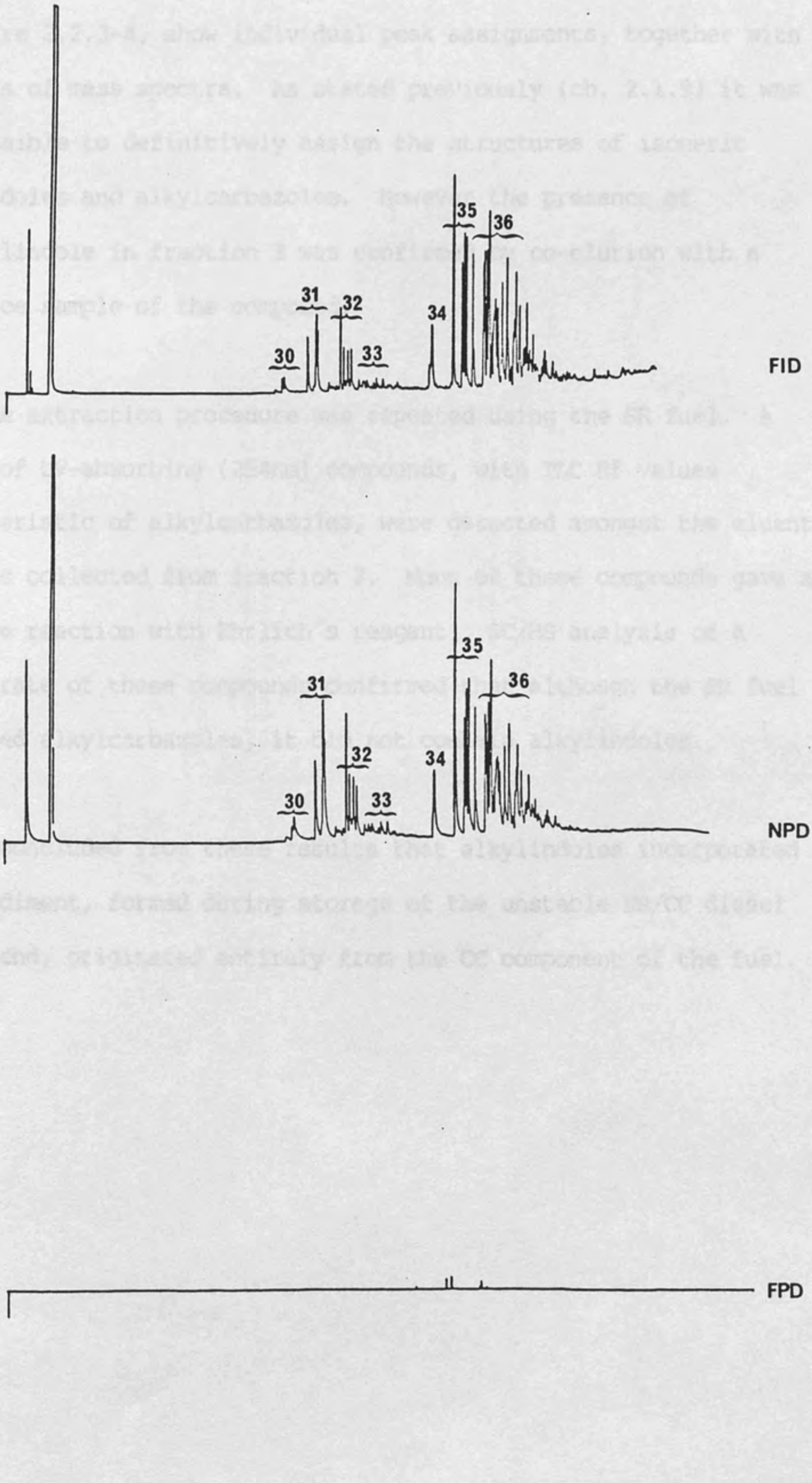


Figure 2.2.3-3 GC analysis of CC fuel fraction 3 with FID (top), NPD (middle) and FPD (bottom) detection. Peak identification given in table 2.2.2-2. (GC temperature programme, 1 min. @ 50°C, 50-270°C @ 6°C/min., 3 min. @ 270°C)



The close similarity of the FID and NPD traces and the lack of peaks in the FPD trace, confirmed that fraction 3 consisted almost entirely of compounds containing nitrogen. Fraction 3 was analysed in detail by GC/MS. Figure 2.2.3-4 shows the total ion chromatogram of fraction 3, whilst figures 2.2.3-5 and 2.2.3-6, expanded versions of figure 2.2.3-4, show individual peak assignments, together with examples of mass spectra. As stated previously (ch. 2.1.9) it was not possible to definitively assign the structures of isomeric alkylindoles and alkylcarbazoles. However the presence of 2-methylindole in fraction 3 was confirmed by co-elution with a reference sample of the compound.

The same extraction procedure was repeated using the SR fuel. A series of UV-absorbing (254nm) compounds, with TLC Rf values characteristic of alkylcarbazoles, were detected amongst the eluent portions collected from fraction 2. None of these compounds gave a positive reaction with Ehrlich´s reagent. GC/MS analysis of a concentrate of these compounds confirmed that although the SR fuel contained alkylcarbazoles, it did not contain alkylindoles.

It was concluded from these results that alkylindoles incorporated into sediment, formed during storage of the unstable SR/CC diesel fuel blend, originated entirely from the CC component of the fuel.

Figure 2.2.3-4 GC/MS total ion chromatogram of CC fuel fraction 3.
(GC temperature programme, 2min. @ 100°C, 100-270°C @ 4°C/min., 5 min. @ 270°C)

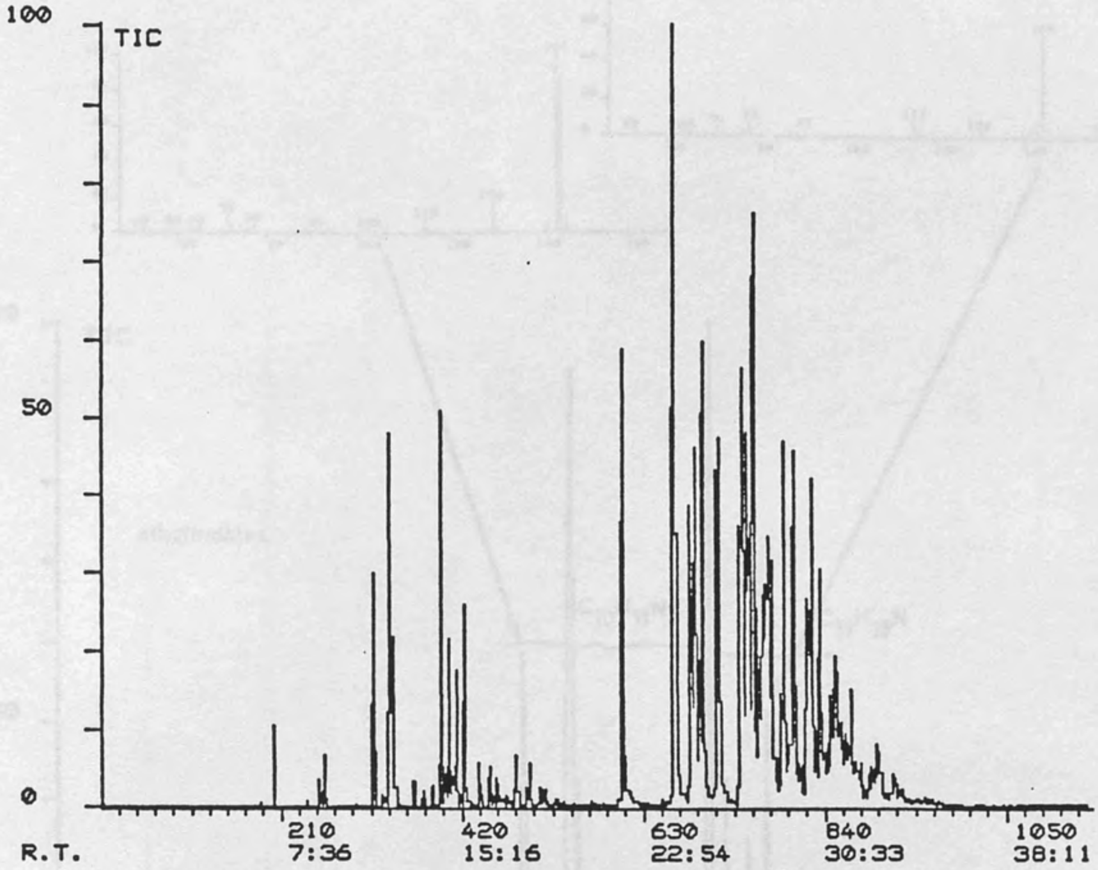


Figure 2.2.3-5 GC/MS total ion chromatogram of CC fuel fraction 3, showing elution of indoles.

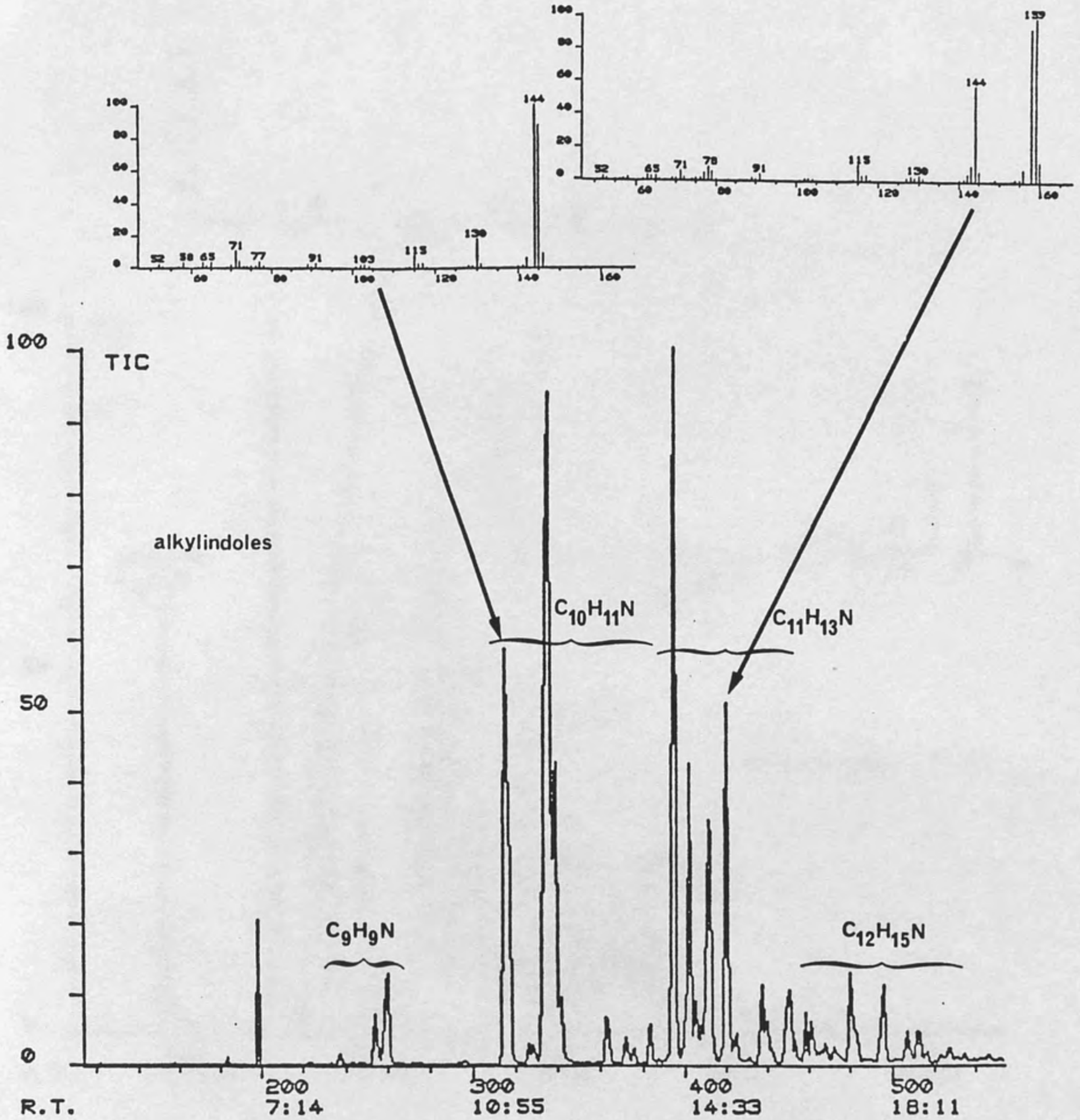
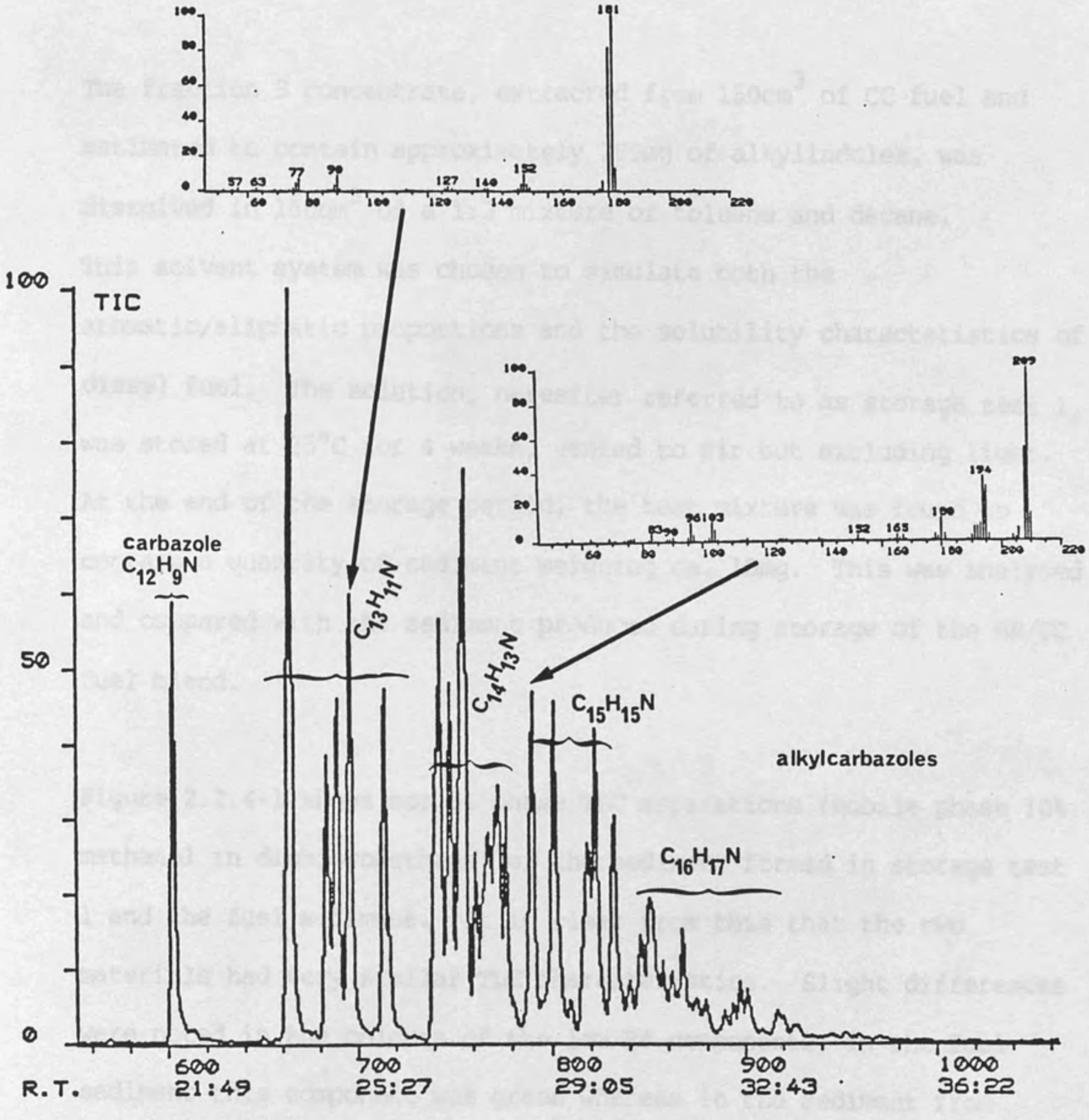


Figure 2.2.3-6 GC/MS total ion chromatogram of CC fuel fraction 3, showing elution of carbazoles.



2.2.4 Storage tests using fraction 3 of the CC fuel

A series of speculative experiments were carried out to observe the effect of storing nitrogen compounds extracted from the CC fuel in hydrocarbon solvents. This was an attempt to simulate diesel fuel instability using a simplified model fuel system containing some of the compounds known to be involved in sediment formation.

The fraction 3 concentrate, extracted from $150cm^3$ of CC fuel and estimated to contain approximately 300mg of alkylindoles, was dissolved in $150cm^3$ of a 1:3 mixture of toluene and decane. This solvent system was chosen to simulate both the aromatic/aliphatic proportions and the solubility characteristics of diesel fuel. The solution, hereafter referred to as storage test 1, was stored at 25°C for 4 weeks, vented to air but excluding light. At the end of the storage period, the test mixture was found to contain a quantity of sediment weighing ca. 10mg. This was analysed and compared with the sediment produced during storage of the SR/CC fuel blend.

Figure 2.2.4-1 shows normal phase TLC separations (mobile phase 10% methanol in dichloromethane) of the sediment formed in storage test 1 and the fuel sediment. It is clear from this that the two materials had very similar TLC characteristics. Slight differences were noted in the colours of the low Rf components; in the fuel sediment this component was green whereas in the sediment from storage test 1, it was blue/green. The storage test 1 sediment also contained slightly more material which did not move from the TLC baseline. The mass spectrum of the pyrolysis products of the sediment produced in storage test 1, shown in figure 2.2.4-2,

Figure 2.2.4-1 TLC separation of sediment produced in storage test 1 (left) and the fuel sediment (right)

Figure 2.2.4-2 Mass spectrum of pyrolysis products of storage test 1 sediment

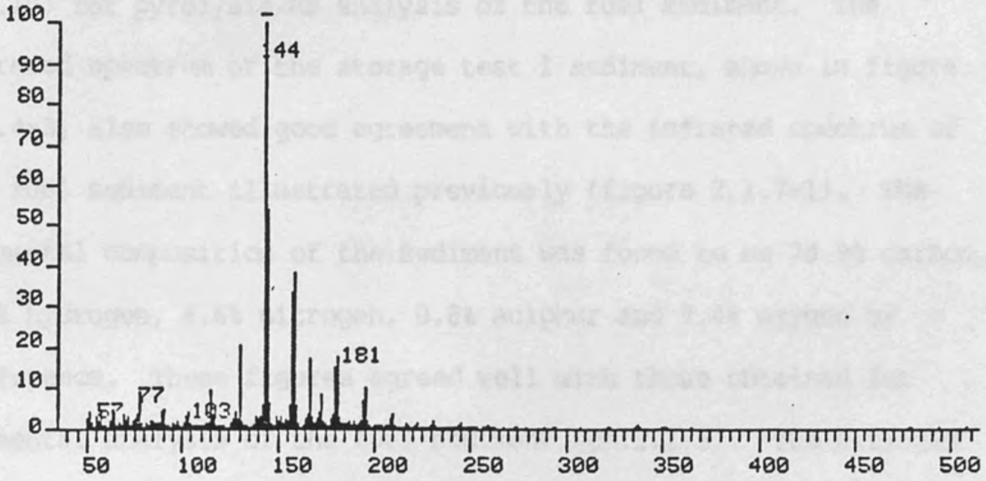
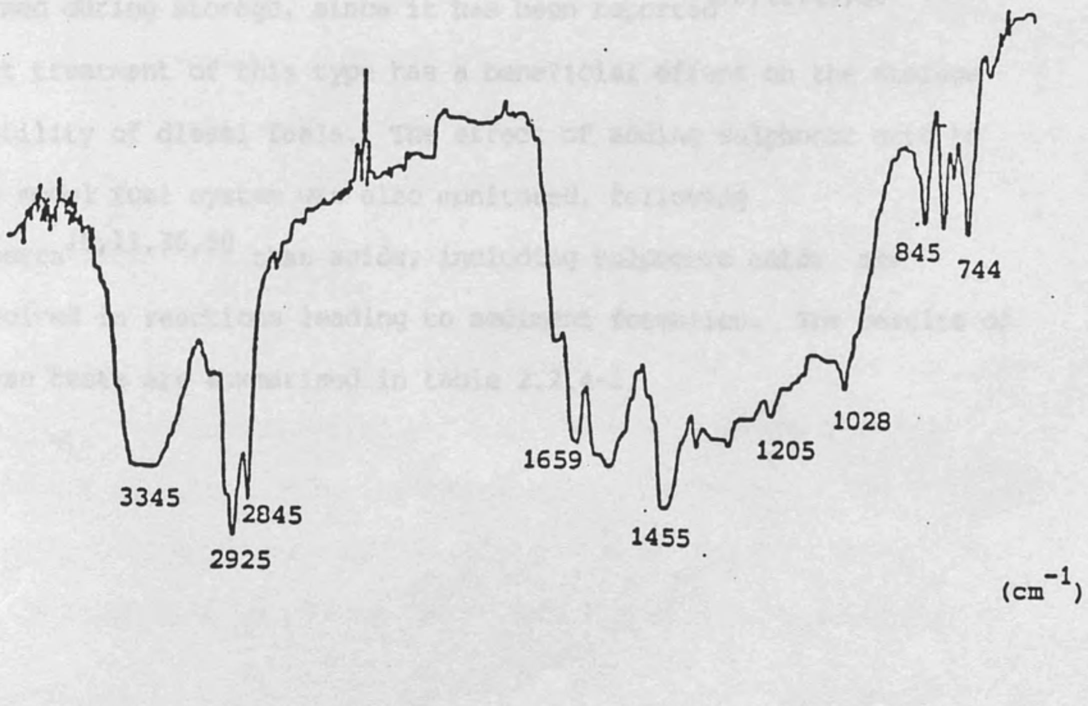


Figure 2.2.4-3 Infrared spectrum of storage test 1 sediment



was dominated by ion-currents attributed to alkylindoles. Very low ion currents occurred in the spectrum at higher relative molecular masses. Similar spectral features were noted previously (ch. 2.1.10) for pyrolysis/MS analysis of the fuel sediment. The infrared spectrum of the storage test 1 sediment, shown in figure 2.2.4-3, also showed good agreement with the infrared spectrum of the fuel sediment illustrated previously (figure 2.1.7-1). The elemental composition of the sediment was found to be 78.9% carbon, 6.4% hydrogen, 4.6% nitrogen, 0.8% sulphur and 9.4% oxygen by difference. These figures agreed well with those obtained for elemental analysis of the fuel sediment (ch.2.1.5). The nitrogen content of this sediment was slightly higher than that of the fuel sediment but still considerably lower than that of alkylindoles (typically ca. 10%).

Storage test 1 was repeated, and further tests were carried out in order to observe whether extraction of the solution of fraction 3 in toluene/decane (1:3) with base would reduce the amount of sediment formed during storage, since it has been reported[10,11,49,50] that treatment of this type has a beneficial effect on the storage stability of diesel fuels. The effect of adding sulphonic acid to the model fuel system was also monitored, following reports[10,11,36,50] that acids, including sulphonic acids, are involved in reactions leading to sediment formation. The results of these tests are summarised in table 2.2.4-1.

Table 2.2.4-1 Results of model fuel system storage experiments (all tests stored for 4 weeks at 25°C in the dark, vented to air)

Test number	Composition of storage test	Weight of precipitate
1	CC fuel fraction 3 in 150cm^3 toluene/decane (1:3)	10mg
2	CC fuel fraction 3 in 150cm^3 toluene/decane (1:3) extracted with 40% sodium hydroxide	<0.1mg
3	CC fuel fraction 3 in 150cm^3 toluene/decane (1:3) extracted with 40% sodium hydroxide plus 3mg (20ppm) 2-naphthalene sulphonic acid	11.7mg

These results clearly showed that removal of acidic species from the model fuel system inhibited sediment formation whereas deliberate addition of sulphonic acid promoted sediment formation. The sediment formed in test 3, ie. sulphonic acid addition, was analysed by TLC and found to consist almost entirely of the low Rf blue/green component of the sediment formed in test 1. It was later noted that addition of mineral acids, such as hydrochloric acid, to fraction 3 of the CC fuel also promoted rapid formation of the blue/green component of the sediment. It was considered likely therefore that sediment formation in test 1 was promoted by trace levels of HCl which were almost certainly present in the dichloromethane solvent used to extract fraction 3 from the CC fuel.

From these results, it was concluded that fraction 3 of the CC fuel contained species which, when dissolved in decane/toluene and stored at room temperature in the dark for 4 weeks, reacted to form an insoluble material with analytical characteristics consistent with those of the fuel sediment produced by a blend of the CC SR fuels. The reactions were inhibited by removing acidic compounds and promoted by addition of acids to the system. Although it has already been established that alkylindoles and alkylcarbazoles made up the bulk of fraction 3, only about 3% by weight of this fraction was converted to insoluble material during storage test 1. In addition, although pyrolysis experiments showed that the sediment contained alkylindoles, its nitrogen content was too low for it to be composed entirely of such compounds. These observations suggested that fraction 3 contained low levels of hitherto unidentified compounds which participated in reactions leading to the formation of sediment.

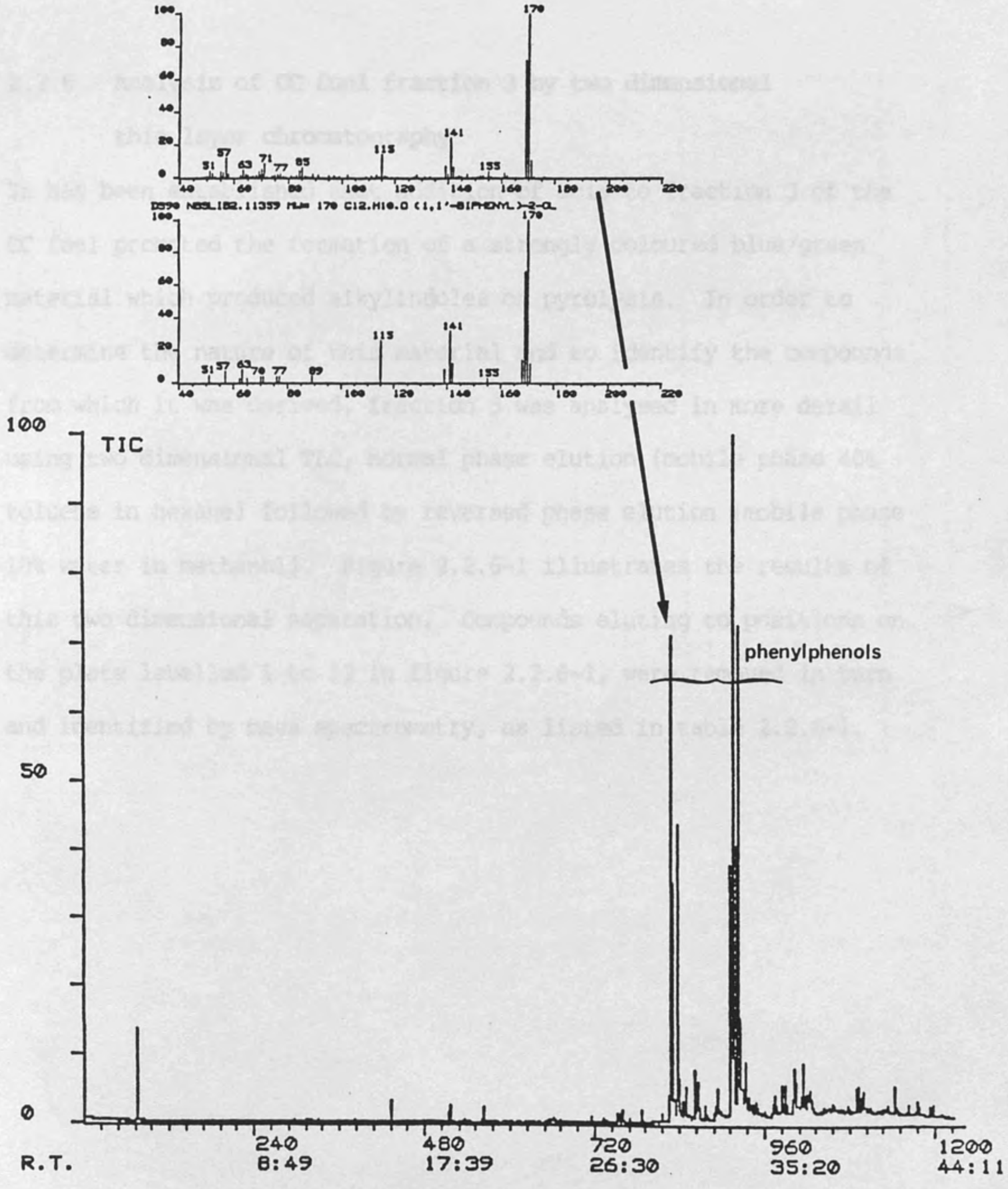
The following sections describe a more detailed analysis of fraction 3, aimed at detecting and identifying such species.

2.2.5 Analysis of organic acids extracted from CC fuel fraction 3

The CC fuel fraction 3 was extracted with 40% aqueous sodium hydroxide to ensure complete removal of acidic compounds. After acidification of the aqueous phase with hydrochloric acid, the organic compounds, hereafter refered to as fraction 3(a), were extracted into dichloromethane and concentrated.

Analysis of fraction 3(a) by normal phase TLC, using a variety of different mobile phases, showed that it consisted entirely of compounds with similar, though on average slightly more polar, retention characteristics to those of alkylindoles. Analysis of the fraction by GC/MS revealed the presence of three homologous series of compounds, which were identified by library matching of mass spectra[43] as alkylphenylphenols ($C_nH_{2n-14}O$, n=12-14) together with much smaller amounts of alkylphenols ($C_nH_{2n-6}O$, n=6-9) and alkylnaphthols ($C_nH_{2n-12}O$, n=11-12). Figure 2.2.5-1 shows the total ion chromatogram of fraction 3(a) and the mass spectrum of one of the chromatographic peaks, an unsubstituted phenylphenol together with the mass spectrum its library match (1,1′-biphenyl)-2-ol. This identification was confirmed by GC and TLC retention measurements with an authentic sample.

Figure 2.2.5-1 GC/MS total ion chromatogram of CC fuel fraction 3(a)
(GC temperature programme, 2 min. @ 30°C, 30-270°C @ 4°C/min., 5 min. @ 270°C)

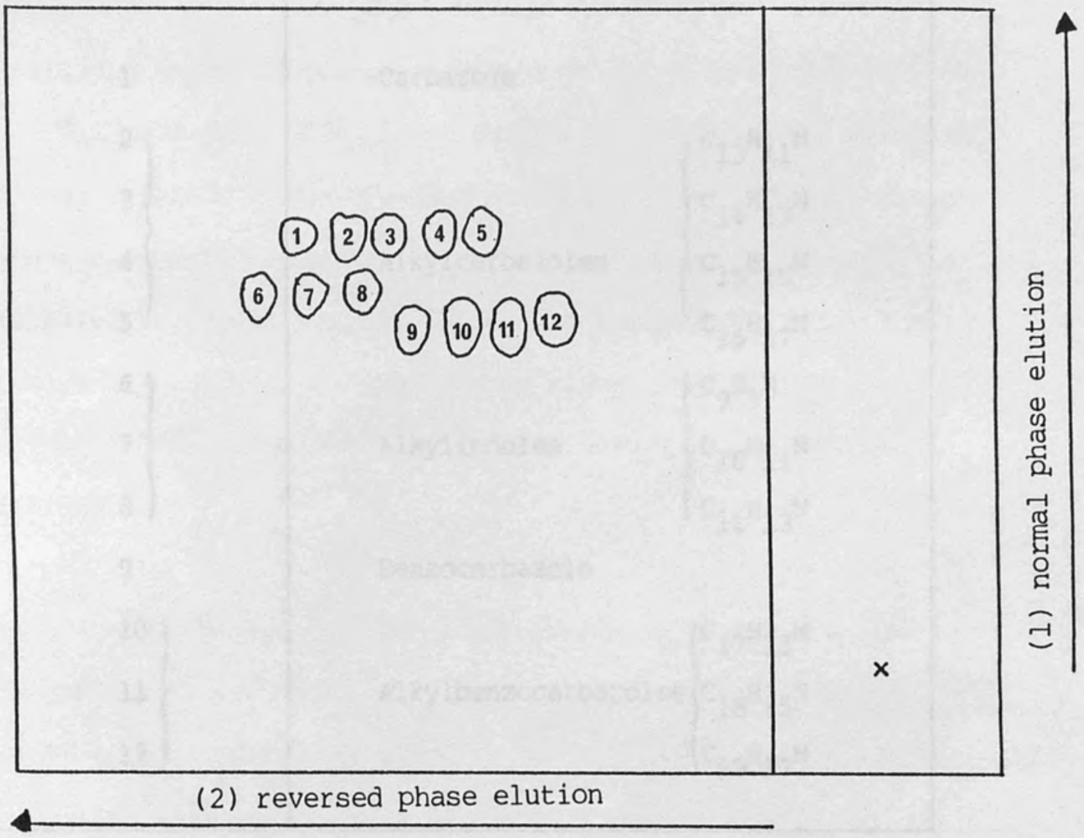


The presence of trace amounts of these compounds in fraction 3 and the observation that fraction 3 was stabilised after their removal, does not necessarily implicate them in sediment formation. The possibility still remained (ch. 2.2.4) that trace acid impurities originating from solvents contributed to sediment formation in storage test 1.

2.2.6 **Analysis of CC fuel fraction 3 by two dimensional thin layer chromatography**

It has been established that addition of acid to fraction 3 of the CC fuel promoted the formation of a strongly coloured blue/green material which produced alkylindoles on pyrolysis. In order to determine the nature of this material and to identify the compounds from which it was derived, fraction 3 was analysed in more detail using two dimensional TLC, normal phase elution (mobile phase 40% toluene in hexane) followed by reversed phase elution (mobile phase 10% water in methanol). Figure 2.2.6-1 illustrates the results of this two dimensional separation. Compounds eluting to positions on the plate labelled 1 to 12 in figure 2.2.6-1, were removed in turn and identified by mass spectrometry, as listed in table 2.2.6-1.

Figure 2.2.6-1 Two dimensional TLC separation of CC fuel fraction 3 (see table 2.2.6-1 for compound identification)



TLC spots 1-12 detected by illumination of the plate with UV light (254nm)

Table 2.2.6-1 Identification of compounds separated by two dimensional TLC (see figure 2.2.6-1)

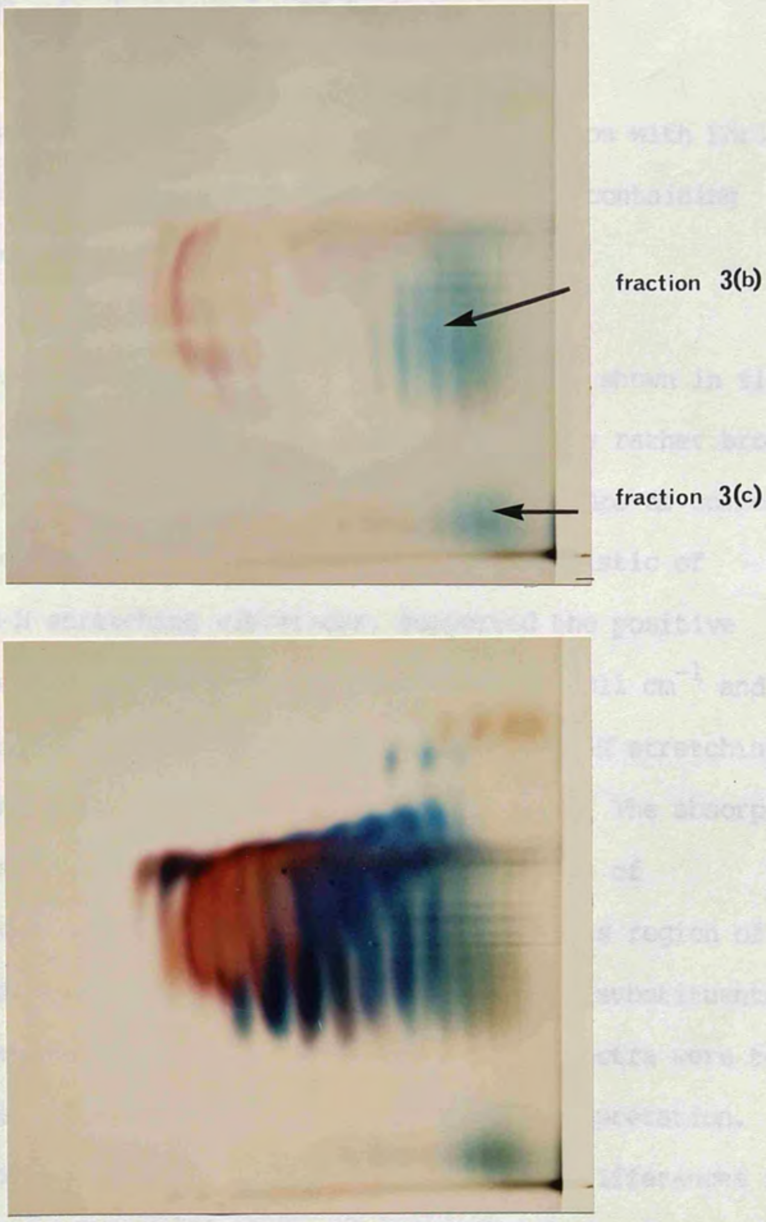
TLC spot number	Identification	
1	Carbazole	
2	Alkylcarbazoles	$C_{13}H_{11}N$
3		$C_{14}H_{13}N$
4		$C_{15}H_{15}N$
5		$C_{16}H_{17}N$
6	Alkylindoles	C_9H_9N
7		$C_{10}H_{11}N$
8		$C_{11}H_{13}N$
9	Benzocarbazole	
10	Alkylbenzocarbazoles	$C_{17}H_{13}N$
11		$C_{18}H_{15}N$
12		$C_{19}H_{17}N$

Although the presence of alkylindoles and alkylcarbazoles had already been established using GC/MS analysis, compounds of the next benzologue series, benzocarbazoles, were not detected in earlier GC/MS analysis because of their relative involatility.

The two dimensional TLC analysis was repeated, deliberately overloading the TLC plate with respect to the compounds listed in table 2.2.6-1, in order to optimise the conditions for the detection of any trace components in the mixture. An acidic TLC spray reagent, 25% concentrated HCl in methanol, was used in an attempt to locate the compounds in fraction 3 known to react with acid to produce the blue/green coloured sediment. Figure 2.2.6-2 shows two photographs of the two dimensional TLC separation, the first taken immediately after spraying with the acidic spray reagent and the second showing the same plate several hours later. The first photograph shows the presence of two groups of compounds (Rf 0.45/0.18 and Rf 0.06/0.13) which reacted rapidly with the spray reagent to produce blue/green coloured material. These compound groups are hereafter referred to as fractions 3(b) and 3(c), as indicated in figure 2.2.6-2. The major components of fraction 3 reacted with the spray reagent more slowly, but eventually also produced strongly coloured material as shown in the second photograph.

The coloured species produced by treatment of fractions 3(b) and 3(c) with methanolic HCl were removed from the TLC plate and re-chromatographed using normal phase TLC (mobile phase 10% methanol in dichloromethane) together with the diesel fuel sediment and the sediments formed in storage tests 1 and 3. The presence of co-eluting Rf blue/green materials at Rf 0.2 in all the samples confirmed that fractions 3(b) and 3(c) of the CC fuel did indeed contain the compounds which reacted with acid, producing the coloured, polar component of the diesel fuel sediment.

Figure 2.2.6-2 Two dimensional TLC separation of CC fuel fraction 3, immediately after spraying with acid (top) and several hours later (bottom)



2.2.7 **Analysis of fractions 3(b) and 3(c) of the CC fuel**

Fractions 3(b) and 3(c) were selectively extracted from CC fuel fraction 3 using a combination of low pressure normal and reversed phase liquid chromatography. This extraction process yielded less than 3mg of each fraction, equivalent to ca. 1% w/w of fraction 3 and ca. 0.002% w/w of the whole CC fuel.

Fractions 3(b) and 3(c) both gave a positive reaction with Ehrlich´s reagent, which indicated the presence of compounds containing pyrrolic nitrogen functional groups.

The infrared spectra of fractions 3(b) and 3(c) are shown in figure 2.2.7-1. The absorptions were noted to be generally rather broad, which suggested that each fraction contained a mixture of compounds. The presence of absorptions at 3399 cm^{-1}, characteristic of alkylindole N-H stretching vibrations, supported the positive results of the Ehrlich spot test. Absorptions at 2911 cm^{-1} and 2845 cm^{-1} were attributed to methyl and methylene C-H stretching vibrations associated with alkyl functional groups. The absorptions between 800 cm^{-1} and 650 cm^{-1} were attributed to out of plane aromatic C-H bending vibrations. Although this region of the spectrum is often used to establish the position of substituents on aromatic rings, the absorption patterns in these spectra were too complex and not sufficiently resolved for such interpretation. Nonetheless, it was clear that there were distinct differences in the aromatic substitution patterns of compounds in the two fractions.

Figure 2.2.7-1 Infrared spectra of CC fuel fractions 3(b) (top) and 3(c) (bottom)

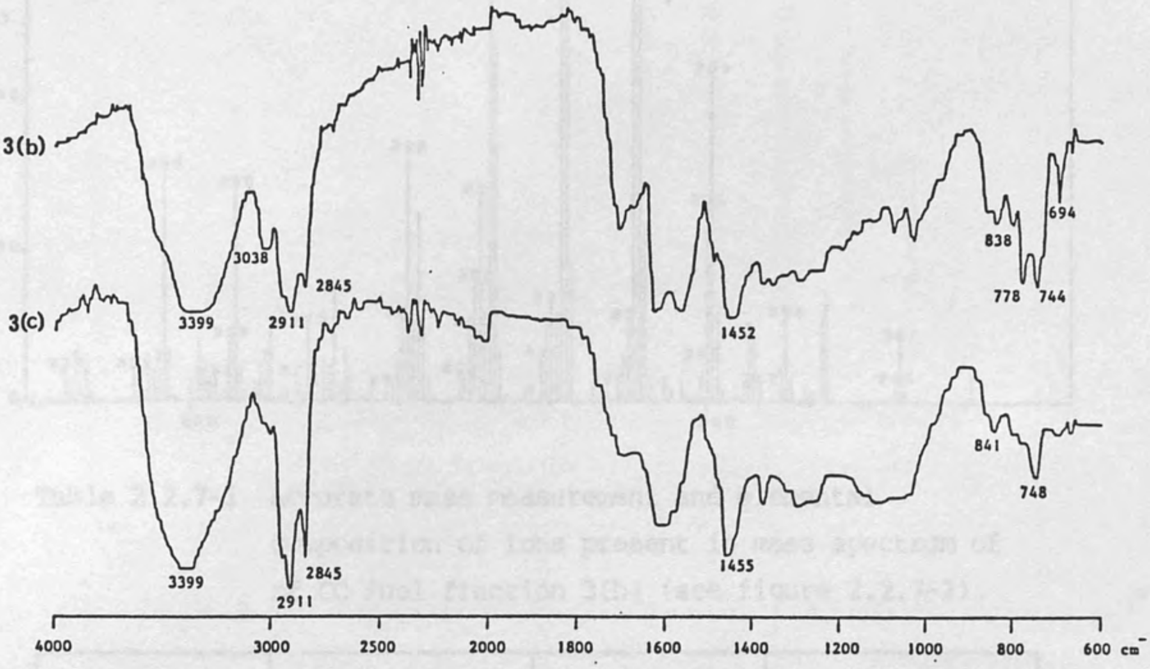


Figure 2.2.7-2 Mass spectrum of CC fuel fraction 3(b)

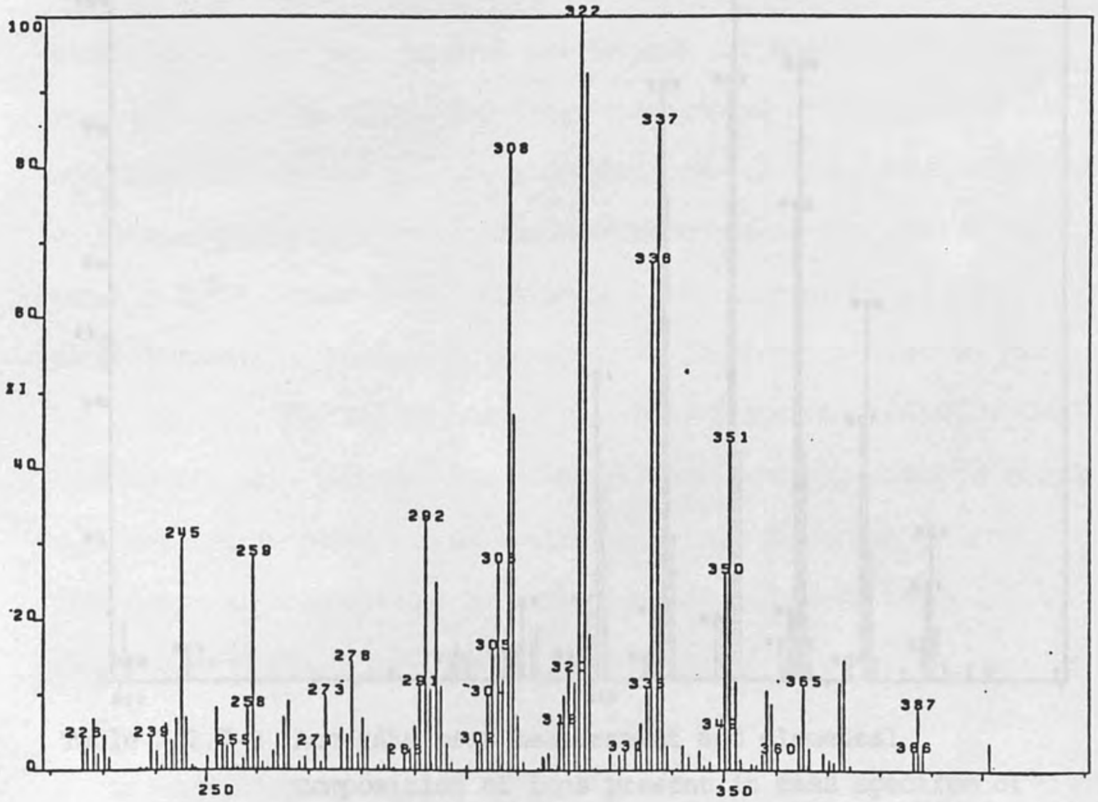


Table 2.2.7-1 Accurate mass measurement and elemental composition of ions present in mass spectrum of of CC fuel fraction 3(b) (see figure 2.2.7-2)

Nominal mass	Accurate mass	Elemental composition	Deviation (mmu)
308	308.1434	$C_{23}H_{18}N$	+ 0.5
309	309.1500	$C_{23}H_{19}N$	+ 1.7
322	322.1567	$C_{24}H_{20}N$	+ 2.8
323	323.1643	$C_{24}H_{21}N$	+ 3.1
336	336.1736	$C_{25}H_{22}N$	+ 1.6
337	337.1802	$C_{25}H_{23}N$	+ 2.9
350	350.1882	$C_{26}H_{24}N$	+ 2.6
351	351.1979	$C_{26}H_{25}N$	+ 0.8

Figure 2.2.7-3 Mass spectrum of CC fuel fraction 3(c)

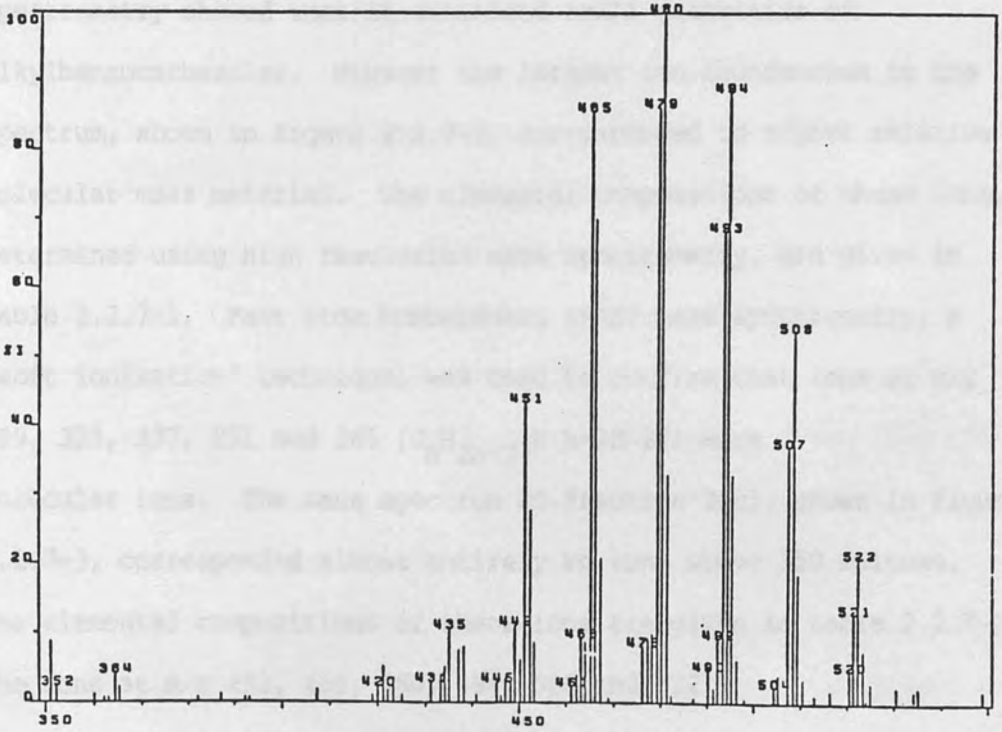


Table 2.2.7-2 Accurate mass measurement and elemental composition of ions present in mass spectrum of of CC fuel fraction 3(c) (see figure 2.2.7-3)

Nominal mass	Accurate mass	Elemental composition	Deviation (mmu)
451	451.2184	$C_{33}H_{27}N_2$	- 1.0
452	452.2230	$C_{33}H_{28}N_2$	+ 2.2
465	465.2311	$C_{34}H_{29}N_2$	+ 2.0
466	466.2369	$C_{34}H_{30}N_2$	+ 3.9
479	479.2485	$C_{35}H_{31}N_2$	+ 0.2
480	480.2532	$C_{35}H_{32}N_2$	+ 3.4
493	493.2661	$C_{36}H_{33}N_2$	- 1.8
494	494.2738	$C_{36}H_{34}N_2$	- 1.6
507	507.2732	$C_{37}H_{35}N_2$	+ 2.3
508	508.2840	$C_{37}H_{36}N_2$	+ 3.8
521	521.2897	$C_{38}H_{37}N_2$	+ 1.5
522	522.3002	$C_{38}H_{38}N_2$	+ 3.3

Analysis of fraction 3(b) by electron impact (EI) ionisation mass spectrometry showed that it contained small quantities of alkylbenzocarbazoles. However the largest ion abundancies in the spectrum, shown in figure 2.2.7-2, corresponded to higher relative molecular mass material. The elemental compositions of these ions, determined using high resolution mass spectrometry, are given in table 2.2.7-1. Fast atom bombardment (FAB) mass spectrometry, a "soft ionisation" technique, was used to confirm that ions at m/z 309, 323, 337, 351 and 365 ($C_nH_{2n-27}N$ n=23-27) were molecular ions. The mass spectrum of fraction 3(c), shown in figure 2.2.7-3, corresponded almost entirely to ions above 350 Daltons. The elemental compositions of these ions are given in table 2.2.7-2. The ions at m/z 452, 466, 480, 494, 508 and 522 ($C_nH_{2n-38}N_2$ n=33-38) were confirmed to be molecular ions using FAB mass spectrometry. The absence of significant abundancies of fragment ions in the EI spectra of fractions 3(b) and 3(c), together with the high ratio of carbon to hydrogen found in the molecular ions, suggested that the fractions contained compounds with highly aromatic structures. It was noted that the mass differences between the molecular ions of the two series of compounds was equivalent to that which would be expected if the higher mass series was related to the lower mass series by the addition of an alkyl derivative of indole. The IR and spot test results discussed earlier are consistent with the presence of compounds of this type. In addition, if it is assumed that fraction 3(c) contained compounds whose structure incorporated two alkylindole units and fraction 3(b) contained compounds whose structure incorporated only one alkylindole unit, then the remaining unassigned material in each compound group would contain carbon and hydrogen in the ratio expressed by the general formula C_nH_{2n-16}.

Fraction 3(b) was analysed by GC/MS in an attempt to obtain mass spectra of single homologues and if possible, single isomers of compounds present in the fraction. However the major components of fraction 3(b), compounds with the general formula $C_nH_{2n-27}N$, were found to be thermally labile, decomposing in the vapourising split injector of the GC. The ion chromatogram resulting from this analysis, shown in figure 2.2.7-4, therefore consisted mainly of the thermal breakdown products of these compounds, together with benzocarbazoles present as contaminants in the sample. A small proportion of the undegraded compounds eluted through the column at high temperatures, but the chromatographic resolution in this region was not good enough to completely separate individual homologues. Consequently mass spectra corresponding to peaks in this region of the chromatogram were all composite spectra of at least two compounds, as shown by the examples illustrated in figure 2.2.7-4. The peaks in the early part of the chromatogram, shown in more detail in figure 2.2.7-5, were found to correspond almost entirely to two homologous series of compounds. Individual peak assignments are given in table 2.2.7-3.

Figure 2.2.7-4 GC/MS total ion chromatogram of CC fuel fraction 3(b). (GC temperature programme, 2 min. @ 100°C, 100-320°C @ 8°C/min., 5 min. @ 320°C)

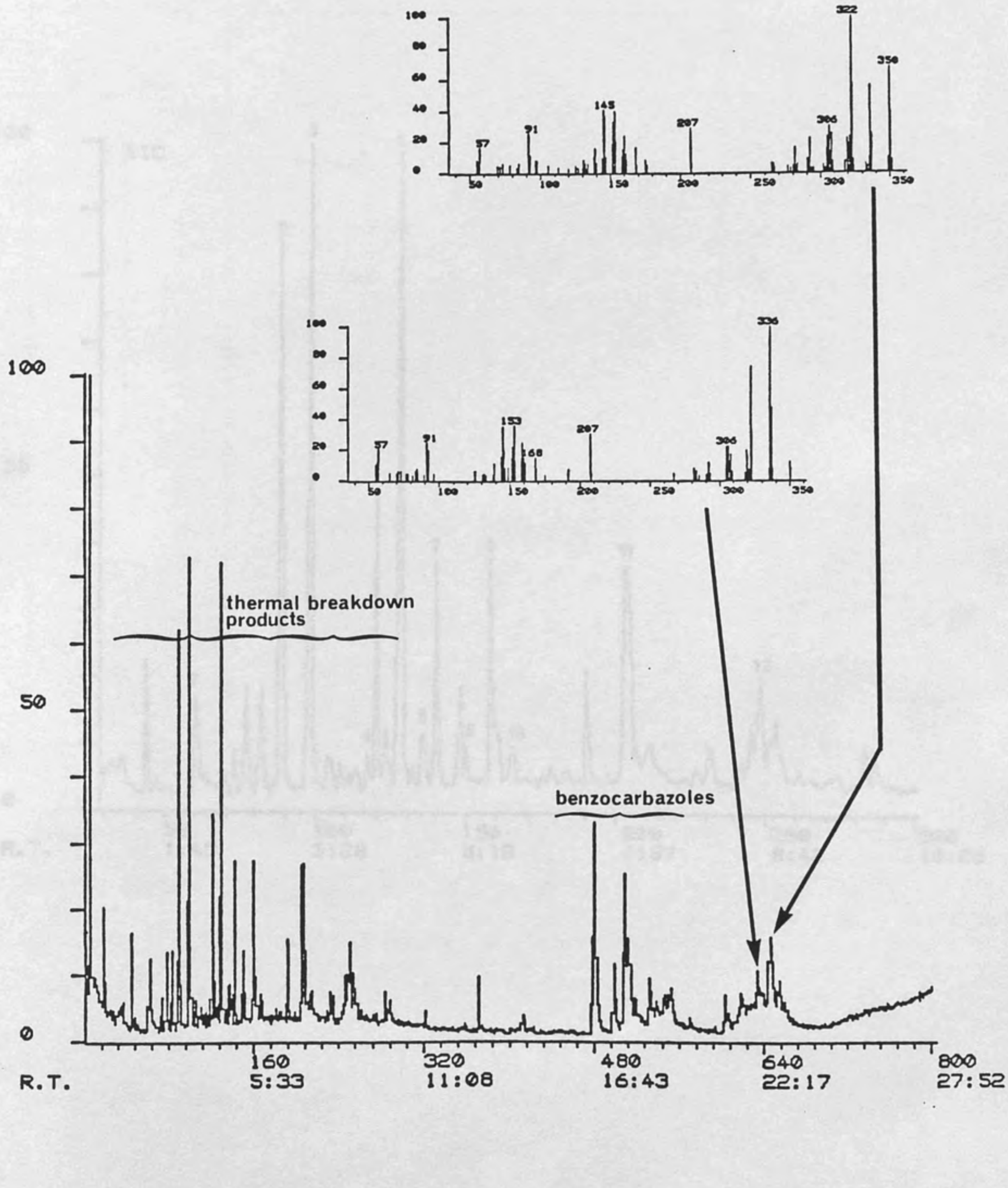


Figure 2.2.7-5 GC/MS total ion chromatogram of the thermal breakdown products of CC fuel fraction 3(b). Peak identifications given in table 2.2.7-3. (GC temperature programme, as figure 2.2.7-4)

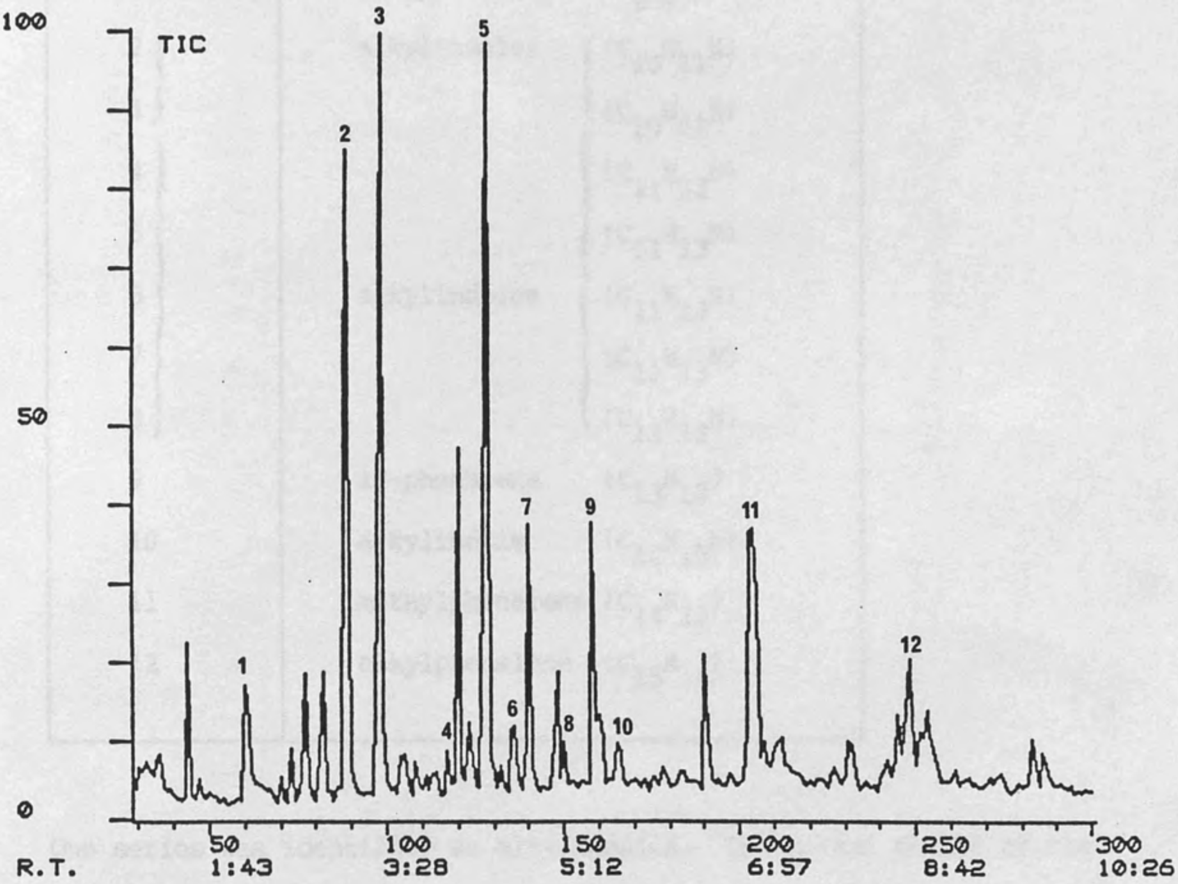
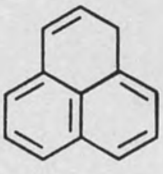


Table 2.2.7-3 Identification of peaks detected by GC/MS analysis of CC fuel fraction 3(b) (see figure 2.2.7-5)

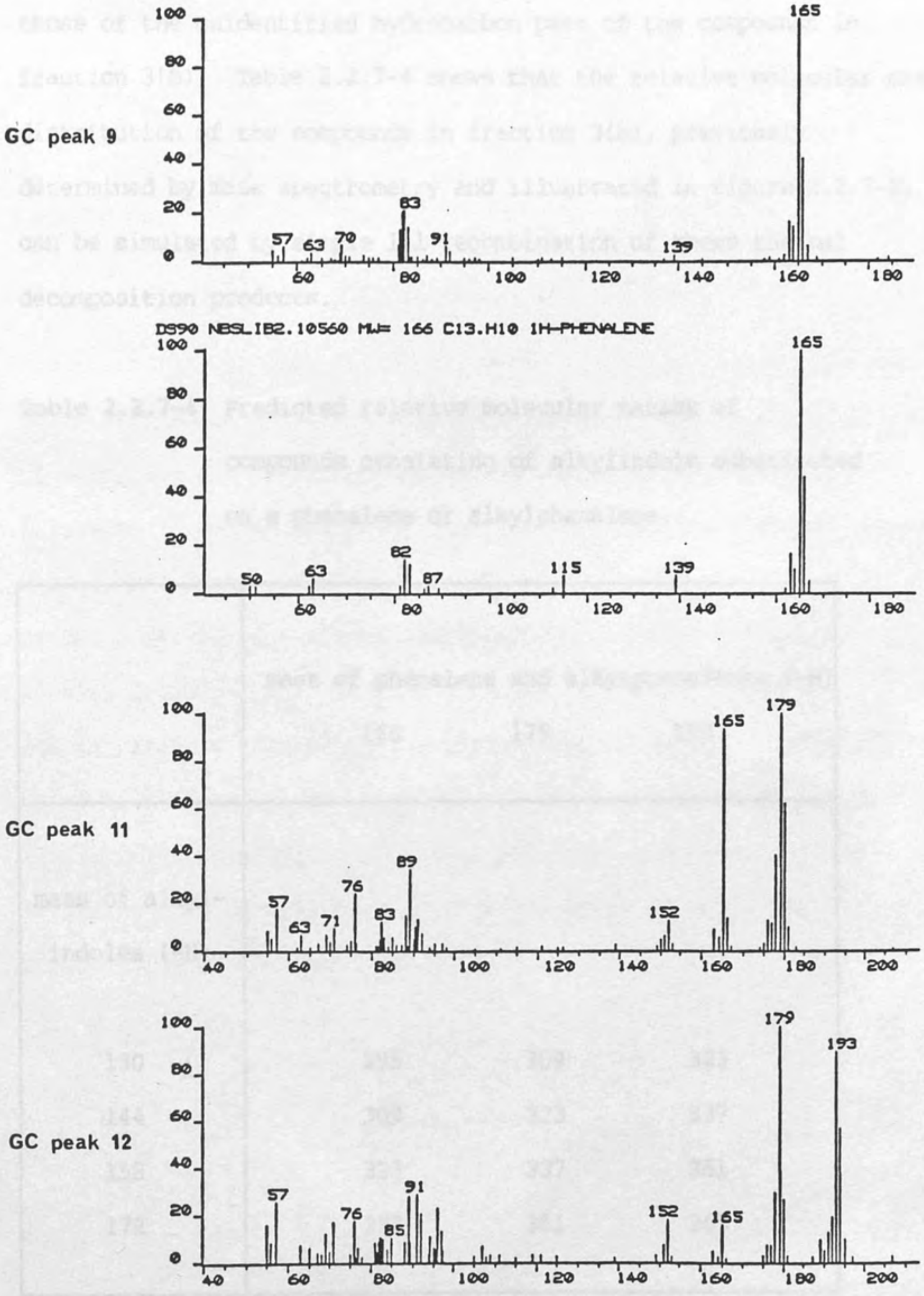
Peak number	Identification	
1	methylindole	(C_9H_9N)
2	alkylindoles	($C_{10}H_{11}N$)
3		($C_{10}H_{11}N$)
4	alkylindoles	($C_{11}H_{13}N$)
5		($C_{11}H_{13}N$)
6		($C_{11}H_{13}N$)
7		($C_{11}H_{13}N$)
8		($C_{11}H_{13}N$)
9	1H-phenalene	($C_{13}H_{10}$)
10	alkylindole	($C_{12}H_{15}N$)
11	methylphenalene	($C_{14}H_{12}$)
12	alkylphenalene	($C_{15}H_{14}$)

One series was identified as alkylindoles. The parent member of the second series, peak number 9, was identified as 1H-phenalene (I) by matching its mass spectrum against a library reference spectrum[43], shown in figure 2.2.7-6. The mass spectra of the first and second alkyl homologues of phenalene, peak numbers 11 and 12 respectively, are also shown in figure 2.2.7-6.



(I)

Figure 2.2.7-6 Mass spectrum of GC peak 9, library spectrum of 1H-phenalene, and mass spectra of GC peaks 11 and 12 (see figure 2.2.7-5)

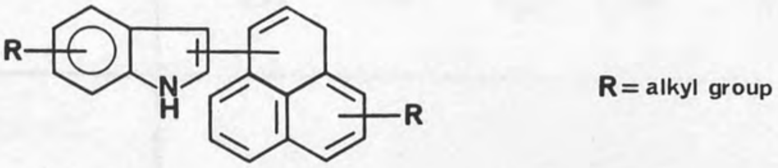


The presence of alkylindoles amongst the decomposition products of fraction 3(b), was consistent with earlier results. The elemental compositions of the other thermal breakdown products, phenalene and its homologues (C_nH_{2n-16} n=13-15), corresponded precisely to those of the unidentified hydrocarbon part of the compounds in fraction 3(b). Table 2.2.7-4 shows that the relative molecular mass distribution of the compounds in fraction 3(b), previously determined by mass spectrometry and illustrated in figure 2.2.7-2, can be simulated by simple 1:1 recombination of these thermal decomposition products.

Table 2.2.7-4 Predicted relative molecular masses of compounds consisting of alkylindole substituted on a phenalene or alkylphenalene.

	mass of phenalene and alkylphenalenes (-H)		
mass of alkyl-indoles (-H)	165	179	193
130	295	309	323
144	309	323	337
158	323	337	351
172	337	351	365

These results suggested that the compounds with the general formula C_nH_{2n-27} n=23-27 consisted of alkylindoles directly substituted on phenalene or alkylphenalene ring systems, ie. alkyl derivatives of indolylphenalene.

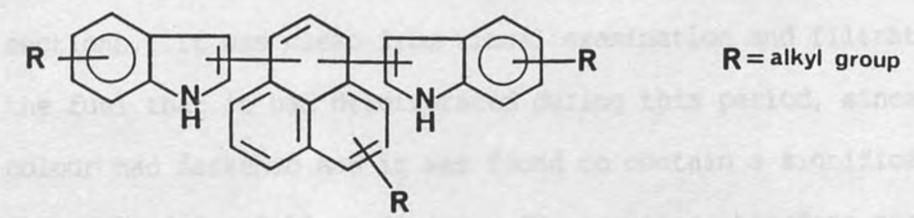


Fraction 3(c) was also found to contain thermally labile compounds which decomposed to mainly alkylindoles, with only very low levels of phenalene and alkylphenalenes. It was suggested earlier, following IR and MS analysis, that compounds in fraction 3(c) with the general formula $C_nH_{2n-38}N_2$ n=33-38, may be related by the addition of a second alkylindole, to compounds with the general formula $C_nH_{2n-27}N$ n=23-27 found in fraction 3(b) and now tentatively identified as alkylindolylphenalenes. Table 2.2.7-5 shows that compounds of this type, derived from the addition of alkylindoles to alkylindolylphenalenes, have the same relative molecular mass distribution as those detected by MS analysis of fraction 3(c), shown in figure 2.2.7-3.

Table 2.2.7-5 Predicted relative molecular masses of compounds consisting of alkylindole substituted on alkylindolylphenalene.

	mass of alkylindolylphenalenes (-H)					
mass of alkyl-indoles (-H)	294	308	322	336	350	364
130	424	438	452	466	480	494
144	438	452	466	480	494	508
158	452	466	480	494	508	522
172	466	480	494	508	522	536

It was deduced from these observations that the compounds in fraction 3(c) consisted of alkylbis(indolyl)phenalenes.



The virtual absence of phenalenes amongst the thermal decomposition products of fraction 3(c), was not inconsistent with the suggestion that the fraction was composed of alkyl derivatives of bis(indolyl)phenalenes. It would be more likely that thermal decomposition would produce alkylindoles and alkylindolylphenalenes rather than alkylindoles and alkylphenalenes since the latter would require the breaking of both indole/phenalene bonds.

These results did not unequivocally confirm the identification of compounds in fractions 3(b) and (3c) of the CC fuel as alkyl derivatives of indolylphenalene and bis(indolyl)phenalene respectively. Further analytical investigations of these species were limited by the amount of material available and by the fact that it was not possible to collect samples of individual compounds from the complex mixture of homologues and isomers. Indolylphenalene, bis(indolyl)phenalene and their alkyl derivatives are not documented in the literature. Therefore, in order to confirm or refute these assignments, an alkylindolylphenalene and an alkylbis(indolyl)phenalene were synthesised, characterised and compared with the compounds present in fractions 3(b) and 3(c) of the CC fuel. These results are discussed in section 2.3.

The CC fuel, from which fractions 3(b) and 3(c) were extracted, had been stored in sealed 5dm^3 metal containers at room temperature for several months before the analyses described in the preceding sections. It was clear from visual examination and filtration of the fuel that it had deteriorated during this period, since its colour had darkened and it was found to contain a significant quantity of insoluble sediment. The question therefore arose, were the compounds in fractions 3(b) and 3(c), which reacted with acid to produce the sediment characteristic of fuel storage instability and thought to be alkyl derivatives of indolylphenalene and bis(indolyl)phenalene, indigenous fuel species or were they formed during fuel storage by reactions of other indigenous fuel species ? To answer this question, a fresh, undegraded batch of essentially the same CC fuel was obtained directly from the refinery and immediately examined for the presence or absence of these compounds.

Small ($100cm^3$) samples of this fresh CC fuel were stored under liquid nitrogen whilst a larger quantity ($40 \times 5dm^3$) was stored at -20°C, in order to minimise degradation of the fuel and to provide a source of relatively undegraded fuel for future analysis.

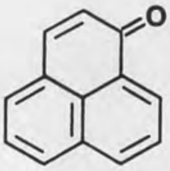
2.2.8 **Analysis of undegraded CC fuel**

A sample of CC fuel was analysed when it was less than 48 hours old. The fuel was found to be very similar to the previous batch of CC fuel, both in terms of its physical properties and gross chemical composition. However, as expected for a freshly produced fuel, it showed no evidence of storage instability. GC analysis with nitrogen selective detection showed that the distribution of nitrogen compounds in the fuel, predominantly alkylindoles and alkylcarbazoles, was almost identical to that observed previously in the partially degraded fuel. The fuel was separated, as before, into fractions using liquid chromatography. Fraction 3 was qualitatively examined for the presence of fractions 3(b) and 3(c) using the two dimensional TLC technique described in ch. 2.2.6. After both normal and reversed phase elution, the plate was sprayed with methanolic HCl. The immediate development of a weak blue/green colouration at Rf 0.45/0.18 indicated the presence of a low concentration of fraction 3(b) (containing compounds thought to be indolylphenalenes). However the absence of colouration at Rf

0.06/0.13 indicated that undegraded CC fuel did not contain detectable amounts of fraction 3(c). An identical analysis of this fuel was carried out after it had been stored at room temperature for several months. It was then found to contain a few milligrams of both fractions 3(b) and 3(c).

The increase in concentration of fractions 3(b) and 3(c) during storage of the second batch of CC fuel was not quantified. Nonetheless, it was clear that the compounds in these fractions (thought to be indolylphenalenes and bis(indolyl)phenalenes) were not indigenous fuel species but were produced by reactions of other fuel components, most probably indoles and derivatives of phenalene, which occurred during storage of the fuel.

The presence of alkylindoles in both undegraded and degraded CC fuel has already been established. The analysis of CC fuel for the presence of phenalene and derivatives of phenalene was pre-empted by series of experiments carried out by Dr. R.W. Hiley to investigate the nature of coloured compounds which formed during the storage of unstable fuel. Several bright yellow compounds were extracted from partially degraded CC fuel, one of which was identified as phenalenone (II), an oxidised derivative of phenalene.



(II)

The following section describes the extraction, analysis and identification of phenalenone and related compounds present in partially degraded CC fuel.

2.2.9 Detection of phenalenone in CC fuel*

A concentrate containing polar compounds, CC fuel fraction 4, was prepared from a sample of partially degraded CC fuel using the extraction scheme illustrated in figure 2.2.9-1. This was analysed by two dimensional TLC, normal phase elution (mobile phase toluene) followed by reversed phase elution (mobile phase 10% water in methanol). This separation showed that fraction 4 consisted almost entirely of a series of yellow compounds which were clearly visible on the TLC plate viewed in natural light. The elution characteristics of these compounds are illustrated diagramatically in figure 2.2.9-2. Examination of the plate under UV light showed that the compounds in fractions 4(1) to 4(7) absorbed strongly at 254nm and exhibited bright green, yellow and blue fluorescence when illuminated with long wave UV light (365nm). A photograph illustrating the fluorescence of these compounds is also shown in figure 2.2.9-2.

Fraction 4 of the CC fuel was separated on a larger scale into sub-fractions 4(1) to 4(7) using normal phase followed by reversed phase liquid chromatography. The sub-fractions were then analysed by IR and GC/MS.

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*The work described in this section was carried out by Dr. R.W. Hiley, Royal Aircraft Establishment, Cobham, Surrey, UK.

Figure 2.2.9-1 Extraction procedure used to prepare CC fuel fraction 4.

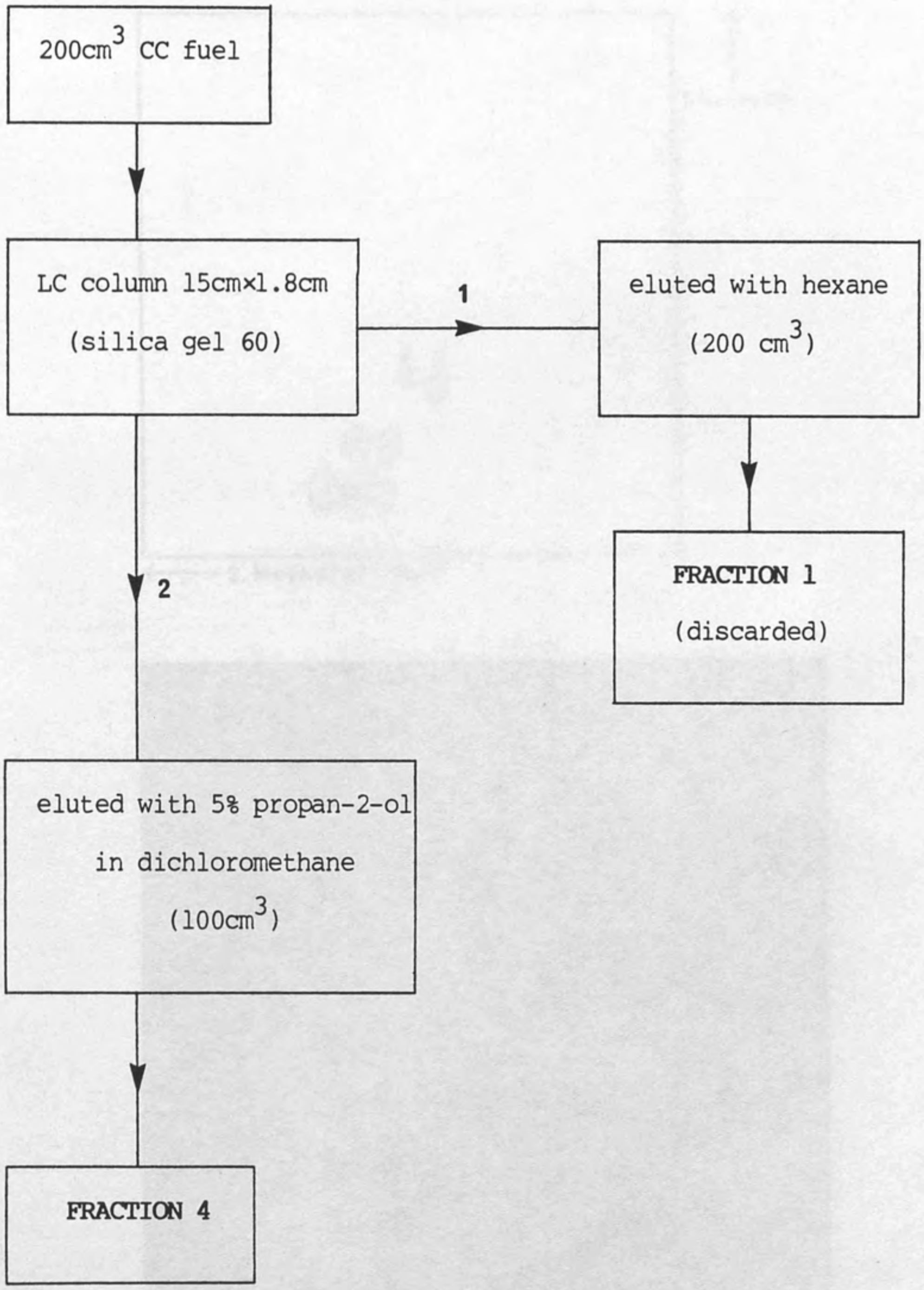


Figure 2.2.9-2 Two dimensional TLC separation of CC fuel fraction 4, diagram (top) and photographed under UV (365nm) light (bottom)

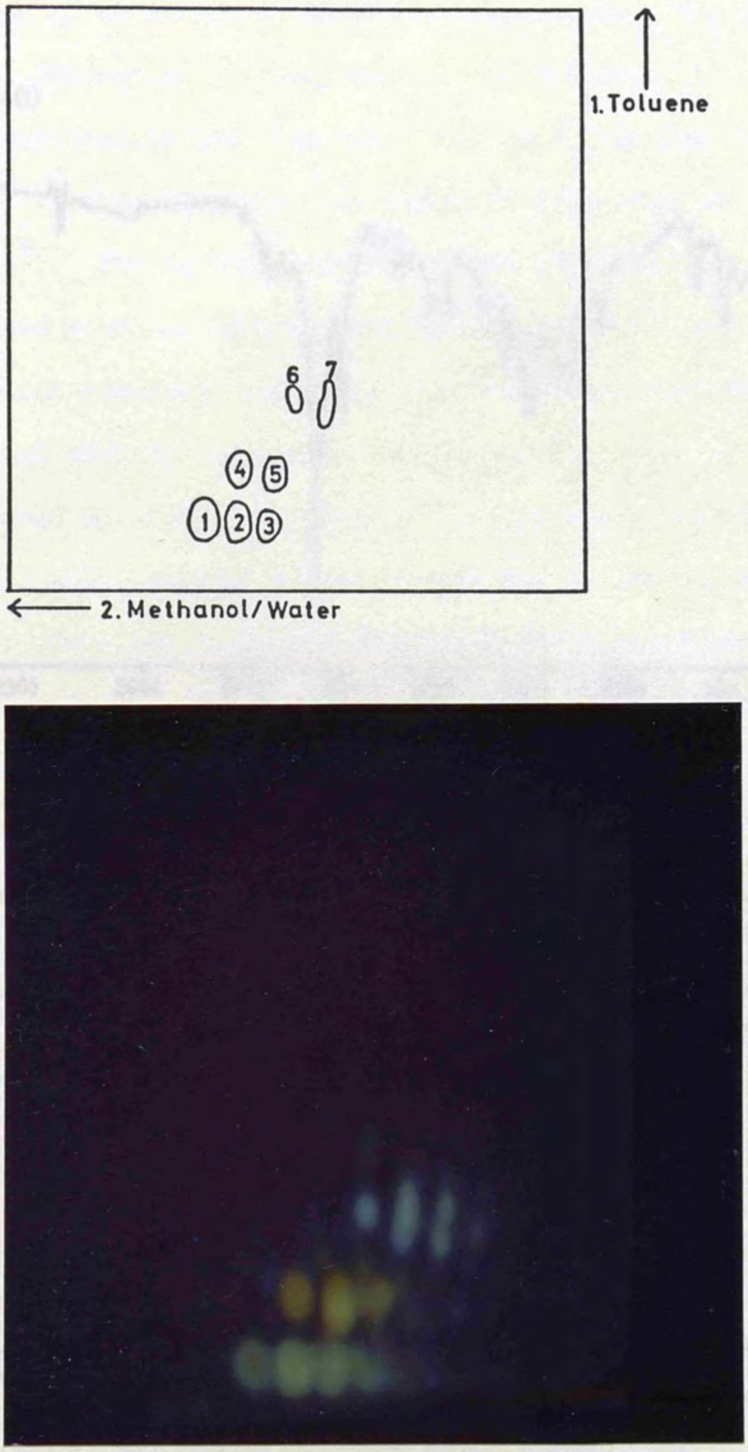
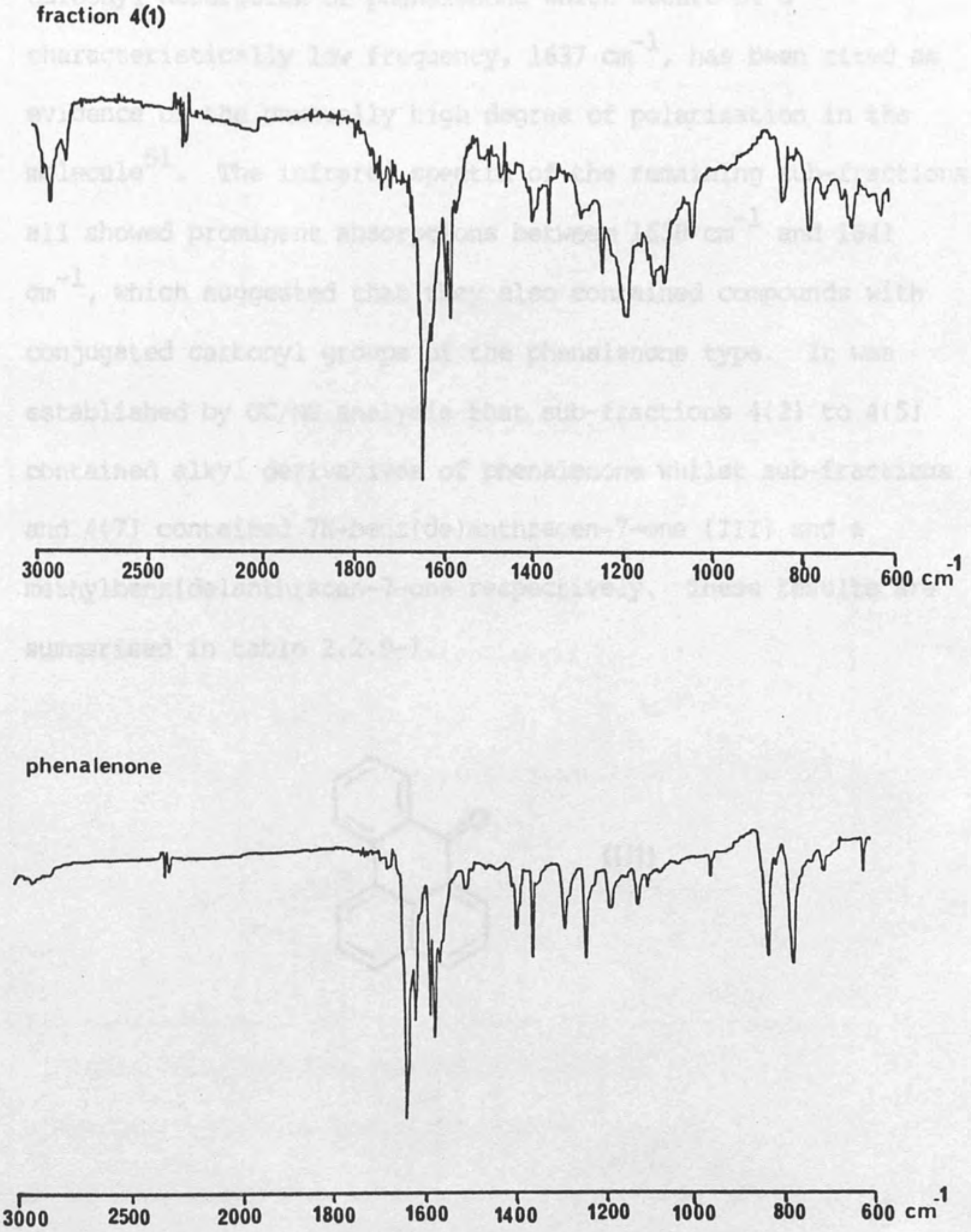
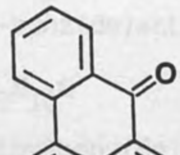


Figure 2.2.9-3 Infrared spectra of CC fuel fraction 4(1) (top) and phenalenone (bottom)



Sub-fraction 4(1) was found to consist of a single compound, identified as phenalenone by matching its TLC, GC, MS and IR characteristics with those of an authentic sample of this compound. Figure 2.2.9-3 shows the infrared spectrum of fraction 4(1) together with that of an authentic sample of phenalenone. The infrared carbonyl absorption of phenalenone which occurs at a characteristically low frequency, 1637 cm^{-1}, has been cited as evidence of the unusually high degree of polarisation in the molecule[51]. The infrared spectra of the remaining sub-fractions all showed prominent absorptions betweem 1638 cm^{-1} and 1641 cm^{-1}, which suggested that they also contained compounds with conjugated carbonyl groups of the phenalenone type. It was established by GC/MS analysis that sub-fractions 4(2) to 4(5) contained alkyl derivatives of phenalenone whilst sub-fractions 4(6) and 4(7) contained 7H-benz(de)anthracen-7-one (III) and a methylbenz(de)anthracen-7-one respectively. These results are summarised in table 2.2.9-1.



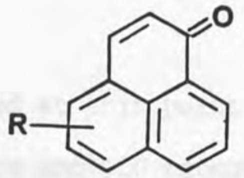
(III)

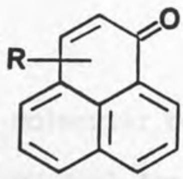
Table 2.2.9-1 Identification of phenalenone derivatives detected by GC/MS analysis of CC fuel sub-fractions 4(1) to 4(7).

Sub-fraction number	Compound identification	number of isomers
4(1)	Phenalenone* $C_{13}H_8O$	
4(2)	Methylphenalenone $C_{14}H_{10}O$	3
4(3)	Dimethyl-/ethylphenalenone $C_{15}H_{12}O$	2
4(4)	Methylphenalenone $C_{14}H_{10}O$	1
4(5)	Dimethyl-/ethylphenalenone $C_{15}H_{12}O$	2
4(6)	7H-benz(de)anthracen-7-one* $C_{17}H_{10}O$	
4(7)	Methylbenz(de)anthracen-7-one $C_{18}H_{12}O$	3

*identified by matching MS and GC retention characteristics with authentic samples

The presence of two distinct groups of alkylphenalenones, 4(2), 4(3) and 4(4), 4(5), differing in their normal phase TLC retention characteristics and fluorescence colours, may arise from alkyl substitution in aromatic and quinoid rings respectively. However this has not yet been confirmed experimentally.





R = alkyl

fractions 4(2) and 4(3)

fractions 4(4) and 4(5)

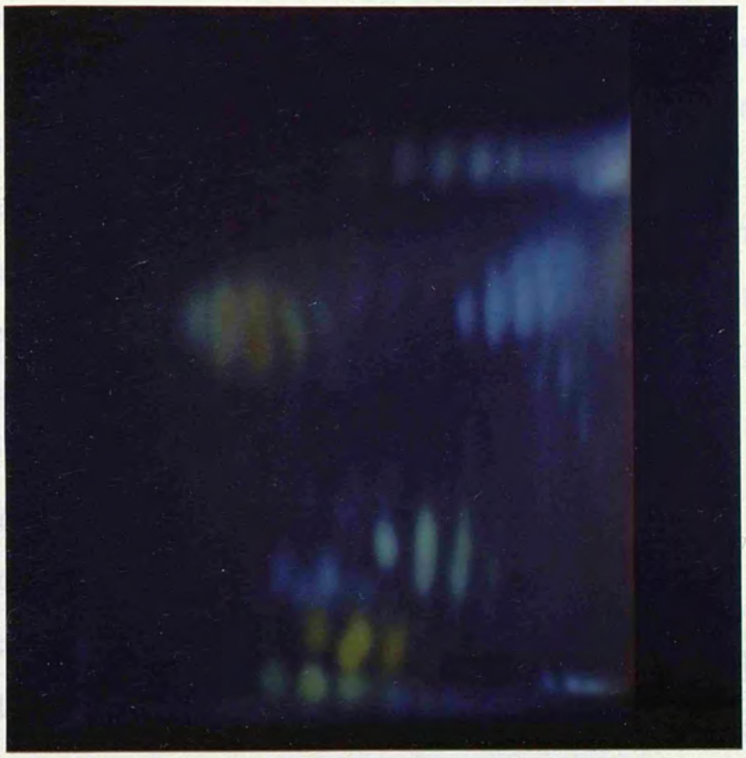
The total concentration of phenalenone derivatives in the partially degraded CC fuel was estimated, using IR absorbance measurements, to be approximately 200ppm. Similar measurements on a sample of undegraded CC fuel showed that the concentration of these species was approximately 50ppm.

Reid[51], in a review of the chemistry of phenalene and related compounds, cited several papers describing the facile formation of phenalenone by autooxidation or mild chemical oxidation of phenalene. Boekelheide and Larrabee[52] reported that white crystals of phenalene, when exposed to air, began to discolour within a few hours and were completely black after a few days. Phenalenone was identified amongst the autooxidation products of phenalene.

Therefore it is possible that the increase in concentration of phenalenone derivatives observed during storage of CC fuel arose from autooxidation of hydrocarbons containing the phenalene ring system. The implication of this would be that undegraded CC fuel contained phenalene and derivatives thereof. The following section describes the analysis of undegraded CC fuel, carried out to investigate this possibility.

It was noted at this point of the study, that the molecular mass, fluorescence and TLC retention characteristics of CC fuel fractions 4(1) to 4(7) were identical to those of compounds detected, but not identified, amongst the pyrolysis products of sediment (ch. 2.1.9). The pyrolysis/TLC experiment was therefore repeated, using two dimensional TLC to separate the pyrolysis products rather than the one dimensional separation described previously. Figure 2.2.9-4 shows a photograph of the TLC plate, illuminated with UV light (365nm). It was clear from comparison of figure 2.2.9-4 with figure 2.2.9-2 (TLC and fluorescence characteristics of CC fuel fractions 4(1) to 4(7)), that some of the previously unidentified sediment pyrolysis products included phenalenone together with its alkyl- and benz- derivatives. This finding was entirely consistent with indications that phenalene derivatives were involved in reactions leading to sediment formation in the unstable diesel fuel.

Figure 2.2.9-4 Two dimensional TLC separation of sediment pyrolysis products viewed under UV (365nm) light.



2.2.10 **Detection of phenalene in CC fuel**[*]

The literature contains no reference to the detection of phenalene itself in petroleum-derived fuels. However the phenalenyl radical has been identified, by Stehling and Bartz[53], in the aromatic fraction of a catalytically cracked fuel using electron spin resonance (ESR) spectroscopy. Bennett[54], also using ESR spectroscopy, found that this unusually stable radical was produced by pyrolysis of various petroleum-derived materials, noting in particular that a diesel fuel (of unspecified origin) gave rise to the radical at a lower pyrolysis temperature (450°C) than other materials tested such as spectroscopic grade cyclohexane (650-750° C). Huckel molecular orbital calculations by Pettit[55] and others, have shown that the stability of the symmetrical phenalenyl radical can be explained by the gain in resonance energy when it is formed from the parent hydrocarbon, phenalene.

The analysis for phenalene was carried out using a sample of undegraded CC fuel which was initially separated into the following compound classes using normal phase HPLC; fraction 1a : aliphatics, fraction 1b : single ring aromatics (alkylbenzenes), fraction 1c : two ring aromatics (alkylnaphthalenes) and fraction 1d : polycyclic aromatics/heteroaromatics. Figure 2.2.10-1 shows the chromatogram resulting from this separation. Phenalene and alkyl derivatives of phenalene, if present in the fuel, would be expected to elute after alkylnaphthalenes in this chromatographic system. Therefore fraction 1d was collected in five sub-fractions as shown in figure 2.2.10-1.

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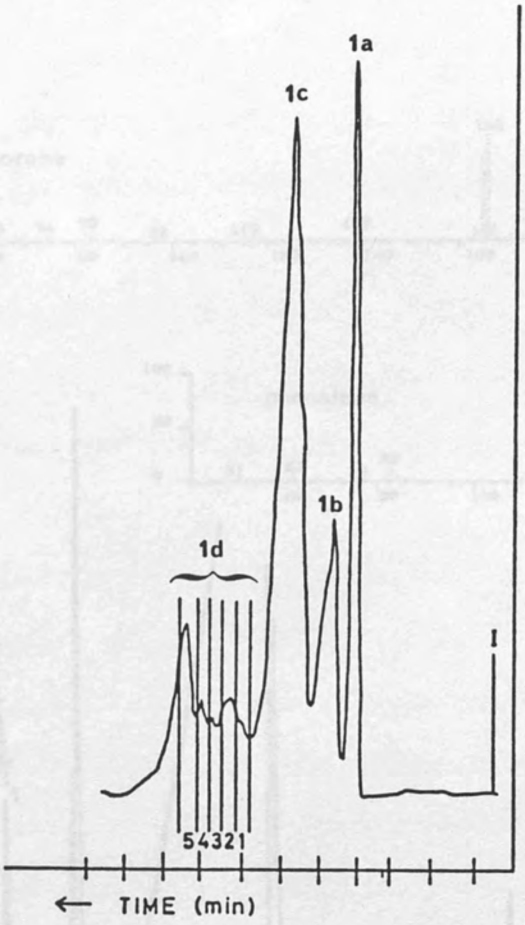
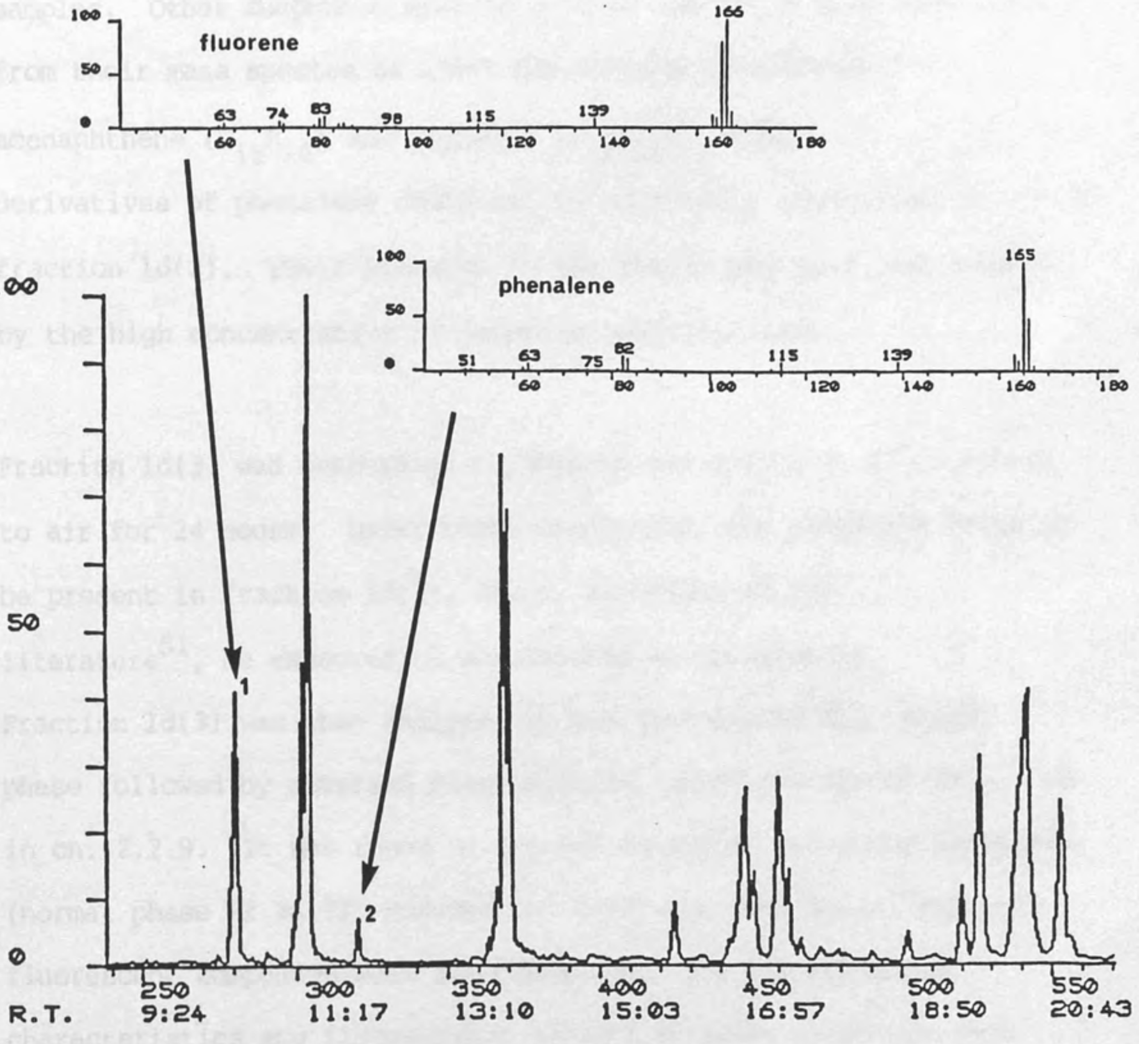
[*] The work described in this section was carried out by Dr. R.W. Hiley, Royal Aircraft Establishment, Cobham, Surrey, UK.

Figure 2.2.10-1 HPLC separation of CC fuel



1a	aliphatics
1b	single ring aromatics (alkylbenzenes)
1c	two ring aromatics (alkylnaphthalenes)
1d	polycyclic aromatics/heteroaromatics

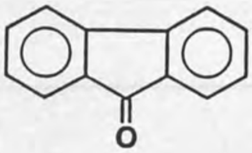
Figure 2.2.10-2 GC/MS total ion chromatogram of CC fuel fraction 1d(3) and mass spectra of GC peaks 1 and 2 (GC temperature programme 2 min. @ 80°C, 80-200°C @ 4°C/min., 5 min. @ 200°C)



Analysis of these sub-fractions by GC/MS showed that phenalene eluted as a minor component of fracton 1d(3). Figure 2.2.10-2 shows the total ion chromatogram of this fraction, together with the mass spectra of compounds corresponding to the GC peaks numbered 1 and 2. These compounds were identified as fluorene ($C_{13}H_{10}$) and phenalene ($C_{13}H_{10}$) respectively by matching their mass spectra and GC retention characteristics with those of authentic samples. Other compounds eluting in fraction 1d(3) were identified from their mass spectra as alkyl derivatives of fluorene, acenaphthene ($C_{12}H_{10}$) and biphenyl ($C_{12}H_{10}$). Alkyl derivatives of phenalene could not be positively identified in fraction 1d(3). Their presence in the sample may have been masked by the high concentration of isomeric alkylfluorenes.

Fraction 1d(3) was evaporated to dryness and stored at 43°C, vented to air for 24 hours. Under these conditions, the phenalene known to be present in fraction 1d(3), would, according to the literature[51], be expected to autooxidise to phenalenone. Fraction 1d(3) was then analysed by two dimensional TLC, normal phase followed by reversed phase elution, using the system described in ch. 2.2.9. It was found to consist mainly of non-polar compounds (normal phase Rf >0.7). However low levels of more polar, strongly fluorescent compounds were also detected. The TLC retention characteristics and fluorescence colours of these compounds were found to be identical to those of the phenalenones identified in CC fractions 4(1) to 4(5) and discussed in ch. 2.2.9. There was insufficient material for further characterisation, but there was little doubt that these compounds arose from autooxidation of phenalene and alkylphenalenes present in fraction 1d(3) of the CC fuel.

Phenalene and its alkyl derivatives have not previously been discussed in the context of middle distillate fuel instability, although aromatic olefins in general are often cited as contributing to fuel instability[6]. Likewise, their oxidation products, phenalenone and alkylphenalenones, have not been mentioned in the literature on this subject. However Bahn, Brinkman, Green and Carley[38] recently reported the detection of other aromatic ketones in undegraded and degraded diesel fuels, in particular 9-fluorenone (IV) and its alkyl homologues were detected and identified by IR and GC/MS analysis.



(IV)

It was suggested that these compounds were produced via the oxidation of fluorene and alkylfluorenes. Observed decreases in the concentration of ketones was put forward as evidence that ketones act as intermediates in oxidation pathways leading to fuel instability, although the specific role of ketones in sediment formation could not be explained.

In the light of the results of these authors, a series of experiments were carried out to determine whether 9-fluorenone and alkylfluorenones, which are isomeric with phenalenone and alkylphenalenones, were present in the CC fuel.

2.2.11 **Analysis of CC fuel for the presence of 9-fluorenone and alkylfluorenones**

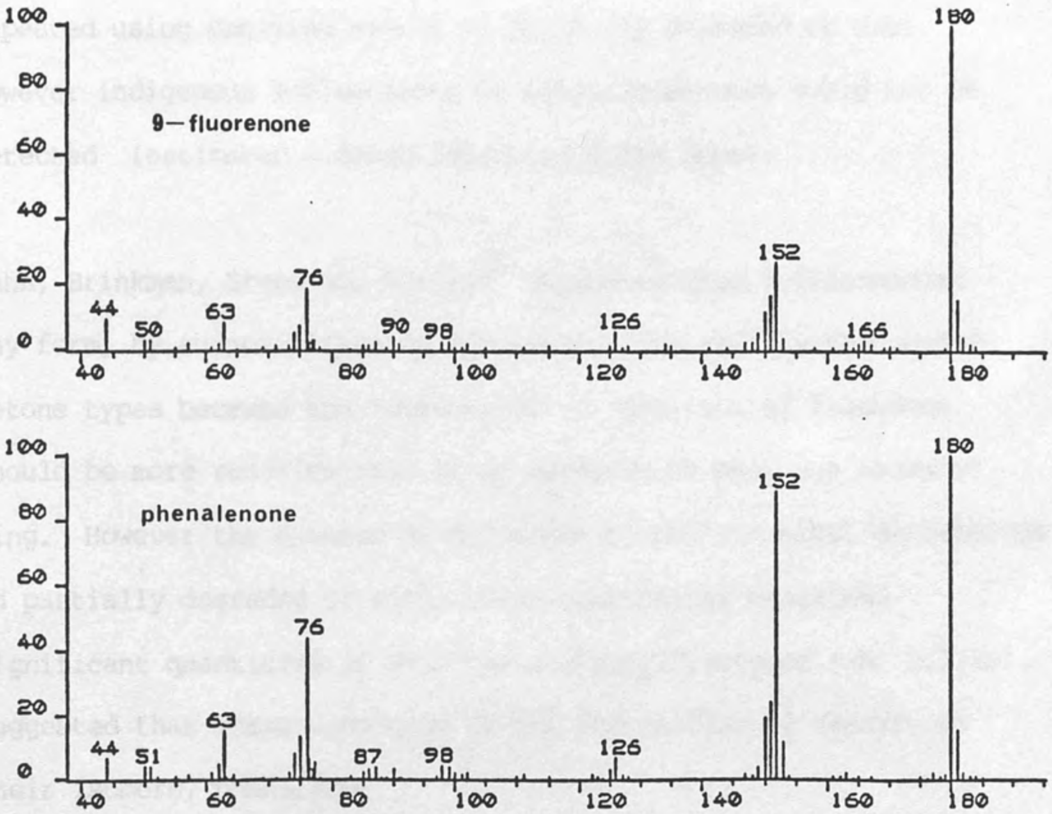
The TLC, GC, IR and MS characteristics of 9-fluorenone were compared with those of phenalenone, to ensure that the two compounds could be unambiguously identified. The mass spectrum of 9-fluorenone was found to be very similar to that of phenalenone, as shown in figure 2.2.11-1. However their TLC, GC and IR characteristics were quite different, as illustrated by the data in table 2.2.11-1.

Table 2.2.11.1 Analytical characteristics of 9-fluorenone and phenalenone

	9-Fluorenone	Phenalenone
Normal phase TLC Rf (mobile phase toluene)	0.46	0.09
Reversed phase TLC Rf (mobile phase 10% water in methanol)	0.47	0.56
Infrared C=O absorption frequency cm^{-1}	1709	1637
GC Kovats retention index (12m BP1 0.2mm ID WCOT column)	1704	1859

In order to determine the extraction characteristics of 9-fluorenone, a sample of partially degraded CC fuel was deliberately spiked with 50ppm of this compound.

Figure 2.2.11-1 Mass spectra of 9-fluorenone (top) and phenalenone (bottom)



The fuel was then fractionated using the extraction scheme previously illustrated in figure 2.2.9-1. CC fuel fraction 4 was analysed by GC/MS. The 9-fluorenone spike was readily detected in the chromatogram. The peak corresponding to 9-fluorenone was well resolved from phenalenone and alkylphenalenones which were present at much higher concentrations in the fraction. The extraction and GC/MS analysis was then repeated using unspiked sample of partially degraded CC fuel. However indigenous 9-fluorenone or alkylfluorenones could not be detected (estimated minimum detection limit 5ppm).

Bahn, Brinkman, Green and Carley[38] suggested that 9-fluorenones may form, by autooxidation of fluorenes, more rapidly than other ketone types because the "dibenzylic" 9- position of fluorenes should be more reactive than sites adjacent to only one aromatic ring. However the absence of 9-fluorenone and its alkyl derivatives in partially degraded CC fuel, which nonetheless contained significant quantities of fluorene and alkylfluorenes (ch. 2.2.10), suggested that these compounds do not autooxidise as readily as their isomers, phenalenes.

2.2.12 **Summary**

The main results and conclusions relating to the formation of sediment during fuel storage which arose from the analysis of SR and CC fuel components, can be summarised as follows:

(i) Alkylindoles were present in both undegraded and degraded CC fuel, but were absent from the SR fuel. This indicated that alkylindoles incorporated in fuel sediment originated only from the CC component of the unstable diesel fuel.

(ii) Storage of a fraction of CC fuel, consisting predominantly of alkylindoles and alkylcarbazoles, resulted in the formation of a sediment virtually indistinguishable from sediment formed during storage of the whole CC fuel.

(iii) The formation of this sediment was inhibited by extraction of the CC fuel fraction with base before storage.

(iv) Naphthalenesulphonic acid and hydrochloric acid both promoted the formation of the polar, intensely coloured part of the sediment, by reaction with trace constituents of the fraction thought to be alkyl derivatives of indolylphenalene and bis(indolyl)phenalene.

(v) The concentration of these compounds increased during storage of unstable CC fuel, indicating that they formed by reaction of indigenous fuel components, possibly alkyindoles and derivatives of phenalene.

(vi) Phenalenone, 7H-benz(de)anthracen-7-one and alkyl derivatives of these compounds were detected in the CC fuel. The concentration of these compounds also increased during storage of the unstable fuel.

(vii) Phenalene was detected in undegraded CC fuel.

(viii) This compound was extracted into a fraction of the CC fuel. It was observed to autooxidise to form phenalenone during storage of the fraction in air at 43°C for 24 hours. The "aged" fraction was also found to contain alkylphenalenones, presumably formed by autooxidation of alkylphenalenes.

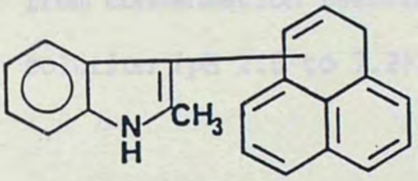
(ix) An isomer of phenalenone, 9-fluoreneone, reported elsewhere[38] to be involved in reactions leading to fuel instability, could not be detected in the CC fuel although the reduced form of the compound, fluorene, an isomer of phenalene, was found to be present in the CC fuel.

It was deduced from these results that sediment formation during storage of the unstable diesel fuel arose, at least in part, from reactions of fuel species resulting in the formation of compounds thought to be alkylderivatives of indolylphenalene and bis(indolyl)phenalene. In order to corroborate this conclusion, it was necessary first to confirm the identity of these compounds and secondly to establish the sequence of reactions leading to their formation in unstable diesel fuel.

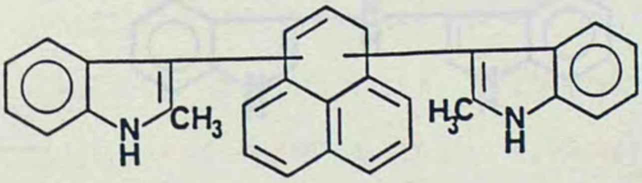
2.3 Synthesis of 2-methylindolylphenalene and bis(2-methylindolyl)phenalene

2.3.1 Introduction

The syntheses of 2-methylindolylphenalene (V) and bis(2-methylindolyl)phenalene (VI) were carried out in order to confirm the suggested structural assignments of compounds detected in CC fuel fractions 3(b) and 3(c) (ch. 2.2.7). Synthetic routes to these compounds, or indeed the compounds themselves, have not been reported in the literature.



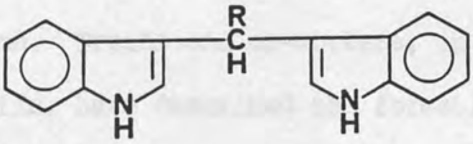
(V)



(VI)

It is well known that indoles are highly reactive towards electrophilic reagents[56]. This reactivity arises from the fact that indoles are π-excessive heteroaromatic compounds[57], ie. the π-electron density on their carbon atoms is greater than that on the carbon atoms of benzene. A variety of theoretical reactivity indices, including total π-electron densities, localization energies and superdelocalizabilties, have been applied to the interpretation of electrophilic substitution in these compounds. All these indicies successfully predict $C_{(3)}$ to be the preferred site of substitution. This prediction holds for both LCAO-MO and SCF calculations[56].

Indoles react readily with both aldehydes and ketones (electrophiles) in the presence of acid, by nucleophilic attack at the carbonyl carbon which carries a substantial positive charge arising from protonation of the carbonyl group. Many reactions of this type have been recorded in the literature[56,58], involving carbonyl groups in widely differing chemical environments. For example, Kamal and Qureshi[59] have described the synthesis of a variety of bis(indolyl)methanes, including VIIa-j, which all arise from condensation reactions of indole with aldehydes in aqueous solution (pH 1.5 to 7.2).



(VII)

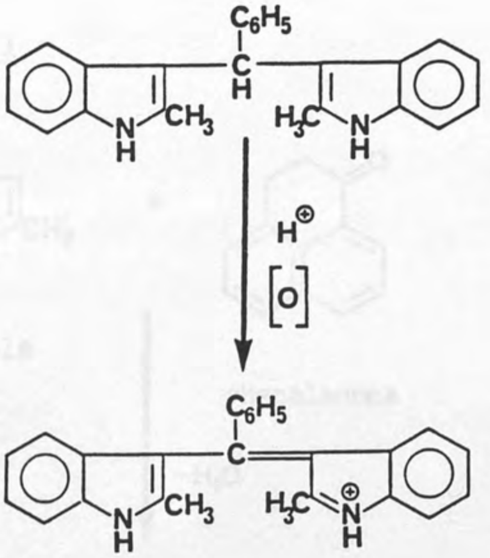
R

(a) H-
(b) CH_3-
(c) $CH_3CH{=}CH$-
(d) C_6H_5-
(e) α-naphthyl:($C_{10}H_7$)-

R

(f) m-$NO_2.C_6H_4$-
(g) $C_6H_5CH{=}CH$-
(h) p-$NO_2.C_6H_4$-
(i) m-$OH.C_6H_4$-
(j) α-furyl-

Oxidation of bis(indolyl)methane derivatives in the presence of acid usually results in the formation of coloured products. For example 3,3′-bis(2-methylindolyl)phenylmethane (VIII) is readily converted by oxygen and acid to "rosindole" (IX)[56,58].



(VIII)

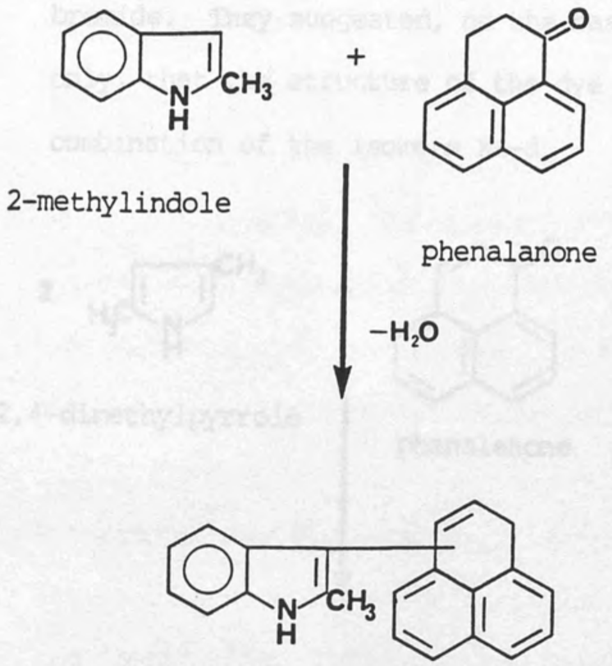
eq. 2.3.1-1

(IX)

The Ehrlich reaction (described in ch. 2.1.6), commonly used as a "spot test" to detect indoles, is another example of this type of reaction. Treibs and co-workers, in attempts to synthesise dyestuffs, have described the formation of coloured species in reactions of pyrroles, and to a lesser extent indoles, with many different carbonyl compounds[eg.60-63].

In the light of this known reactivity of indoles towards carbonyl compounds, the following synthetic routes to 2-methylindolylphenalenes (V) and bis(2-methylindolyl)phenalenes (VI) may be envisaged.

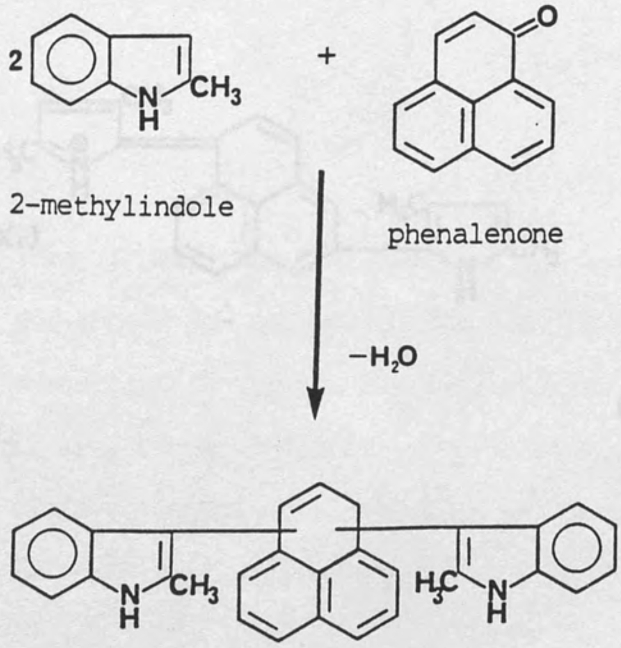
Reaction 1



(V)

eq. 2.3.1-2

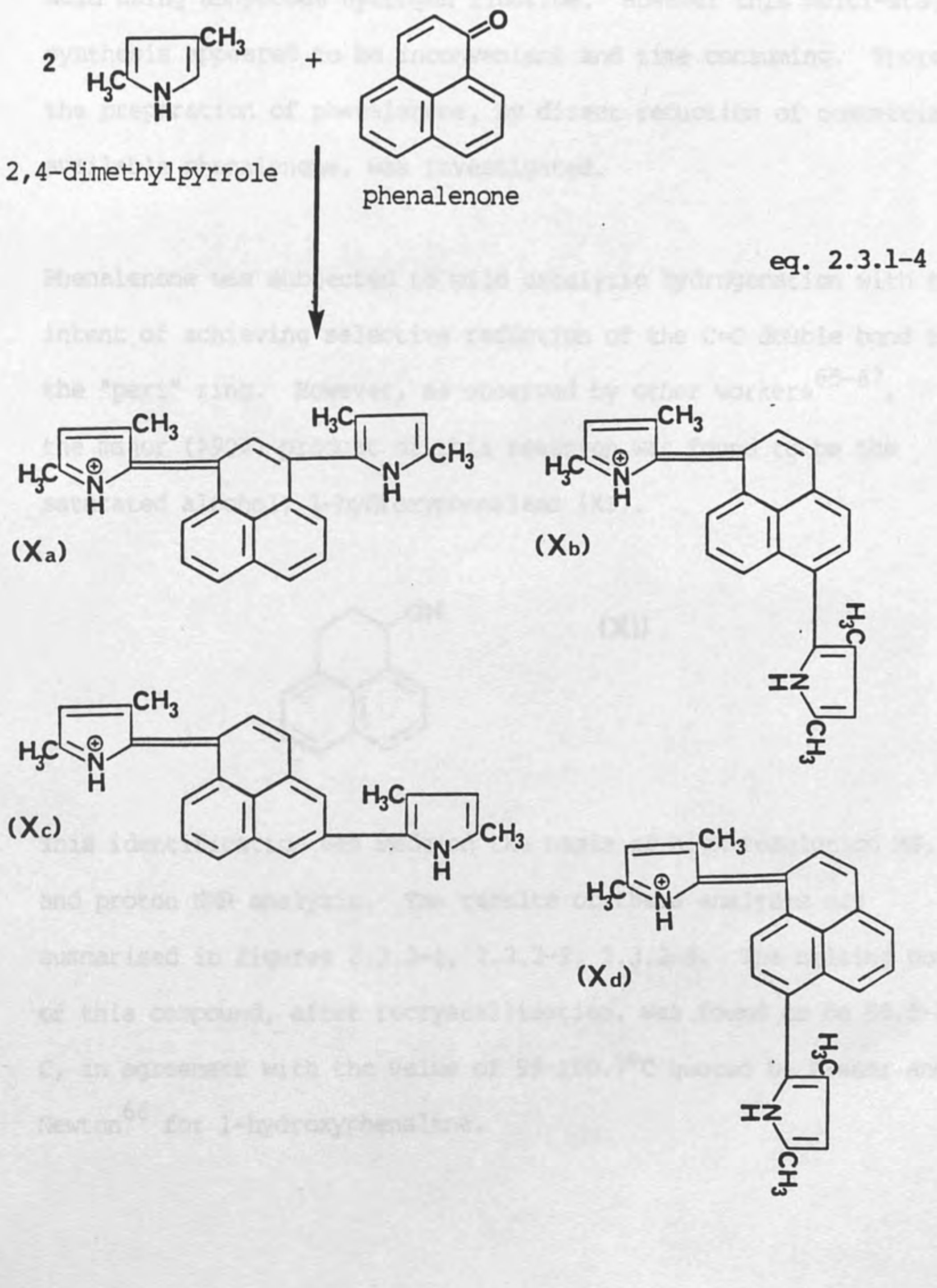
Reaction 2



(VI)

eq. 2.3.1-3

The only reported reaction of a pyrrole derivative with phenalenone was described by Treibs, Herrmann and Meissner[63] in 1958. They described the formation of a blue dye by reaction of 2,4-dimethylpyrrole with phenalenone in the presence of hydrogen bromide. They suggested, on the basis of elemental analysis data only, that the structure of the dye may be either one or a combination of the isomers Xa-d.



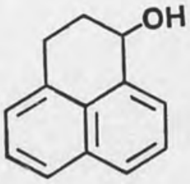
eq. 2.3.1-4

2.3.2 **Reaction 1. Phenalanone with 2-methylindole**

In order to carry out this reaction, it was first necessary to synthesise phenalanone, since this compound is not available commercially.

The best known synthesis of phenalanone is the method of Fieser and Gates[64] which involves cyclisation of β-(1-naphthyl)propionic acid using anhydrous hydrogen fluoride. However this multi-stage synthesis appeared to be inconvenient and time consuming. Therefore the preparation of phenalanone, by direct reduction of commercially available phenalenone, was investigated.

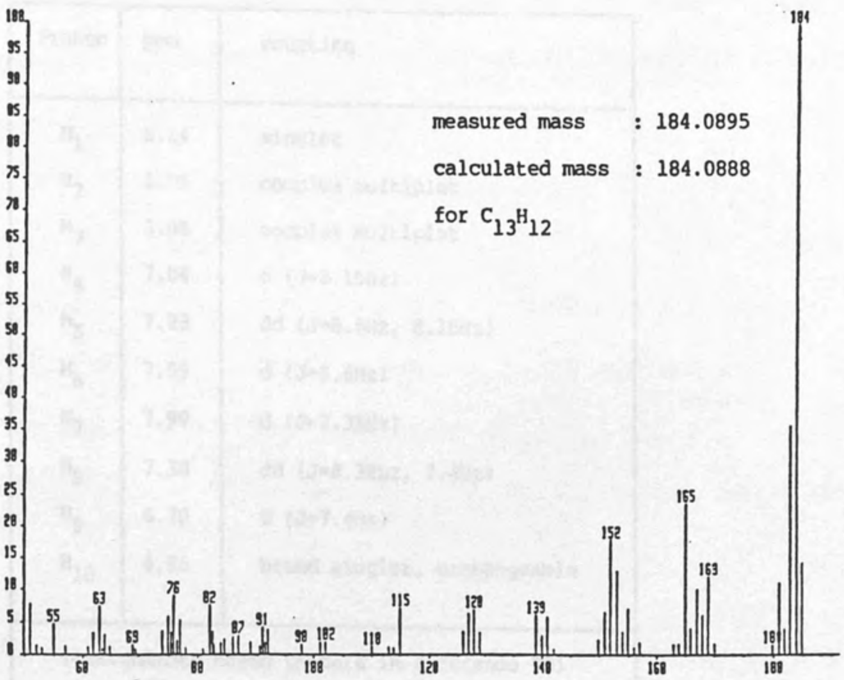
Phenalenone was subjected to mild catalytic hydrogenation with the intent of achieving selective reduction of the C=C double bond in the "peri" ring. However, as observed by other workers[65-67], the major (>90%) product of this reaction was found to be the saturated alcohol, 1-hydroxyphenalane (XI).



(XI)

This identification was made on the basis of high resolution MS, IR and proton NMR analysis. The results of these analyses are summarised in figures 2.3.2-1, 2.3.2-2, 2.3.2-3. The melting point of this compound, after recrystallisation, was found to be 99.5-100° C, in agreement with the value of 99-100.7°C quoted by Fieser and Newton[66] for 1-hydroxyphenalane.

Figure 2.3.2-1 Mass spectrum of 1-hydroxyphenalane


measured mass : 184.0895

calculated mass : 184.0888

for $C_{13}H_{12}$

Figure 2.3.2-2 Infrared spectrum of 1-hydroxyphenalane

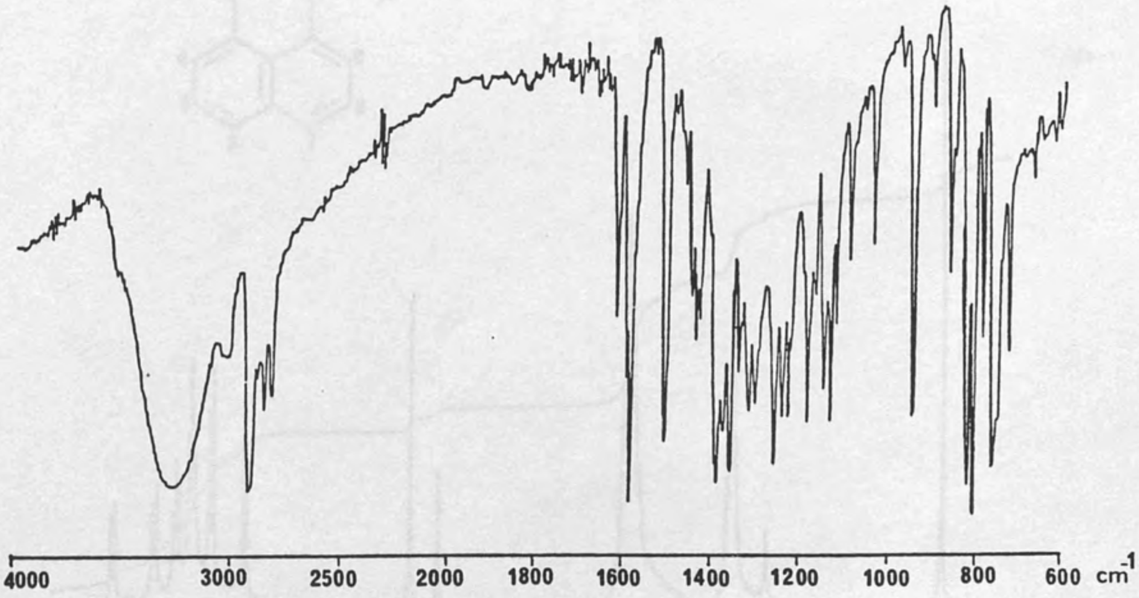
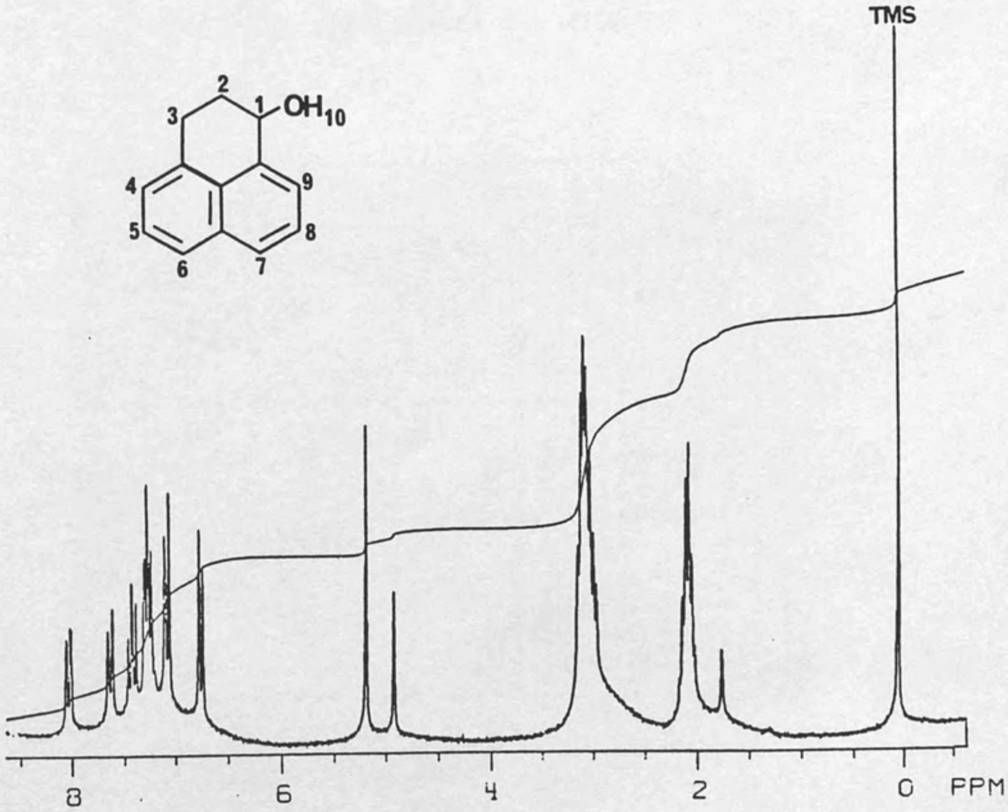


Figure 2.3.2-3 Proton NMR spectrum of 1-hydroxyphenalane

Proton	ppm	coupling
H_1	5.14	singlet
H_2	2.05	complex multiplet
H_3	3.05	complex multiplet
H_4	7.04	d (J=8.15Hz)
H_5	7.23	dd (J=8.6Hz, 8.15Hz)
H_6	7.59	d (J=8.6Hz)
H_7	7.99	d (J=8.38Hz)
H_8	7.38	dd (J=8.38Hz, 7.4Hz)
H_9	6.70	d (J=7.4Hz)
H_{10}	4.86	broad singlet, exchangeable

(assignments based on data in reference 70)



Boudjouk and Johnson[68] have reported the formation of phenalanone, in 28% yield, by reduction of phenalenone with tetramethyldisiloxane. Their synthetic method was repeated and found to be a convenient route to phenalanone (31.6% yield). This product was characterised by high resolution MS, IR and NMR analysis. The results of these analyses, shown in figures 2.3.2-4, 2.3.2-5 and 2.3.2-6, compare well with previously published spectra (IR[68,69], NMR[68,70]). Other compounds isolated from the reaction mixuture included phenalene ($C_{13}H_{10}$) and 1-hydroxyphenalane, together with the starting material phenalenone.

Figure 2.3.2-4 Mass spectrum of phenalanone

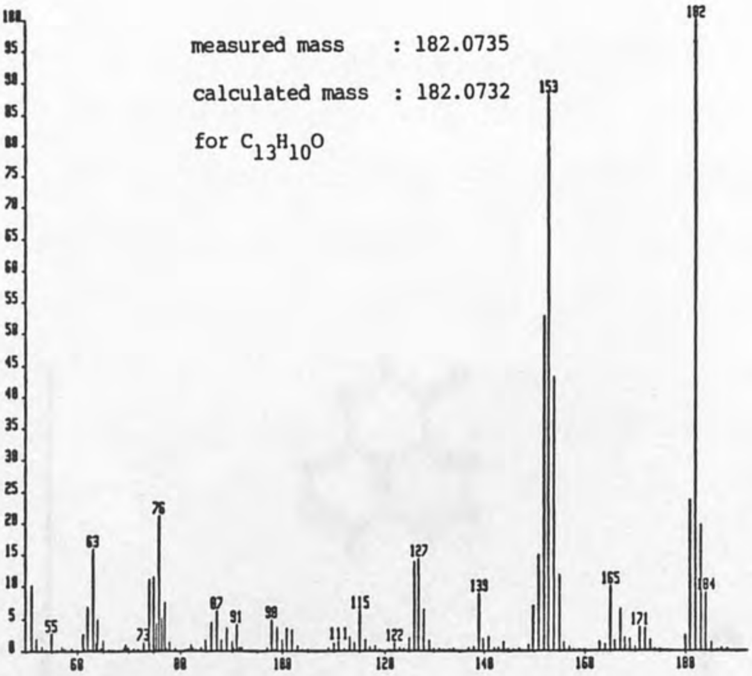


Figure 2.3.2-5 Infrared spectrum of phenalanone

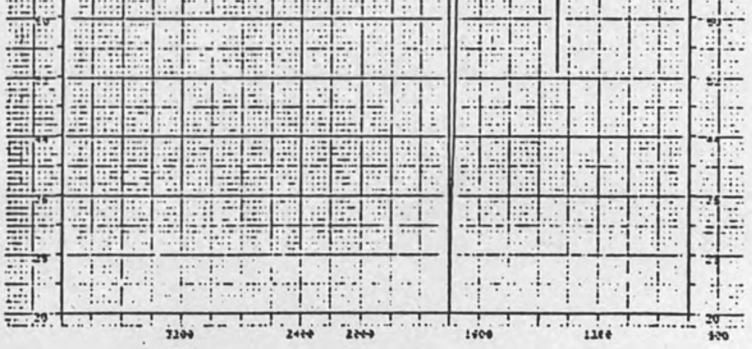
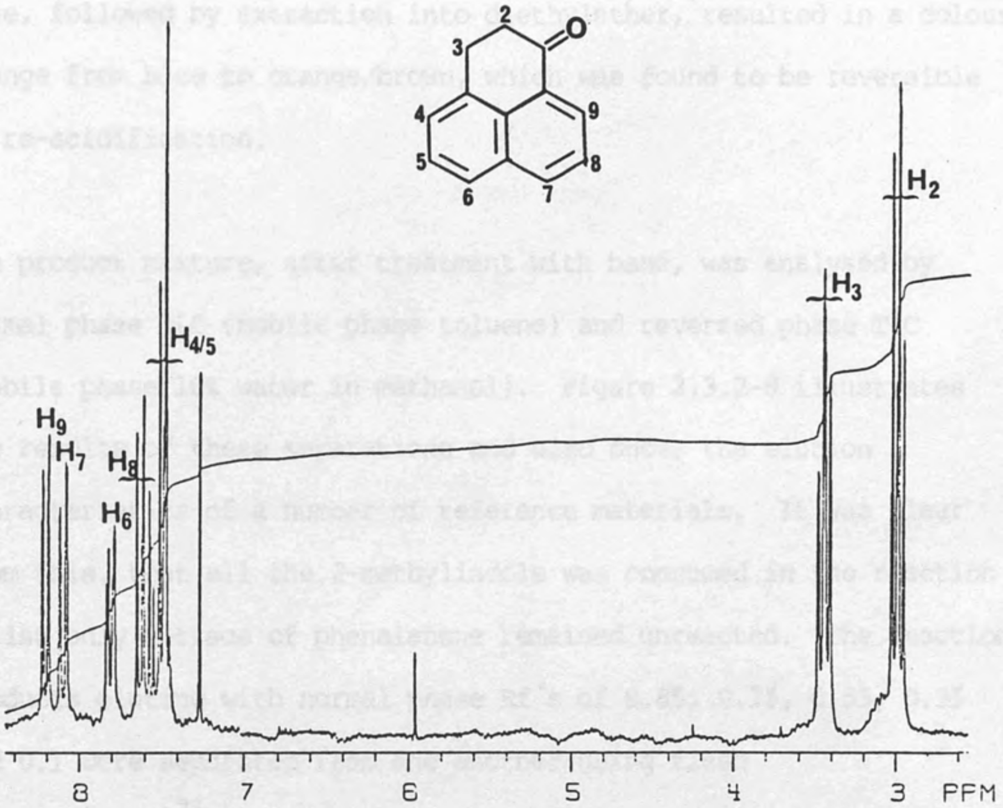


Figure 2.3.2-6 Proton NMR spectrum of phenalanone



The attempted synthesis of 2-methylindolylphenalene was carried out according to the scheme illustrated in figure 2.3.2-7. 2-methylindole was used in this reaction (and in reaction 2) in preference to indole itself since the former compound was known to be present in the CC fuel (ch. 2.2.3). The reaction mixture, initially almost colourless, developed a deep blue colouration over a 24 hour period. Treatment of these coloured products with strong base, followed by extraction into diethylether, resulted in a colour change from blue to orange/brown, which was found to be reversible on re-acidification.

The product mixture, after treatment with base, was analysed by normal phase TLC (mobile phase toluene) and reversed phase TLC (mobile phase 10% water in methanol). Figure 2.3.2-8 illustrates the results of these separations and also shows the elution characteristics of a number of reference materials. It was clear from this, that all the 2-methylindole was consumed in the reaction whilst only a trace of phenalanone remained unreacted. The reaction products eluting with normal phase Rf´s of 0.85, 0.75, 0.55, 0.35 and 0.1 were separated from one another using flash chromatography[71]. Two of the reaction products, Rf 0.85 and Rf 0.1, were identified as phenalene and phenalenone respectively. The other minor products, together with the major product of this reaction, Rf 0.75, immediately developed an intense blue colouration on treatment with methanolic HCl. Similar behaviour was noted (ch. 2.2.6) for CC fuel fractions 3(b) and 3(c), normal phase TLC Rf´s of 0.75 and 0.55 respectively.

Figure 2.3.2-7 Scheme of reaction 1

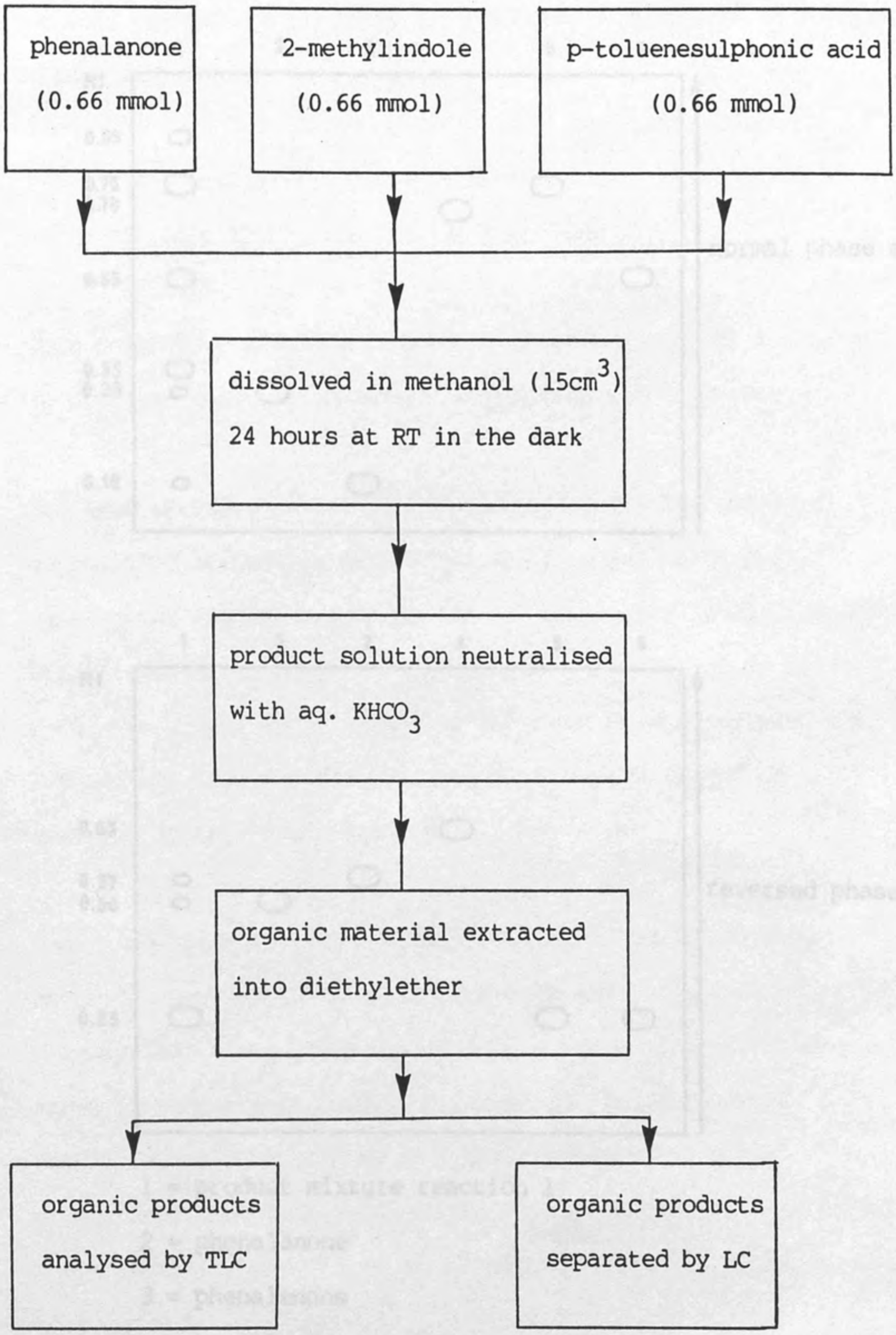
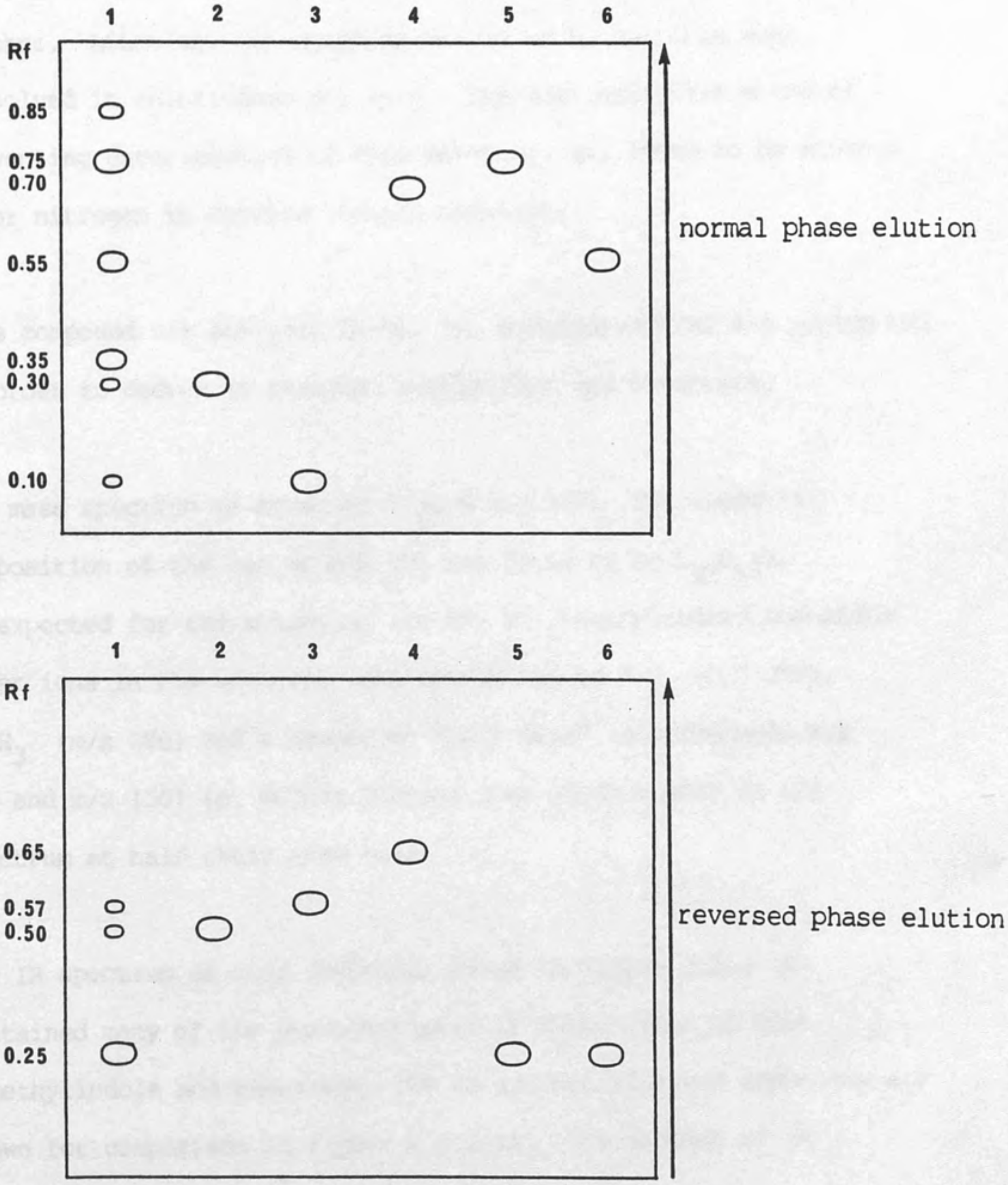


Figure 2.3.2-8 Normal phase (top) and reversed phase (bottom) separation of the products of reaction 1.



1 = product mixture reaction 1

2 = phenalanone

3 = phenalenone

4 = 2-methylindole

5 = CC fuel fraction 3(b)

6 = CC fuel fraction 3(c)

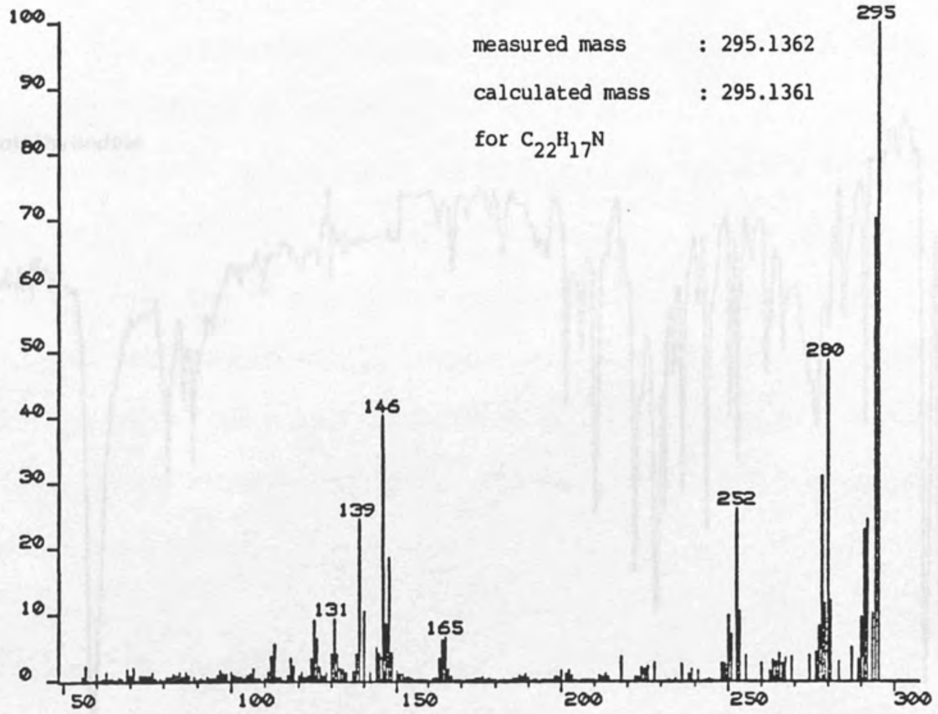
The major product of this reaction, Rf 0.75, could not be purified by recrystallisation. The solid form of the compound was found to readily discolour in contact with glassware even under a nitrogen blanket. Likewise, the compound proved to be unstable when dissolved in chlorinated solvents. The most effective means of preventing deterioration of this material, was found to be storage under nitrogen in chilled toluene solution.

This compound was analysed by MS, IR, pyrolysis/GC/MS and proton NMR in order to deduce it chemical composition and structure.

Its mass spectrum is shown in figure 2.3.2-9. The elemental composition of the ion at m/z 295 was found to be $C_{22}H_{17}N$, as expected for the molecular ion (M) of 2-methylindolylphenalene. Other ions in the spectrum were attributed to M-H (m/z 294), $M-CH_3$ (m/z 280) and a number of "half-mass" ions (between m/z 135 and m/z 150) ie. doubly charged ions which appear in the spectrum at half their true mass.

The IR spectrum of this compound, shown in figure 2.3.2-10, contained many of the characteristic IR absorptions of both 2-methylindole and phenalene. The IR spectra of these compounds are shown for comparison in figure 2.3.2-11. The absence of IR absorbance at 1700 cm^{-1} or 1640 cm^{-1} indicated that the compound did not contain a carbonyl group associated with either a phenalanone (1700 cm^{-1}) or phenalenone (1640 cm^{-1}) ring system.

Figure 2.3.2-9 Mass spectrum of the major product of reaction 1.


measured mass : 295.1362

calculated mass : 295.1361

for $C_{22}H_{17}N$

Figure 2.3.2-10 Infrared spectrum of the major product of reaction 1.

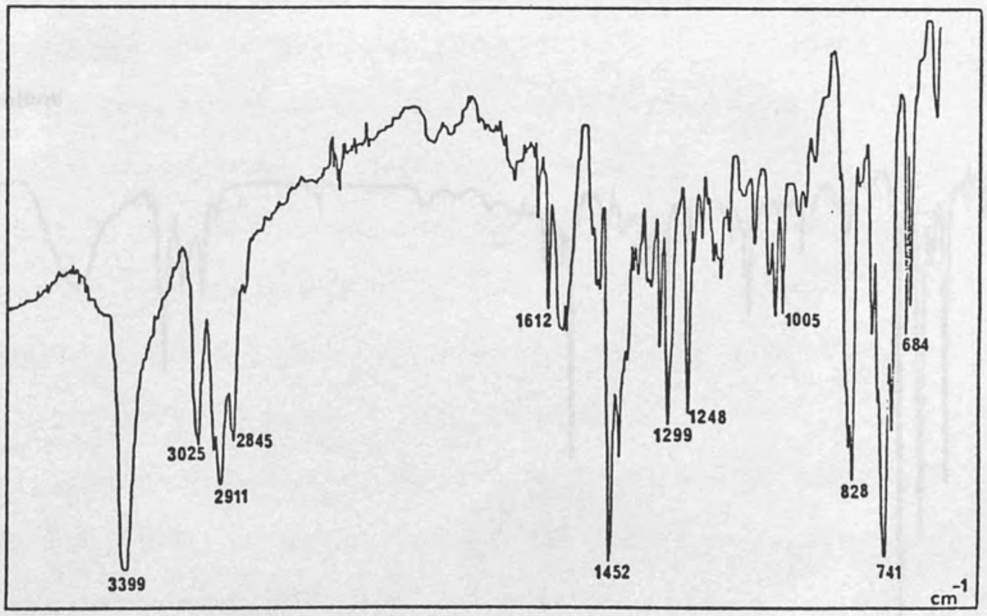
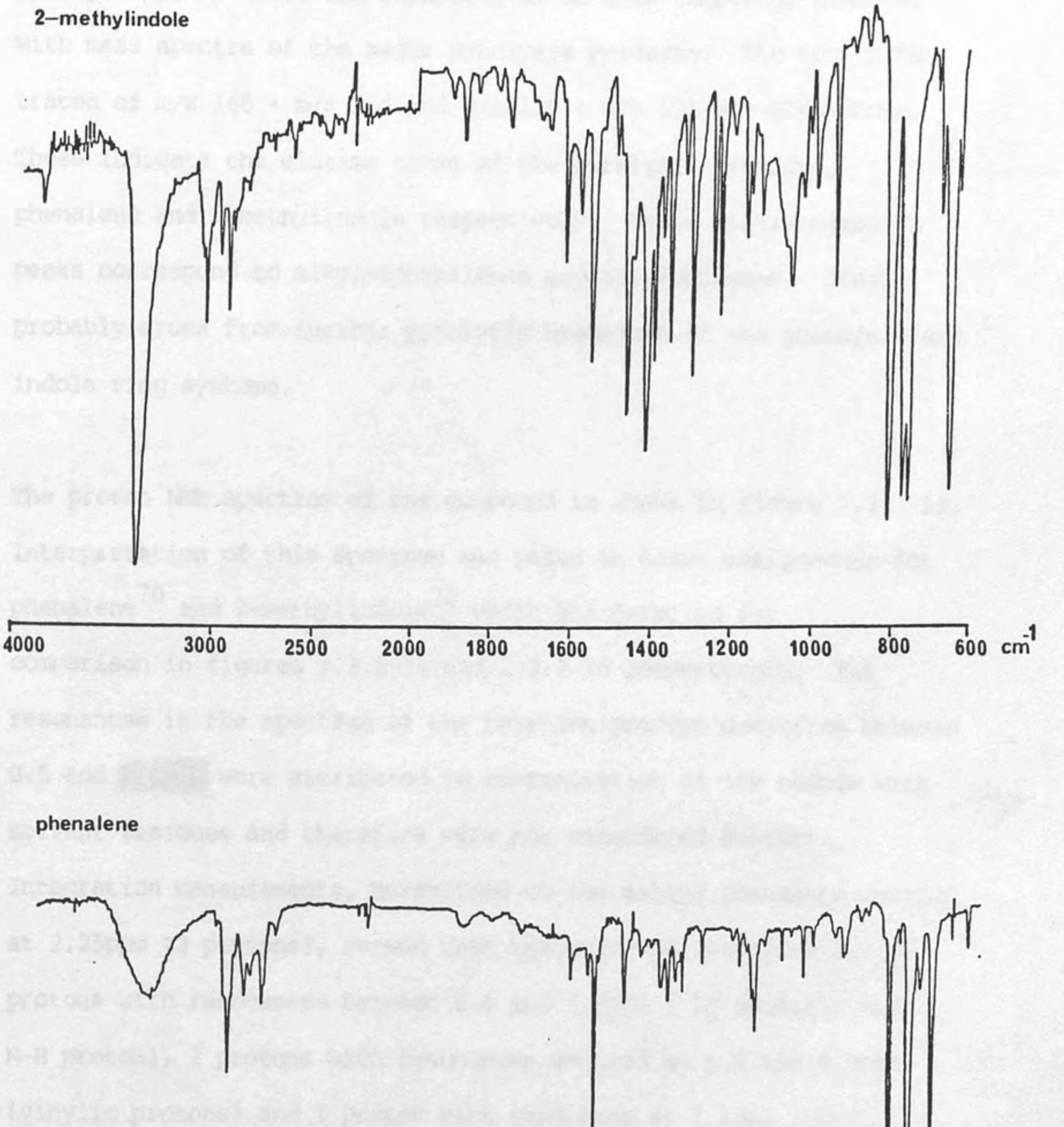


Figure 2.3.2-11 Infrared spectra of 2-methylindole (top) and phenalene (bottom).



Further evidence to suggest that this compound contained 2-methylindole and phenalene ring systems was provided by the results of a pyrolysis/GC/MS experiment. Figure 2.3.2-12 shows the pyrolysis/GC/MS total ion chromatogram of this compound, together with mass spectra of the major pyrolysis products. The ion current traces of m/z 165 + m/z 166 and m/z 130 + m/z 131 are also shown. These indicate the elution times of the pyrolysis products, phenalene and 2-methylindole respectively. Minor chromatographic peaks correspond to alkylnaphthalenes and alkylbenzenes. These probably arose from further pyrolytic breakdown of the phenalene and indole ring systems.

The proton NMR spectrum of the compound is shown in figure 2.3.2-13. Interpretation of this spectrum was based on known assignments for phenalene[70] and 2-methylindole[72] which are detailed for comparison in figures 2.3.2-14 and 2.3.2-15 respectively. The resonances in the spectrum of the reaction product occurring between 0.5 and 1.5ppm were attributed to contamination of the sample with solvent residues and therefore were not considered further. Integration measurements, normalised to the methyl resonance centred at 2.25ppm (3 protons), showed that the compound contained 11 protons with resonances between 6.8 and 7.9ppm (10 aromatic and 1 N-H proton), 2 protons with resonances centred at 6.6 and 6.0ppm (vinylic protons) and 1 proton with resonance at 4.1ppm (methine proton). Integration of the resonance at 4.2ppm and the resonances between 3.5 and 4.0ppm showed that together they corresponded to less than one proton. This also indicated that these resonances were not associated with the major part of the sample and therefore they were not considered further.

Figure 2.3.2-12 Pyrolysis/GC/MS total ion chromatogram of the major product of reaction 1. (GC temperature programme, 1 min. @ 35°C, 35-200°C @ 8°C/min., 1 min. @ 200°C)

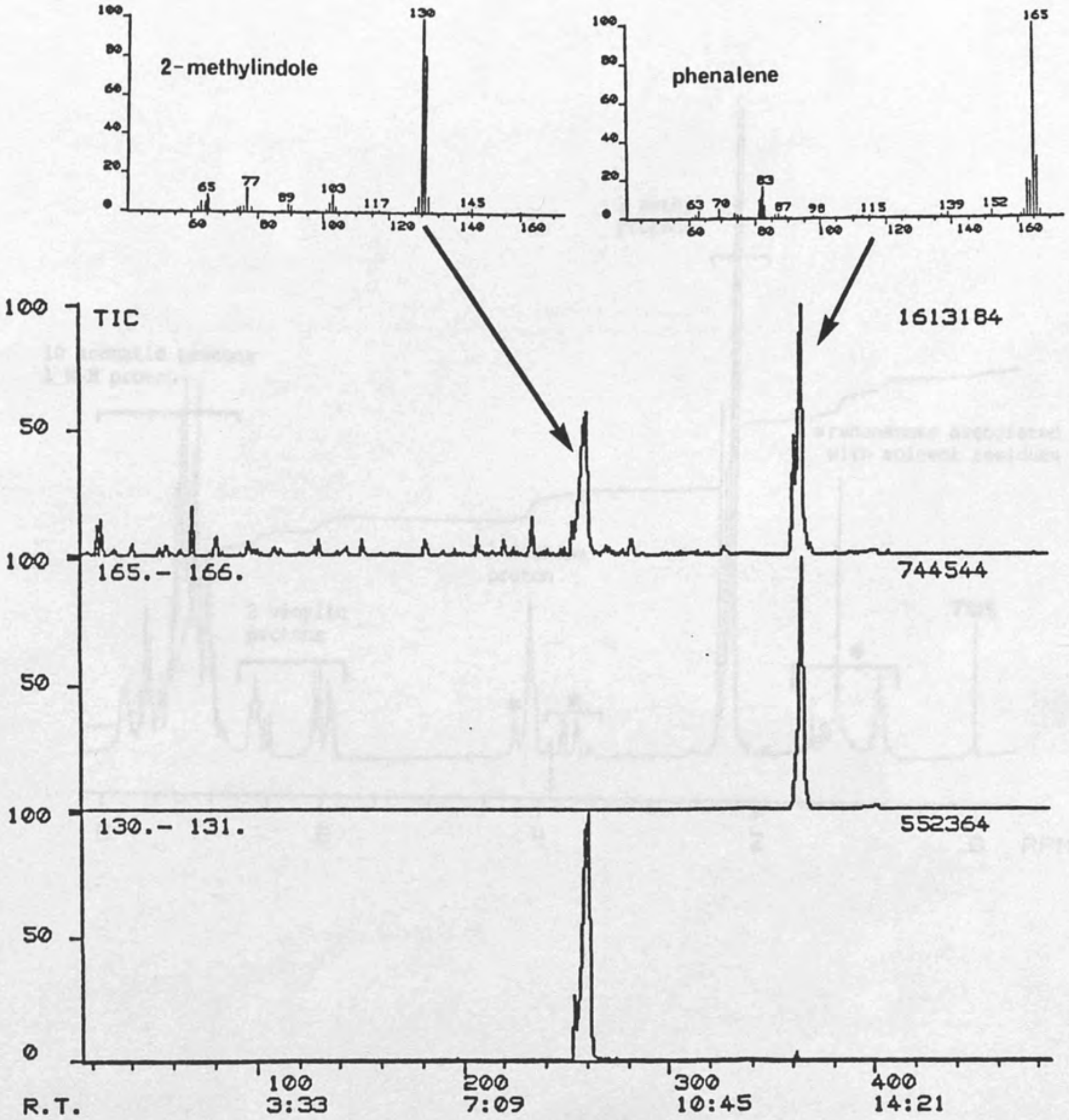


Figure 2.3.2-13 Proton NMR spectrum of the major product of reaction 1.

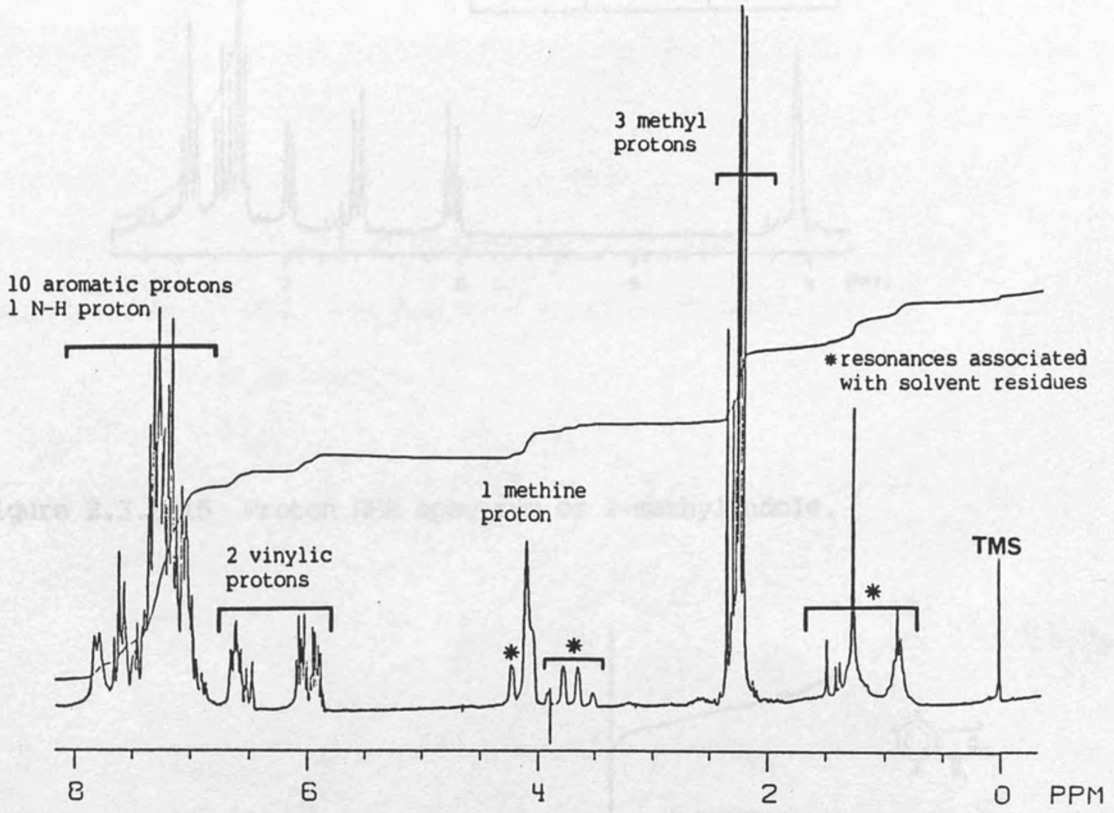
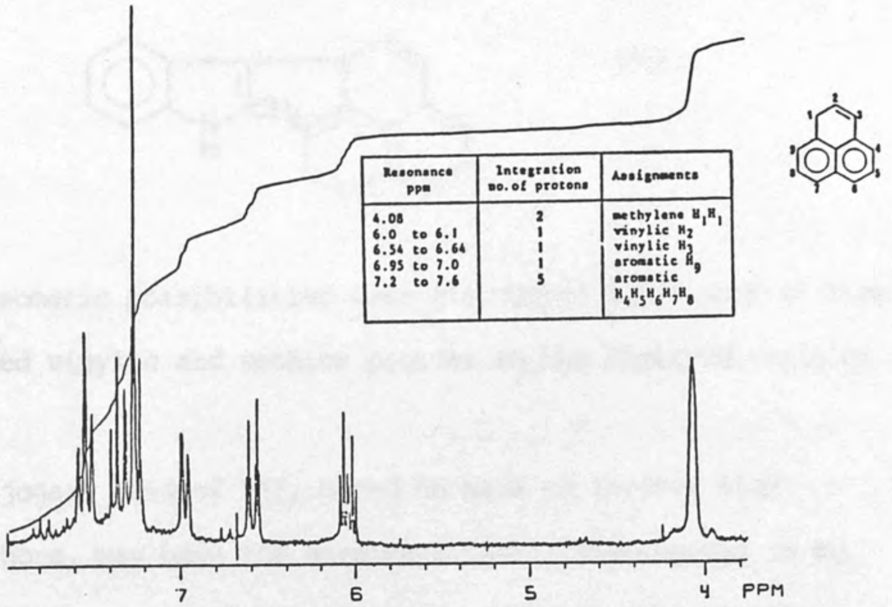
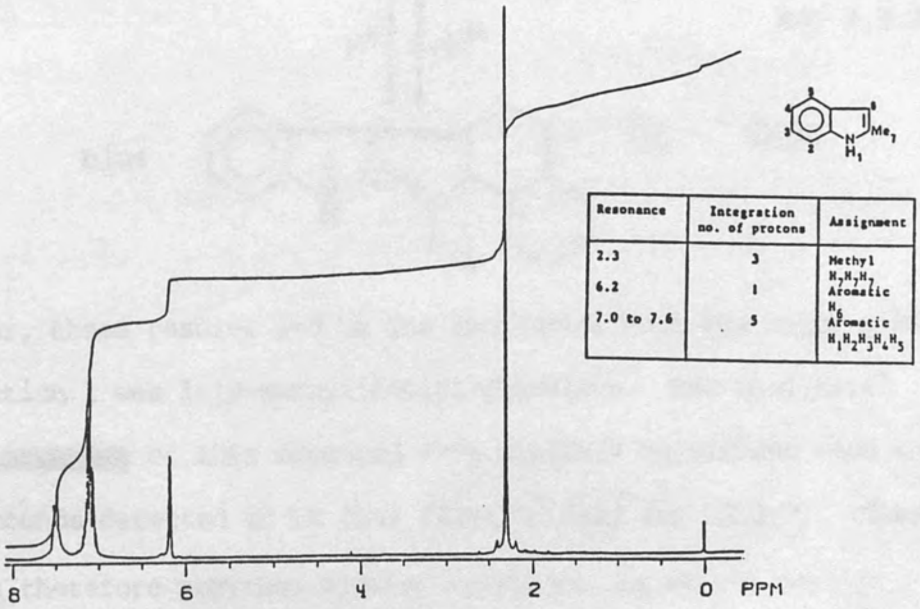


Figure 2.3.2-14 Proton NMR spectrum of phenalene.



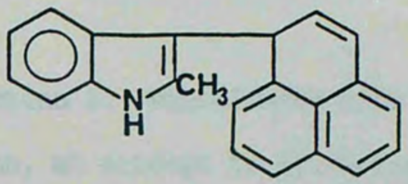
Resonance ppm	Integration no.of protons	Assignments
4.08	2	methylene H_1H_1
6.0 to 6.1	1	vinylic H_2
6.54 to 6.64	1	vinylic H_3
6.95 to 7.0	1	aromatic H_9
7.2 to 7.6	5	aromatic $H_4H_5H_6H_7H_8$

Figure 2.3.2-15 Proton NMR spectrum of 2-methylindole.



Resonance	Integration no. of protons	Assignment
2.3	3	Methyl $H_7H_7H_7$
6.2	1	Aromatic H_6
7.0 to 7.6	5	Aromatic $H_1H_2H_3H_4H_5$

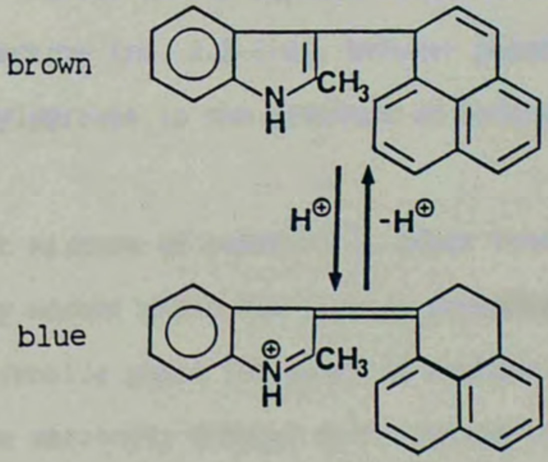
The only 2-methylindolylphenalene structure consistent with these NMR assignments and integrations was 1-(2-methylindolyl)phenalene (XII).



(XII)

Other isomeric possibilities were discounted since none of them contained vinylic and methine protons in the observed ratio of 2:1.

The conjugate acid of XII, noted to have an intense blue chromophore, may have the structure (XIII) illustrated in eq. 2.3.2-1. However it has not been possible to confirm this suggestion experimentally.



(XII)

eq. 2.3.2-1

(XIII)

Together, these results led to the conclusion that the major product of reaction 1 was 1-(2-methylindolyl)phenalene. The analytical characteristics of this compound were entirely consistent with those of compounds detected in CC fuel fraction 3(b) (ch. 2.2.7). These results therefore provided further corroboration of the earlier suggestion that CC fuel fraction 3(b) contained alkyl derivatives of indolylphenalene.

Two minor products of reaction 1, compounds with normal phase TLC Rf´s of 0.55 and 0.35, were also formed in reaction 2. The analysis and identification of these are discussed in the following section.

2.3.3 **Reaction 2. Phenalenone with 2-methylindole**

This reaction, an attempt to synthesis bis(2-methylindolyl)phenalenes, was carried out according to the scheme illustrated in figure 2.3.3-1. The formation of material with an intense blue chromophore was apparent within a few minutes of mixing the reagents. After 24 hours at room temperature, the reaction mixture was treated with strong base and extracted into diethylether. This resulted in a colour change from deep blue to orange brown, which, as observed in reaction 1, was found to be reversible on re-acidification. Treibs, Herrmann and Meissner[63] noted that similar colour changes occur with the products of a related reaction (eq. 2.3.1-4), between phenalenone and 2,4-dimethylpyrrole in the presence of hydrogen bromide.

The product mixture of reaction 2, after treatment with base, was analysed by normal phase TLC (mobile phase toluene) and reversed phase TLC (mobile phase 10% water in methanol). These analyses revealed an extremely complex distribution of products. Figure 2.3.3-2 shows the retention characteristics of only the most abundant species in the mixture, together with a number of reference compounds. Traces of unreacted starting materials were detected, 2-methylindole with normal phase Rf 0.7 and phenalenone with normal phase Rf 0.1.

Figure 2.3.3-1 Scheme of reaction 2

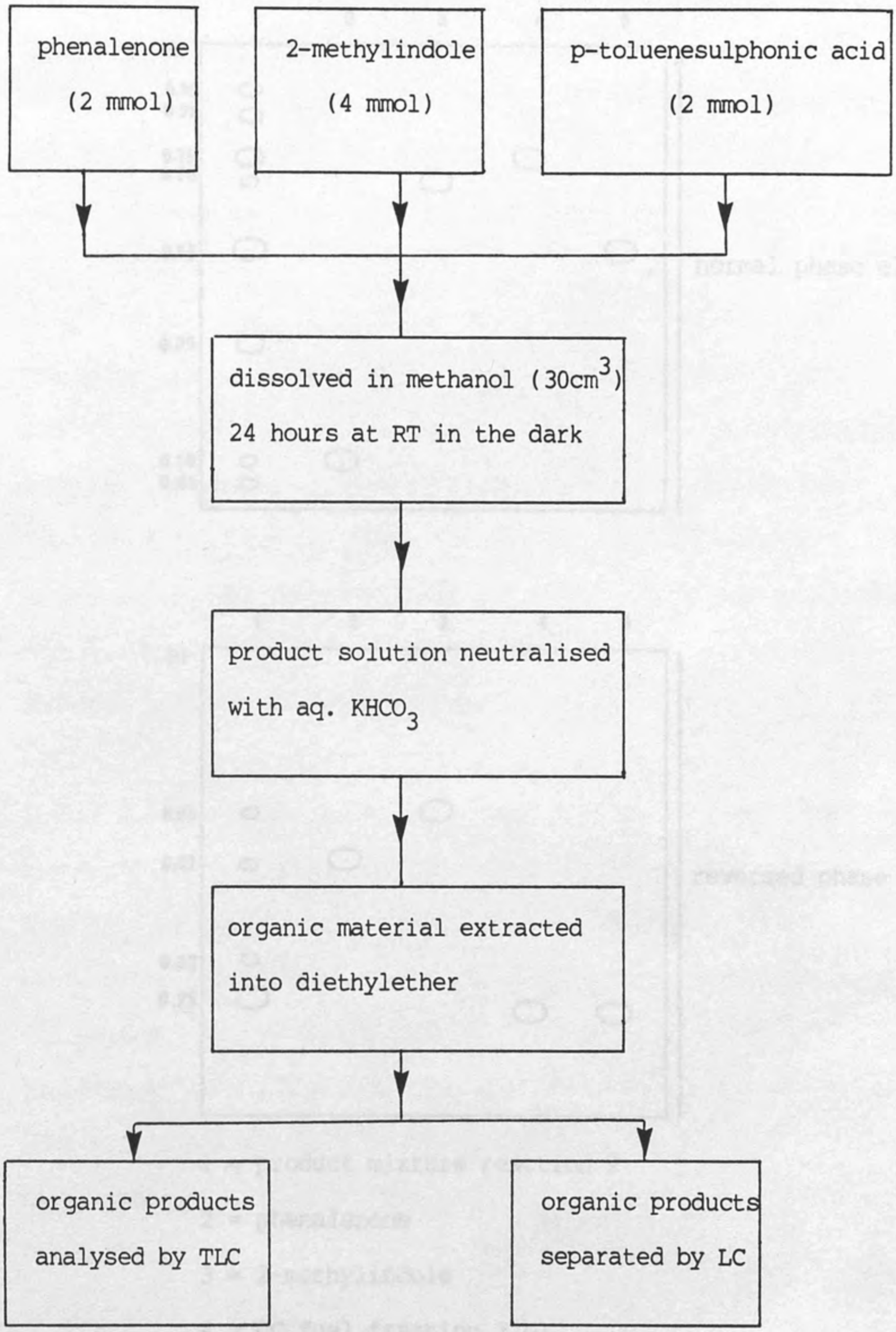
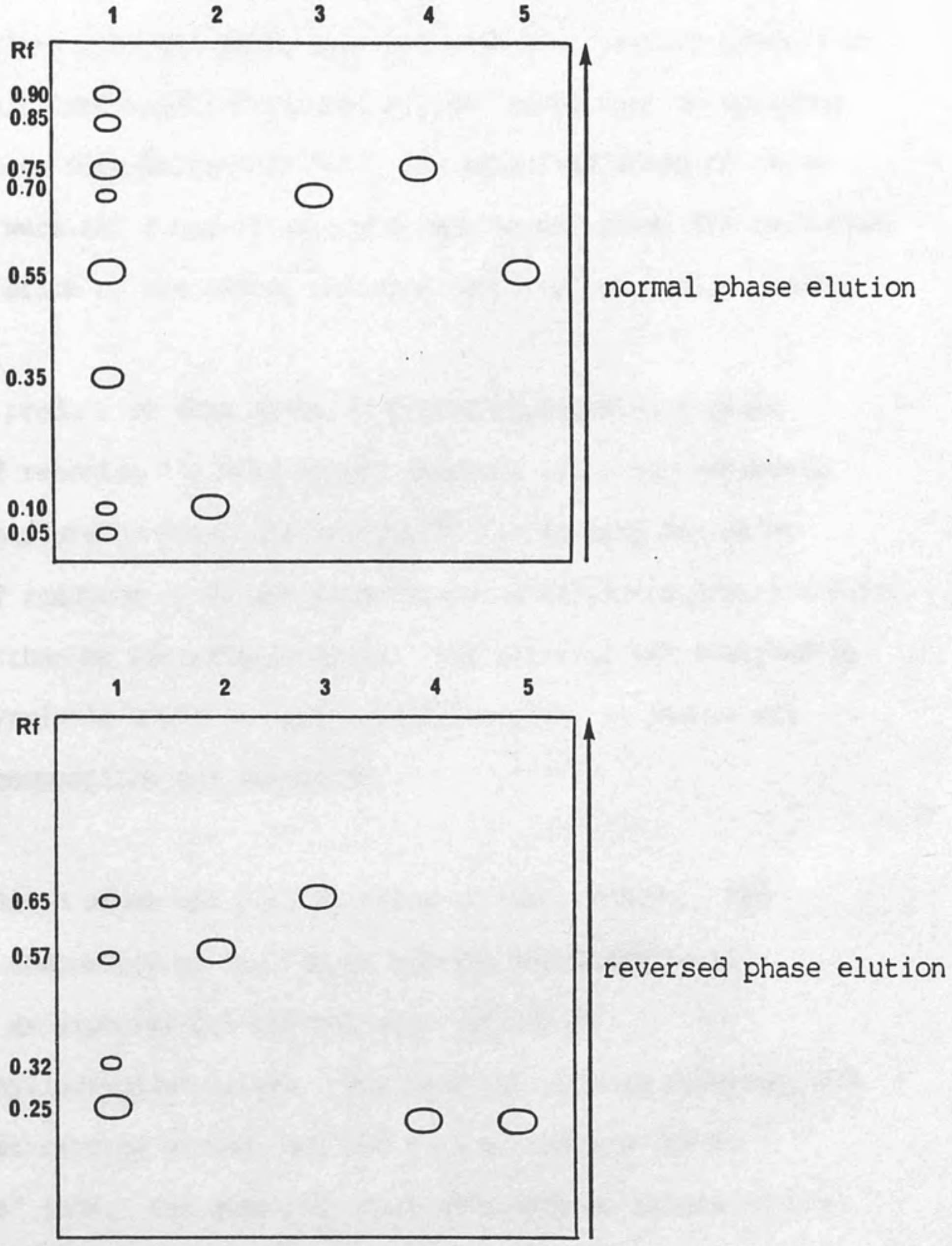


Figure 2.3.3-2 Normal phase (top) and reversed phase (bottom) TLC separation of the products of reaction 2.



1 = product mixture reaction 2

2 = phenalenone

3 = 2-methylindole

4 = CC fuel fraction 3(b)

5 = CC fuel fraction 3(c)

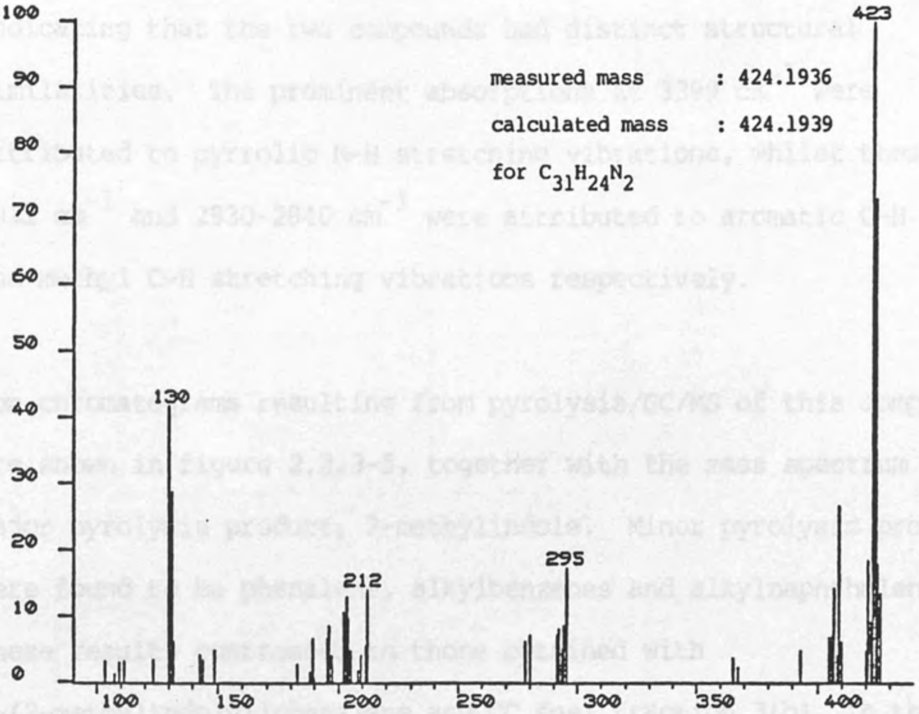
Reaction products were detected with normal phase Rf´s 0.9, 0.85, 0.75, 0.55 (major product), 0.35 and 0.05. The compounds having Rf 0.75 and 0.55 ie. those from the product mixture and those from CC fuel fractions 3(b) and 3(c), together with the reaction product at Rf 0.35, all immediately developed a blue colouration on spraying the TLC plate with methanolic HCl. The acidified forms of these compounds were all found to have the same normal phase TLC retention characteristics as the highly coloured component of fuel sediment.

The major product of this reaction (which appeared as a minor product of reaction 1), with normal phase Rf 0.55, was separated from the mixture by flash chromatography[71]. As with the major product of reaction 1, it was found to be unstable and impossible to purify further by recrystallisation. The material was analysed by MS, IR, pyrolysis/GC/MS and proton NMR, in order to deduce its chemical composition and structure.

Figure 2.3.3-3 shows the mass spectrum of this product. The elemental compositon of the ion at m/z 424 was found to be $C_{31}H_{24}N_2$, as expected for the molcular ion (M) of bis(2-methylindolyl)phenalene. The base ion in this spectrum, m/z 423, was attributed to M-H and the ions around m/z 200 to "half-mass" ions. The measured relative molecular masses of the ions at 131 and 295 Daltons corresponded to C_9H_9N, methylindole and $C_{22}H_{17}N$, methylindolylphenalene respectively.

The infrared spectrum of this compound is shown in figure 2.3.3-4.

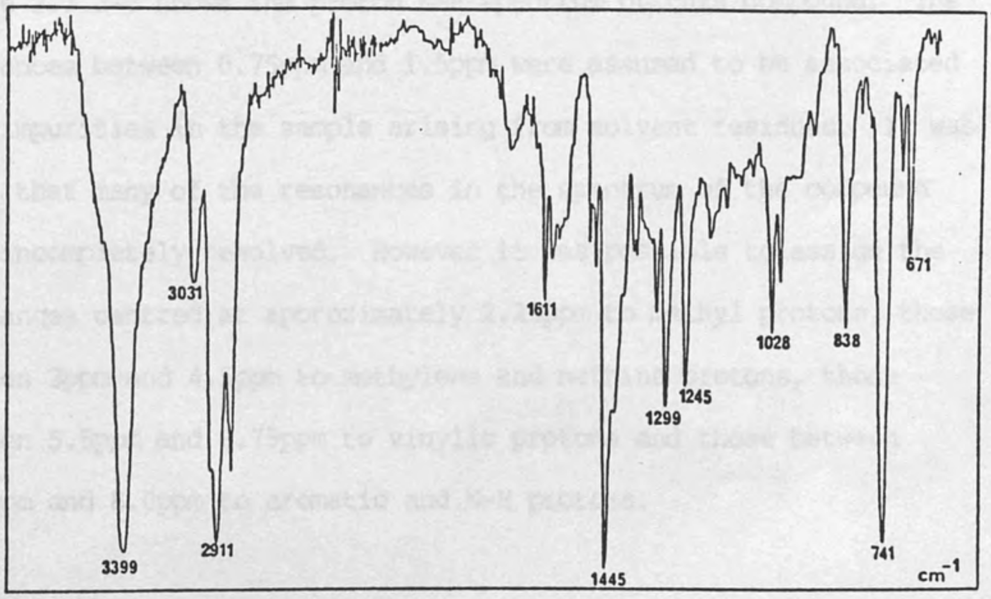
Figure 2.3.3-3 Mass spectrum of the major product of reaction 2.


measured mass : 424.1936

calculated mass : 424.1939

for $C_{31}H_{24}N_2$

Figure 2.3.3-4 Infrared spectrum of the major product of reaction 2.



It showed many of the same features as the spectrum of 1-(2-methylindolyl)phenalene, illustrated in figure 2.3.2-10, indicating that the two compounds had distinct structural similarities. The prominent absorptions at 3399 cm^{-1} were attributed to pyrrolic N-H stretching vibrations, whilst those at 3031 cm^{-1} and 2930-2840 cm^{-1} were attributed to aromatic C-H and methyl C-H stretching vibrations respectively.

Ion chromatograms resulting from pyrolysis/GC/MS of this compound are shown in figure 2.3.3-5, together with the mass spectrum of the major pyrolysis product, 2-methylindole. Minor pyrolysis products were found to be phenalene, alkylbenzenes and alkylnaphthalenes. These results contrasted to those obtained with 1-(2-methylindolyl)phenalene and CC fuel fraction 3(b), in that very little phenalene was produced during pyrolysis. However they compared well with the pyrolysis characterisitcs of CC fuel fraction 3(c) (ch. 2.2.7).

Figure 2.3.3-6 shows the proton NMR spectrum of this compound. The resonances between 0.75ppm and 1.5ppm were assumed to be associated with impurities in the sample arising from solvent residues. It was clear that many of the resonances in the spectrum of the compound were incompletely resolved. However it was possible to assign the resonances centred at approximately 2.25ppm to methyl protons, those between 3ppm and 4.5ppm to methylene and methine protons, those between 5.5ppm and 6.75ppm to vinylic protons and those between 6.75ppm and 8.0ppm to aromatic and N-H protons.

Figure 2.3.2-5 Pyrolysis/GC/MS total ion chromatogram of the major product of reaction 2.
(GC temperature programme, 1 min. @ 35°C, 35-200°C @ 8°C/min., 1 min. @ 200°C)

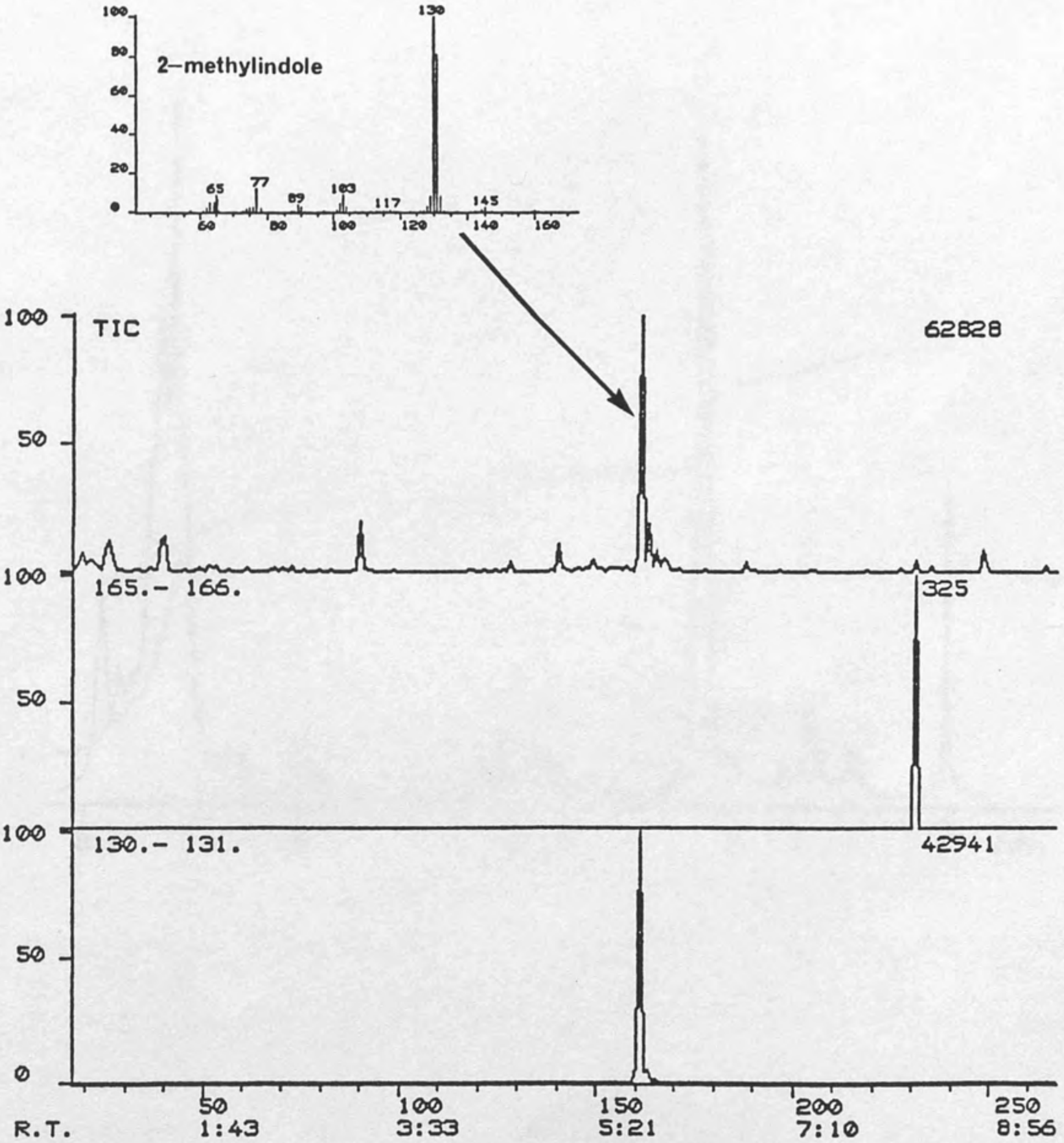
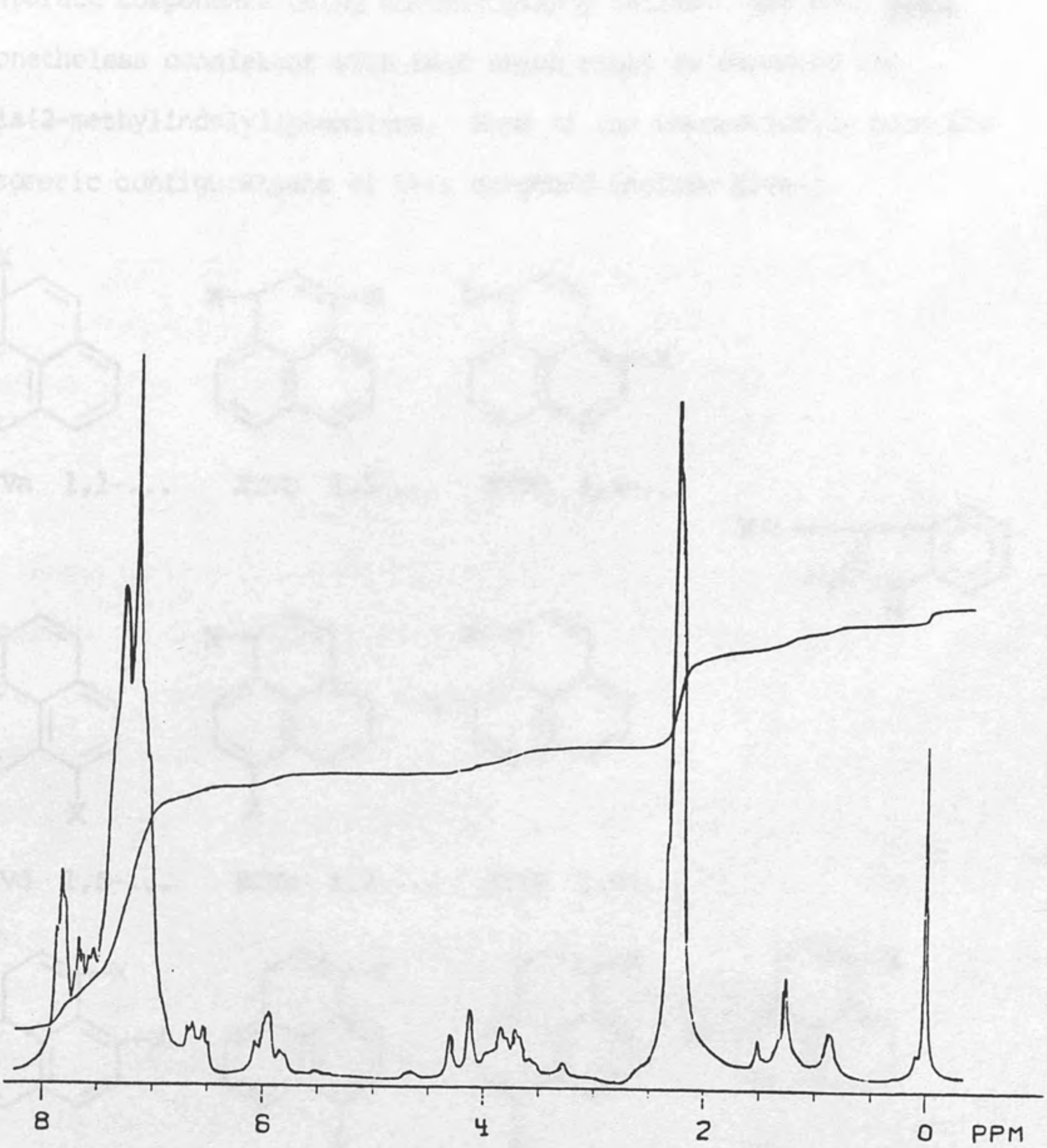
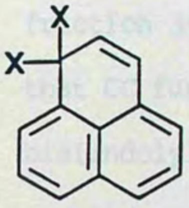


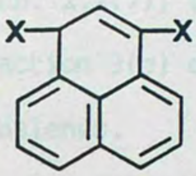
Figure 2.3.3-6 Proton NMR spectrum of the major product of reaction 2.



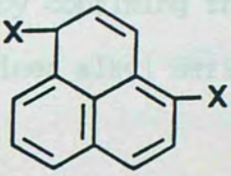
The complexity of the spectrum suggested that the sample consisted of a mixture of compounds, although attempts to resolve it into separate components using chromatography failed. The data were nonetheless consistent with that which might be expected for bis(2-methylindolyl)phenalene. Some of the theoretically possible isomeric configurations of this compound include XIVa-j.



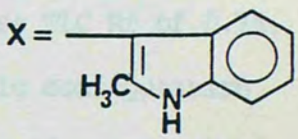
XIVa 1,1-...

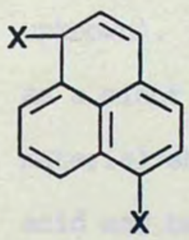


XIVb 1,3-...

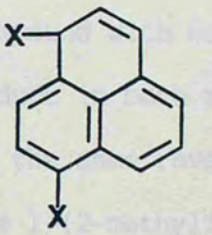


XIVc 1,4-...

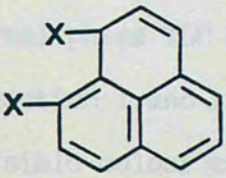




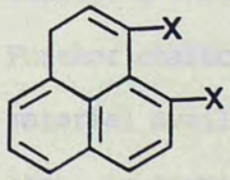
XIVd 1,6-...



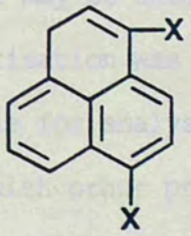
XIVe 1,7-...



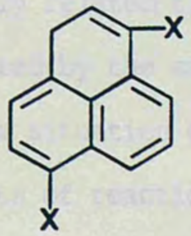
XIVf 1,9-...



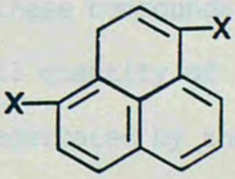
XIVg 3,4-...



XIVh 3,6-...



XIVi 3,7-...



XIVj 3,9-...

However the NMR spectrum of this material, like the spectra of phenalene (figure 2.3.2-14) and 1-(2-methylindolyl)phenalene (figure 2.3.2-13), did appear to contain two vinylic resonances, this limiting the isomeric possibilities to 1,1-..., 1,4..., 1,6..., 1,7... or 1,9-... configurations, although the 1,1... and 1,9... configurations may be considered less likely for steric reasons.

Together, these results showed that the general analytical characteristics of XIV, the major product of reaction 2, were entirely consistent with those of the compounds detected in CC fuel fraction 3(c) (ch. 2.2.7), thereby confiming the earlier suggestion that CC fuel fraction 3(c) contained alkyl derivatives of bis(indolyl)phenalenes.

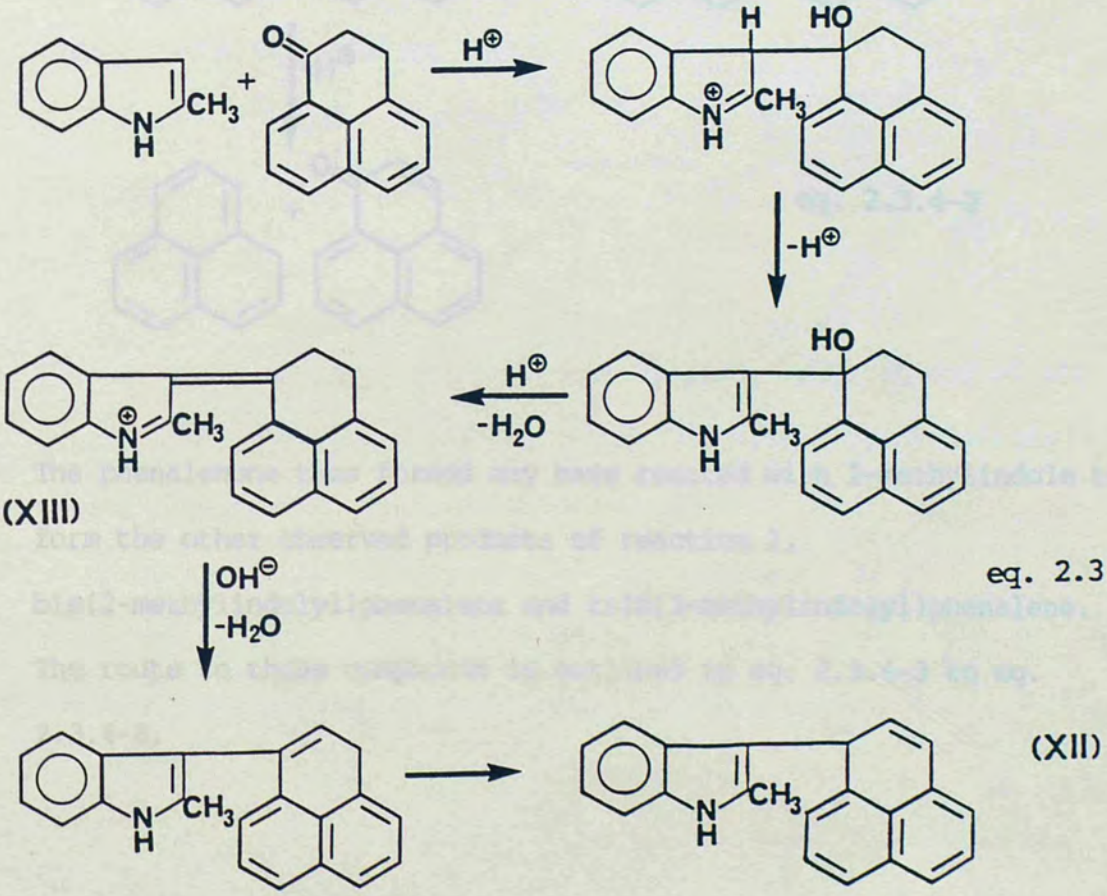
The minor product of reaction 2, with a normal phase TLC Rf of 0.75, was found to be a 2-methylindolylphenalene (isomeric configuration unknown). A compound with normal phase TLC Rf of 0.35 was detected as a minor procduct in both reaction 1 and reaction 2. This material showed the same reversible colour changes when treated with acid and base as 1-(2-methylindolyl)phenalene and 1,X-bis(2-methylindolyl)phenalene (X=1, 4, 6, 7 or 9), which indicated that it may be chemically related to these compounds. Further characterisation was limited by the small quantity of material available for analysis, a situation exacerbated by the fact that, in common with other products of reactions 1 and 2, the compound was found to be unstable. However low resolution MS analysis of a crude sample of this material resulted in the formation of several ions with relative molecular masses in excess of 500 Daltons, including one at m/z 553 which may indicate that this product corresponded to a tris(2-methylindolyl)phenalene.

2.3.4 Rationalisation of reactions 1 and 2

The schemes outlined in eq. 2.3.4-1 to eq. 2.3.4-8 are an attempt to explain the distribution of products observed in reactions 1 and 2. None of the proposed intermediates was isolated and therefore the schemes do not constitute a mechanistic interpretation of these reactions.

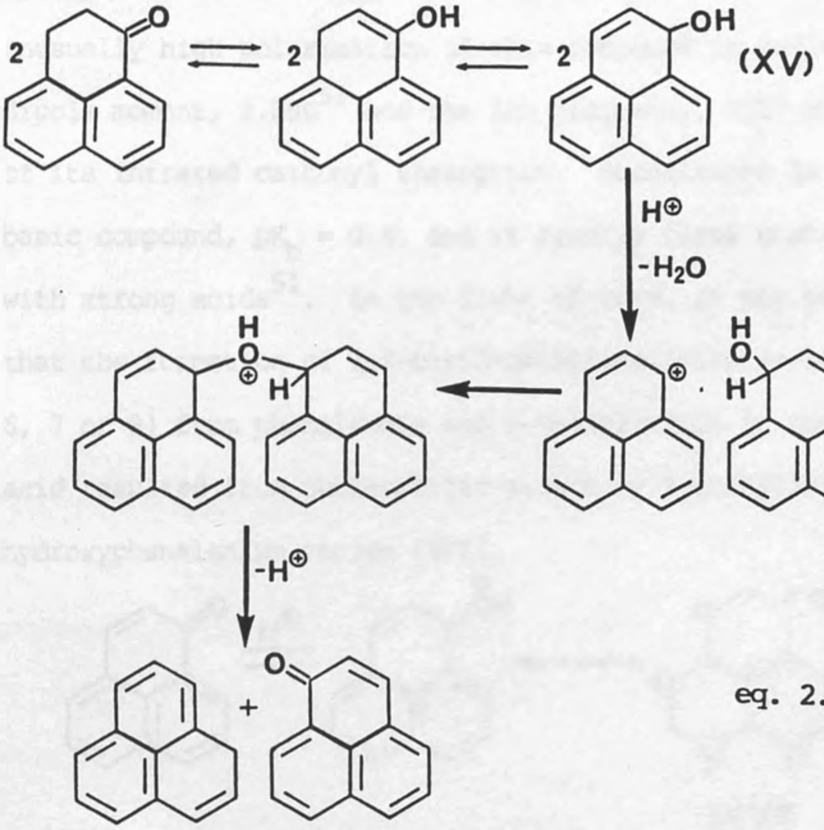
Reaction 1

The formation of 1-(2-methylindolyl)phenalene (XII) in reaction 1 can be explained simply in terms of a reaction involving nucleophilic attack by 2-methylindole on the carbonyl carbon of phenalanone, followed by loss of water.



eq. 2.3.4-1

The presence of phenalene and phenalenone in the product mixture may have arisen from a disproportionation reaction involving 1-hydroxyphenalene (XV)[51].

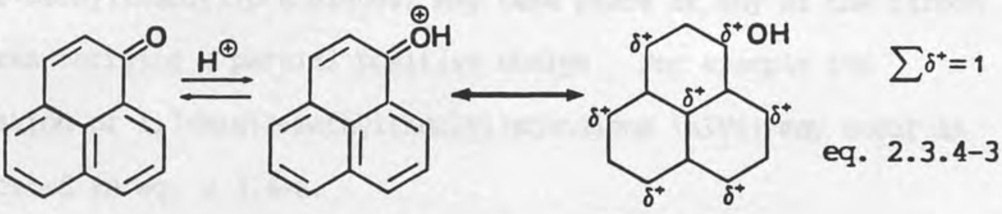


eq. 2.3.4-2

The phenalenone thus formed may have reacted with 2-methylindole to form the other observed products of reaction 1, bis(2-methylindolyl)phenalene and tris(2-methylindolyl)phenalene. The route to these compounds is outlined in eq. 2.3.4-3 to eq. 2.3.4-8.

Reaction 2

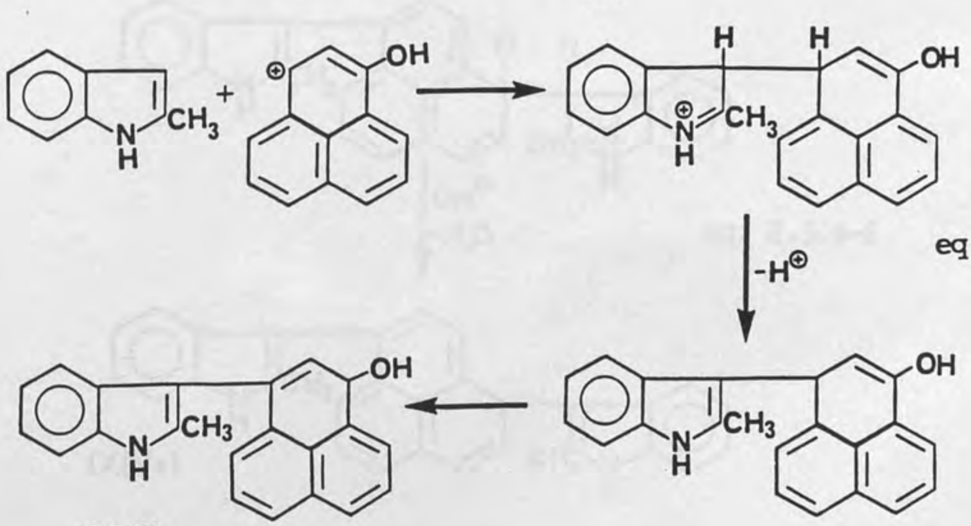
Phenalenone, unlike phenalanone, does not undergo many of the reactions normally associated with ketonic species. For example it does not form a 2,4-dinitrophenylhydrazone[51] and it only forms a hydrazone[73] and an oxime[66] under forcing conditions. The unusually high polarisation of this compound is reflected by its dipole moment, 3.89D[51] and the low frequency, 1637 cm^{-1} [69], of its infrared carbonyl absorption. Phenalenone is a strongly basic compound, $pK_b = 0.4$, and it readily forms stable salts with strong acids[51]. In the light of this, it may be postulated that the formation of 1,X-bis(2-methylindolyl)phenalene (X = 1, 4, 6, 7 or 9) from phenalenone and 2-methylindole in the presence of acid resulted from nucleophilic attack by 2-methylindole on the hydroxyphenalenium cation (XVI).



eq. 2.3.4-3

(XVI)

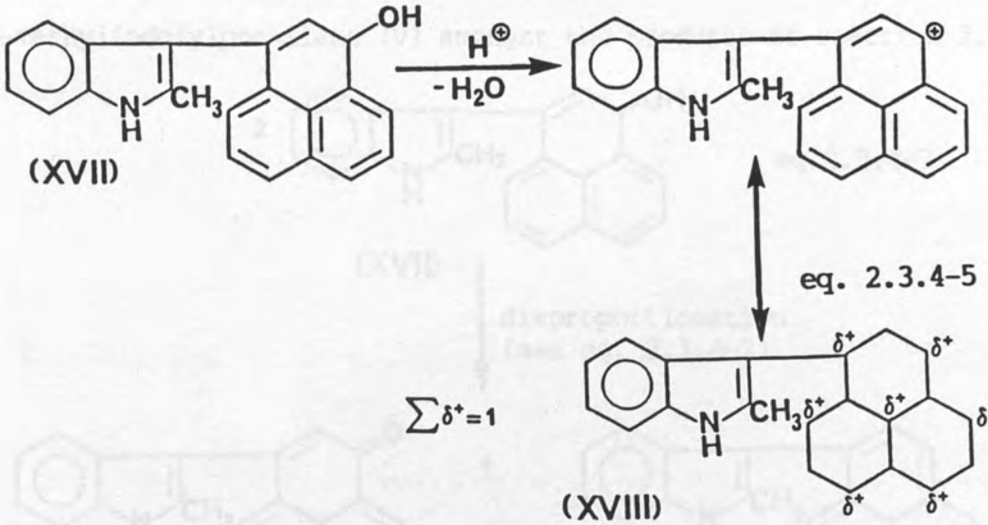
Theoretically nucleophilic substitution could occur at any of the carbon atoms carrying a partial positive charge. The following scheme illustrates substitution at $C_{(3)}$.



eq. 2.3.4-4

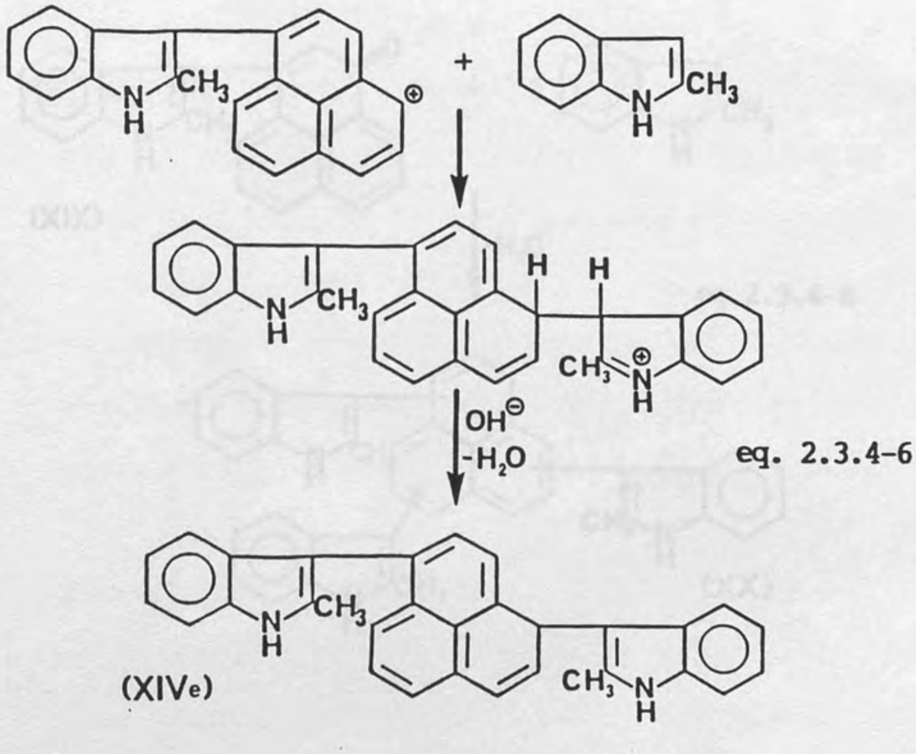
(XVII)

Dehydration of 1-hydroxy-3-(2-methylindolyl)phenalene (XVII) would be expected to lead to the formation of the 2-methylindolylphenalenium cation (XVIII).



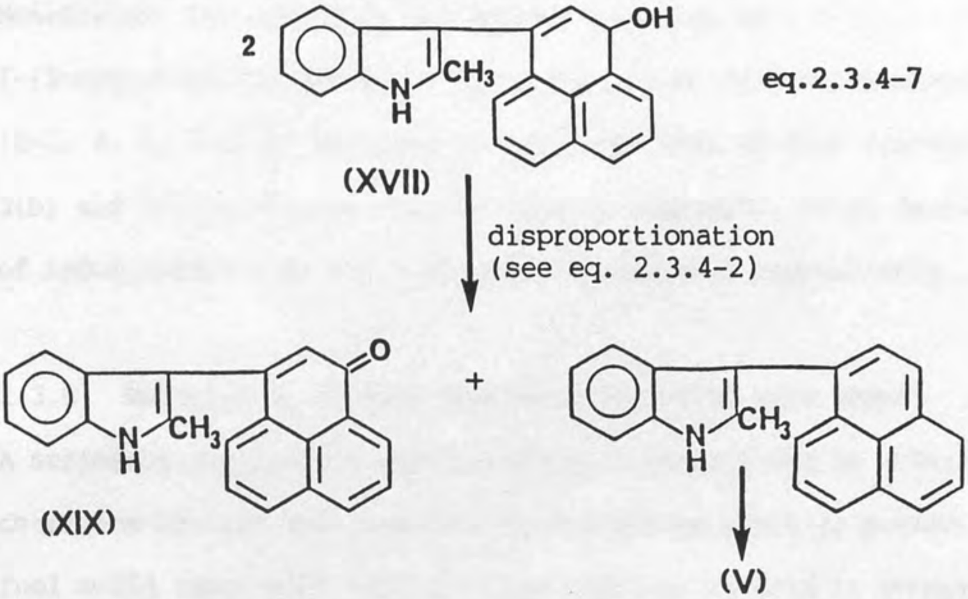
eq. 2.3.4-5

Further nucleophilic substitution, to form bis(2-methylindolyl)phenalenes, may take place at any of the carbon centres carrying a partial positive charge. For example the formation of 1,7-bis(2-methylindolyl)phenalene (XIVe) may occur as indicated in eq. 2.3.4-6.



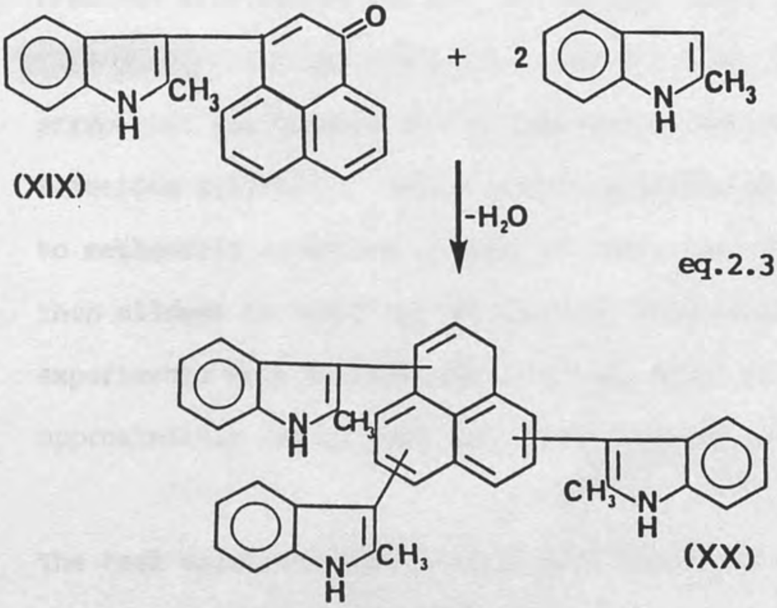
eq. 2.3.4-6

1-Hydroxy-3-(2-methylindolyl)phenalene (XVII) may also undergo a disproportionation reaction of the type indicated previously in eq. 2.3.4-2. This could explain the presence of a 2-methylindolylphenalene (V) amongst the products of reaction 2.



eq.2.3.4-7

Further reaction of 3-(2-methylindolyl)phenalenone (XIX) with two molecules of 2-methylindole would account for the observed formation of tris(2-methylindolyl)phenalene (XX) in both reactions 1 and 2.



eq.2.3.4-8

Clearly more detailed investigations of both reactions 1 and 2 are required in order to develop a thorough mechanistic understanding of the chemical processes which occur in these systems.

Nonetheless the synthesis and characterisation of 1-(2-methylindolyl)phenalene and 1,X-bis(2-methylindolyl)phenalene (X=1, 4, 6, 7 or 9) provided confirmation that CC fuel fractions 3(b) and 3(c) contained closely related compounds, alkyl derivatives of indolylphenalenes and bis(indolyl)phenalenes respectively.

2.3.5 **Reaction 3. CC fuel fractions 4(1)-4(7) with indole**

A series of qualitative experiments were carried out in order to determine whether the phenalenone derivatives actually present in CC fuel would react with indole in the presence of acid to produce coloured products of the same type as those formed in reaction 2.

It was shown in ch. 2.2.9 that phenalenone itself occurred in fraction 4(1) of the CC fuel, whilst its alkyl and benzo derivatives occurred in fractions 4(2)-4(7). Table 2.2.9-1 listed the general structural assignments of the phenalenone derivatives in CC fuel fractions 4(1)-4(7). Indole and p-toluenesulphonic acid were added to methanolic solutions of each of these fuel fractions, which were then allowed to stand for 18 hours at room temperature. These experiments were carried out on a very small scale, since only approximately 2mg of each fuel fraction were available for reaction.

The test solutions involving CC fuel fractions 4(1), 4(2) and 4(3), which were initially bright yellow in colour (characteristic of these phenalenone derivtives), produced intensely coloured blue material under these reaction conditions. The products were analysed by normal phase TLC and found to have the same retention characteristics as the species formed in reaction 2. However the remaining tests, containing fuel fractions 4(4), 4(5), 4(6) and 4(7), did not develop the characteristic strong blue colouration, but remained visually indistinguishable from the initial reactant mixture. The lack of reaction in the test solutions containing CC fuel fractions 4(4), 4(5), 4(6) and 4(7) was confirmed by TLC at the end of the reaction period which showed that they contained only the initial starting materials.

No explanation can be given for the apparent difference in reactivity of these phenalenone derivatives towards indole.

2.3.6 **Summary**

The main results and conclusions arising from experiments carried out to synthesise 2-methylindolylphenalene and bis(2-methylindolyl)phenalene can be summarised as follows:

(i) Mild catalytic hydrogenation of phenalenone yielded 1-hydroxyphenalane as the only significant product.

(ii) Phenalanone was prepared in modest yield by reduction of phenalenone with tetramethyldisiloxane.

(iii) Reaction between 2-methylindole and phenalanone yielded 1-(2-methylindolyl)phenalene as the major product. This compound was unstable and attempts to recrystallise it were unsucessful. In the presence of acid it developed an intense blue chromophore. This colour change was reversible. Other products formed in this reaction included phenalene phenalenone and a bis(2-methylindolyl)phenalene.

(iv) Reaction between 2-methylindole and phenalenone yielded 1,X-bis(2-methylindolyl)phenalene (X = 1, 4, 6, 7 of 9). This compound was also unstable and showed the same colour changes under the influence of acid and base as 1-(2-methylindolyl)phenalene. Several other products were formed in this reaction system. However of these, only a 2-methylindolylphenalene was positively identified.

(v) Alkyl derivatives of phenalenone, extracted from the CC fuel in fractions 4(2) and 4(3), reacted with indole to form products analogous to those formed by reaction of phenalenone with 2-methylindole. However the alkylphenalenones present in CC fuel fractions 4(4) and 4(5), together with the phenalenone derivatives in fractions 4(6) and 4(7), did not react with indole under the same conditions.

(vi) The analytical characteristics of the major products of reactions 1 and 2 were found to be consistent with those of compounds detected in CC fuel fractions 3(b) and 3(c). This therefore supported the conclusions of ch. 2.2.7 that CC fuel fractions 3(b) and 3(c) contained alkyl derivatives of indolylphenalene and bis(indolyl)phenalene.

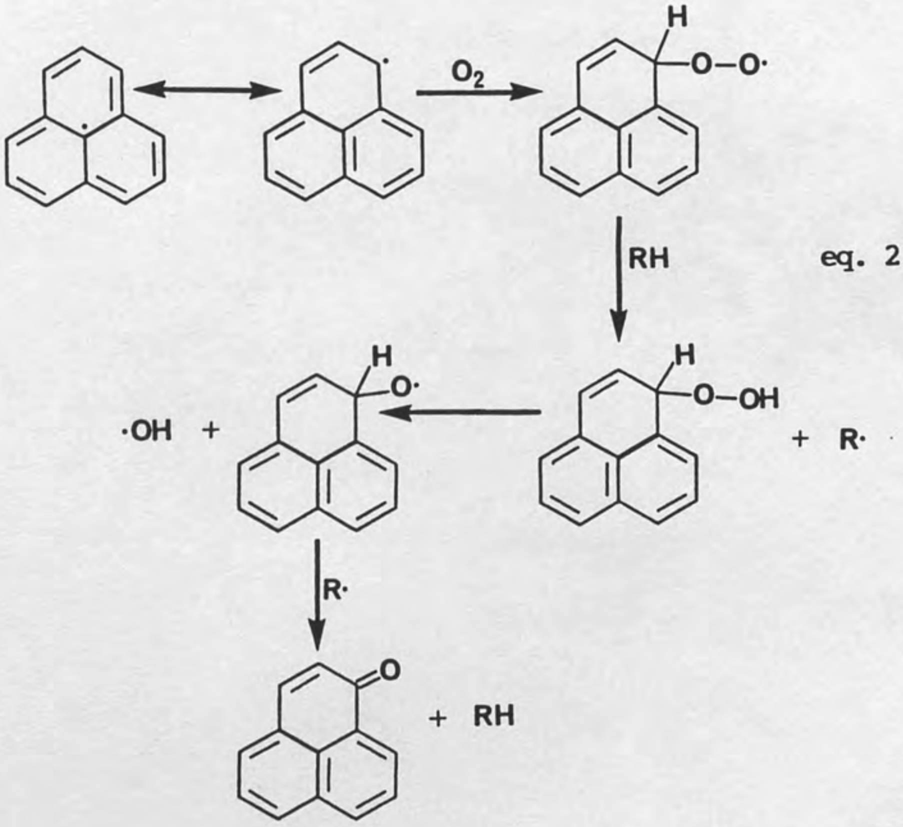
The results of these experiments, together with those arising from sediment analysis and fuel analysis, have been drawn together to form a theory, described in the following chapter, to account for some of the processes leading to sediment formation during storage of an unstable diesel fuel.

2.4 Theory to account for sediment formation in the unstable diesel fuel

2.4.1 Proposed sequence of reactions

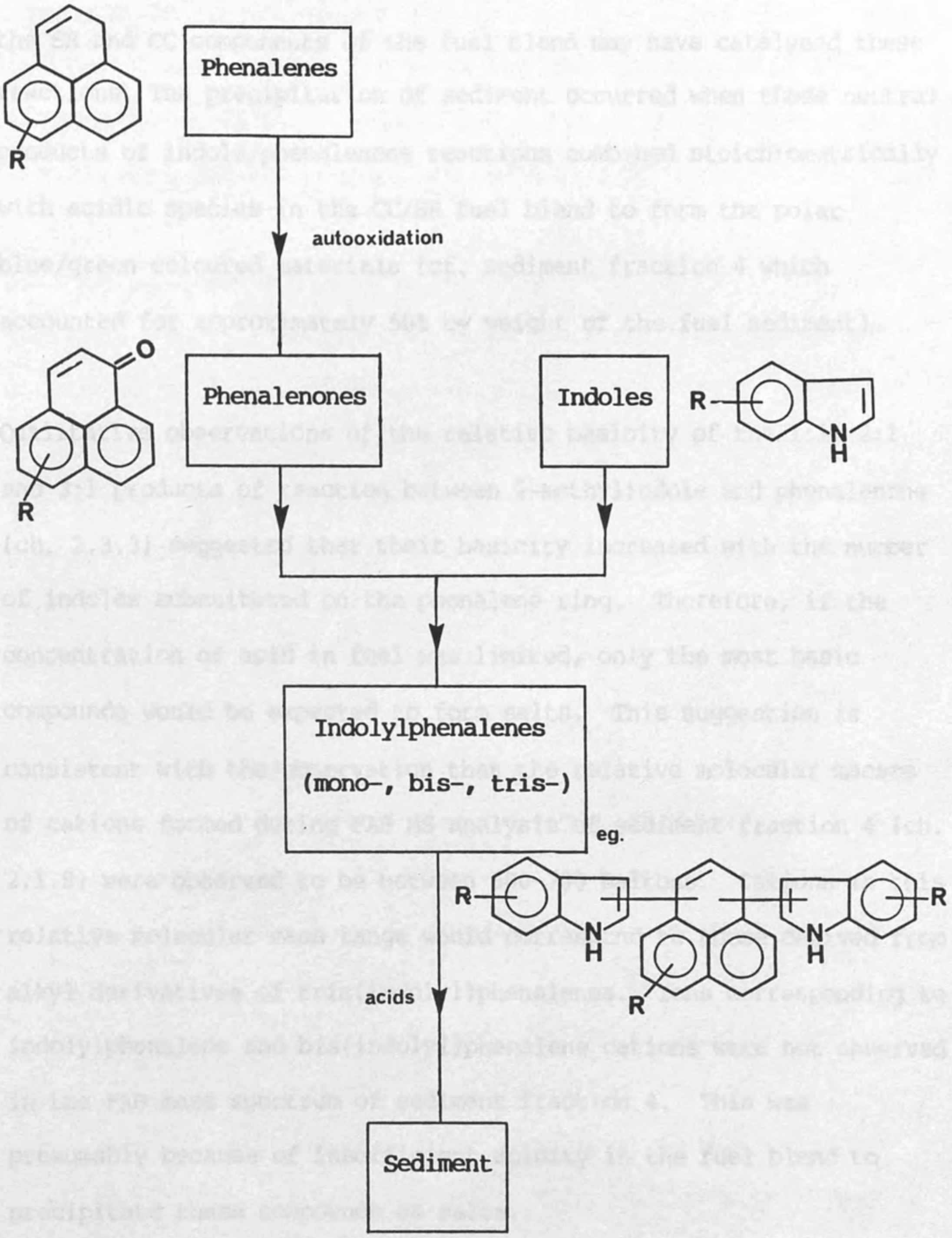
The formation of sediment during storage of unstable diesel fuel, which consisted of a 1:9 blend of catalytically cracked (CC) fuel in North Sea straight run (SR) diesel fuel, can be explained in terms of the reaction sequence outlined in figure 2.4.1-1.

The first stage of the process involved the formation of phenalenones, by autooxidation of phenalenes originally present in the CC portion of the fuel blend. The mechanism of this autooxidation is not known, but it may have involved the unusually stable phenalenyl radical, previously detected in the aromatic fraction of catalyticaly cracked fuels using electron spin resonance techniques[53].



eq. 2.4.1-1

Figure 2.4.1-1 Reaction sequence to account for sediment formation in the unstable diesel fuel.



Alkylindoles, also originating from the CC portion of the fuel blend, reacted with phenalenone and some of its alkyl derivatives (ch. 2.3.5) to form products which included alkylindolylphenalenes and bis(alkylindolyl)phenalenes. Acids present in either or both the SR and CC components of the fuel blend may have catalysed these reactions. The precipitation of sediment occurred when these neutral products of indole/phenalenone reactions combined stoichiometrically with acidic species in the CC/SR fuel blend to form the polar blue/green coloured materials (cf. sediment fraction 4 which accounted for approximately 50% by weight of the fuel sediment).

Qualitative observations of the relative basicity of the 1:1, 2:1 and 3:1 products of reaction between 2-methylindole and phenalenone (ch. 2.3.3) suggested that their basicity increased with the number of indoles substituted on the phenalene ring. Therefore, if the concentration of acid in fuel was limited, only the most basic compounds would be expected to form salts. This suggestion is consistent with the observation that the relative molecular masses of cations formed during FAB MS analysis of sediment fraction 4 (ch. 2.1.8) were observed to be between 600-700 Daltons. Cations in this relative molecular mass range would correspond to those derived from alkyl derivatives of tris(indolyl)phenalenes. Ions corresponding to indolylphenalene and bis(indolyl)phenalene cations were not observed in the FAB mass spectrum of sediment fraction 4. This was presumably because of insufficient acidity in the fuel blend to precipitate these compounds as salts.

The nature of the acids in the fuel blend which were involved in these reactions has not been established. It has been suggested in the literature that sulphonic acids contribute to sediment formation in unstable diesel fuels[10,36,50]. The detection of sulphur dioxide amongst the pyrolysis products of the sediment (ch. 2.1.9) supported the suggestion that sulphur contained in the sediment was in a highly oxidised form. However the low overall sulphur content of the sediment indicated that sulphur containing compounds, acids or otherwise, did not form a significant part of this sediment.

Fraction 1, accounting for approximately 10% by weight of the sediment, was found to have analytical characteristics consistent with those of the bis- or tris(indolyl)phenalenes found in solution in the fuel blend. The detection of this material as a component of the sediment may indicate that it contained additional functional groups which reduced its solubility in diesel fuel. Alternatively a proportion of the bis- and tris(indolyl)phenalenes may have simply co-precipitated with the more polar sediment components.

The nature of fractions 2 and 3 of the sediment remains unclear, although, in common with the other fractions, they have been found to contain alkylindoles. It is possible that they are related to some of the uncharacterised materials formed in reaction 2, phenalenone with 2-methylindole (ch. 2.3.3). Alternatively they may either correspond to other materials, derived from indoles and phenalenones, which form more readily in diesel fuel than in the more polar and acidic conditions of reaction 2, or they may arise from reactions of indoles with fuel species other than phenalenones present in CC fuel.

2.4.2 **Further evidence to support the proposed theory of sediment formation**[*]

A series of fuel storage tests were carried out in order to test the theory of sediment formation described in ch. 2.4.1.

Compounds, representative of those implicated in sediment formation and previously detected only in the CC portion of the unstable fuel blend, were added to 200cm^3 samples of the SR fuel. The composition of each test is given in table 2.4.2-1. The amount of phenalene and 2-methylindole added to the SR fuel was chosen to be approximately equivalent to the expected total concentration of these species in a 1:9 blend of CC in SR fuel.

Table 2.4.2-1 Composition of storage tests 4, 5, 6 and 7

Test number	Composition of test
4	200 cm^3 SR fuel
5	20mg phenalene in 200 cm^3 SR fuel
6	20mg 2-methylindole in 200 cm^3 SR fuel
7	20mg phenalene and 20mg 2-methylindole in 200 cm^3 SR fuel

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[*] The work described in this section was carried out by Dr. R.W. Hiley, Royal Aircraft Establishment, Cobham, Surrey, UK.

The test solutions were filtered after storage for 6 months at 25°C. The weights of sediment produced in this relatively brief period of storage at ambient temperature, were too small for useful comparative measurements to be obtained. However it was clear from the appearance of the filter disks, shown in figure 2.4.2-1, that test 7, containing both phenalene and 2-methylindole, produced the largest amount of sediment (approximately 2mg) during the storage period.

The sediment formed in test 7 was analysed by normal phase TLC (mobile phase 10% water in methanol), MS and IR spectroscopy. TLC separation of the sediment yielded the characteristic blue/green bands at low Rf, together with a small quantity of red/brown material at high Rf. Figure 2.4.2-2 shows a pyrolysis mass spectrum of the sediment from test 7 which was dominated by ions at m/z 130 and m/z 131, attributed to 2-methylindole. The ion at m/z 165 was attributed to phenalene, whilst those at m/z 423, m/z 424 and m/z 552, m/z 553 were attributed to bis(2-methylindolyl)- and tris(2-methylindolyl)phenalene respectively. These spectral features were consistent with those arising from similar analysis of sediment formed during storage of the 1:9 CC/SR fuel blend (see figure 2.4.2-2), except of course that only species corresponding to single methyl homologues were present. Figure 2.4.2-3 shows IR spectra of the sediment from test 7 and, for comparison, the sediment from the CC/SR fuel blend.

Figure 2.4.2-1 Filter disks showing solids produced during storage tests 4, 5, 6 and 7

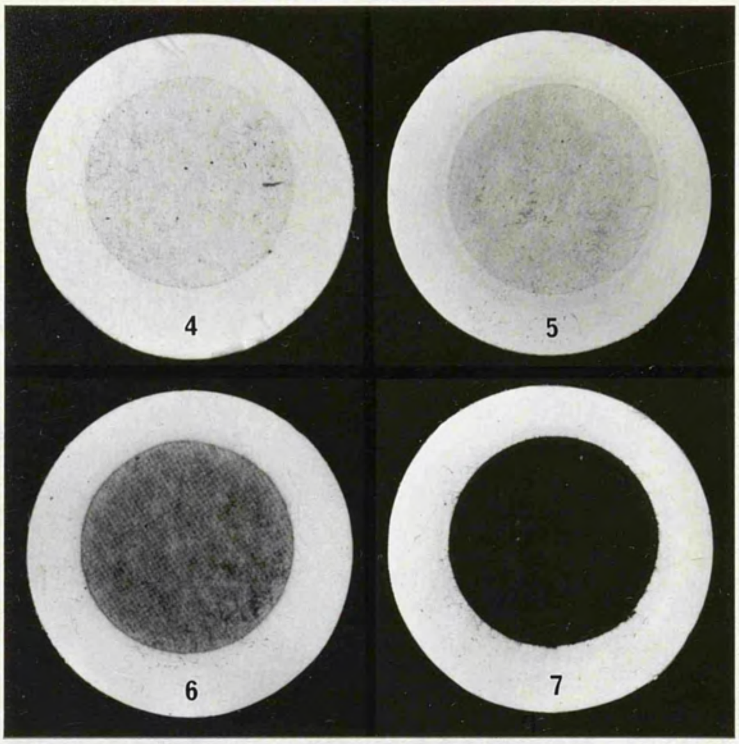
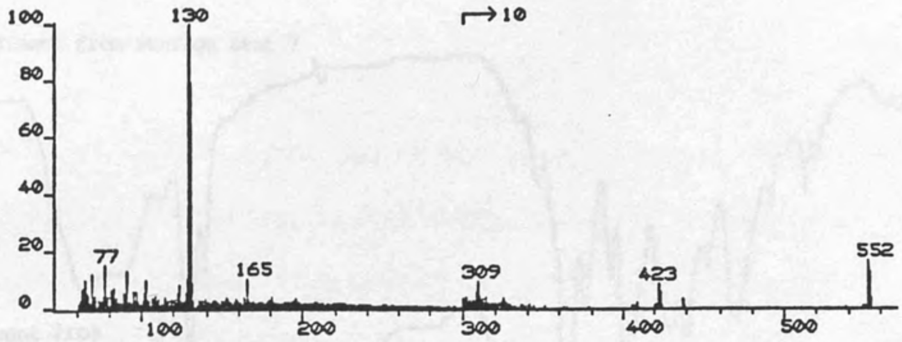


Figure 2.4.2-2 Mass spectra produced by pyrolysis of sediments from storage test 7 (top) and storage of the 1:9 CC/SR fuel blend (bottom)

sediment from storage test 7



sediment from fuel blend

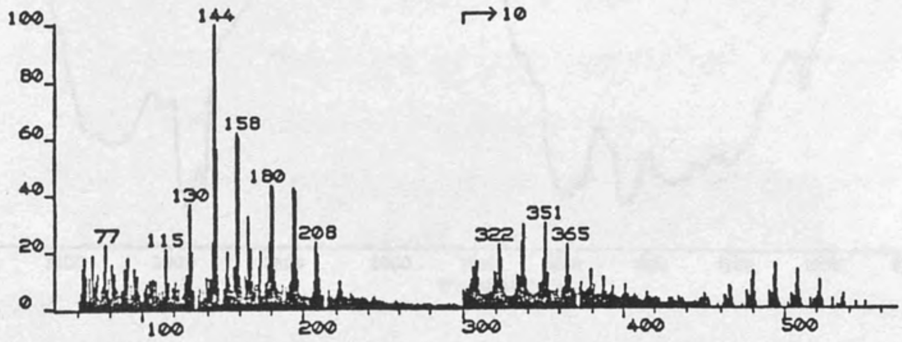
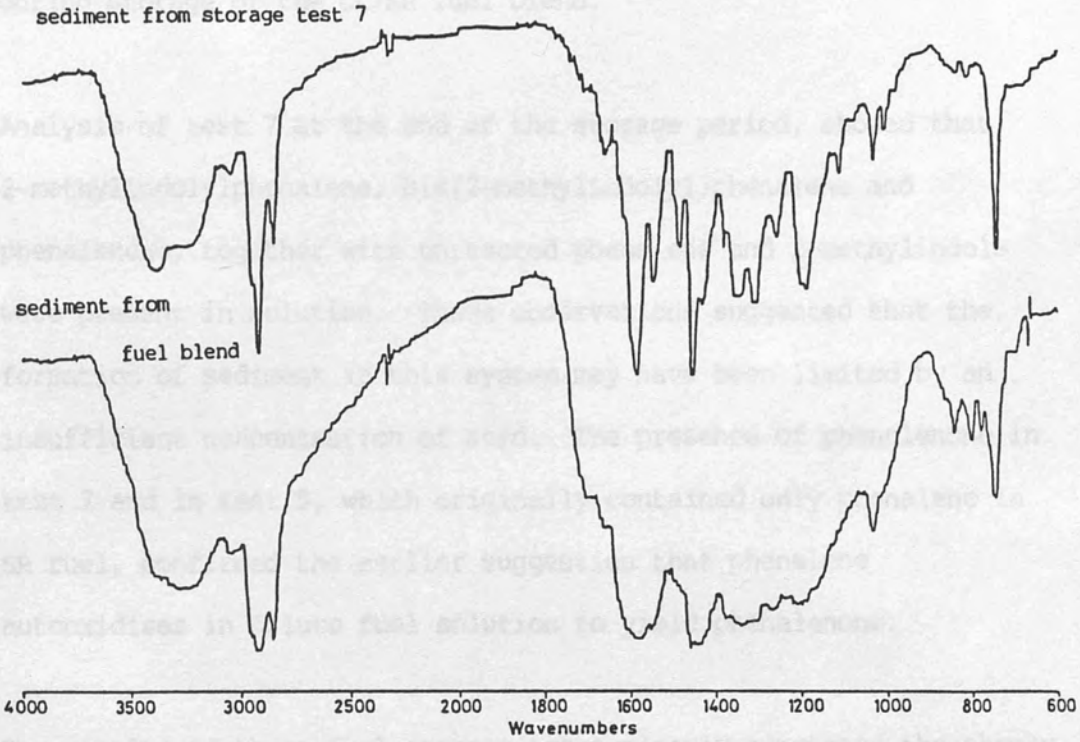


Figure 2.4.2-3 Infrared spectra of sediments from storage test 7 (top) and storage of the 1:9 CC/SR fuel blend (bottom)



The spectrum of the fuel sediment was composed of broad overlapping absorbances whilst the spectrum of sediment formed in test 7 showed relatively well resolved absorbances, indicating that it corresponded to a much simpler mixture of compounds. Nonetheless it is clear that the principal regions of absorbance in the two spectra coincided well, providing further evidence that the sediment produced by the deliberate addition of phenalene and 2-methylindole to the SR fuel was very closely related to the sediment formed during storage of the CC/SR fuel blend.

Analysis of test 7 at the end of the storage period, showed that 2-methylindolylphenalene, bis(2-methylindolyl)phenalene and phenalenone, together with unreacted phenalene and 2-methylindole were present in solution. These observations suggested that the formation of sediment in this system may have been limited by an insufficient concentration of acid. The presence of phenalenone in test 7 and in test 5, which originally contained only phenalene in SR fuel, confirmed the earlier suggestion that phenalene autooxidises in dilute fuel solution to yield phenalenone.

The results of these fuel storage tests clearly supported the theory of sediment formation described in ch. 2.4.1 and summarised in figure 2.4.1-1.

CHAPTER THREE

CONCLUSIONS AND RECOMMENDATIONS

3.1 Conclusions

The work described in this thesis was undertaken with the objective of identifying chemical processes which lead to the formation of sediment during storage of an unstable, petroleum derived diesel fuel.

It has been established that the formation of sediment in one unstable diesel fuel, a 1:9 blend of catalytically cracked (CC) fuel in straight run (SR) fuel, arose predominantly from a series of reactions involving compounds which were present in the fuel blend at concentrations of only a few parts per million. The combined presence of two compounds classes, indoles and phenalenes, both originating entirely from the CC portion of the fuel blend, was found to be particularly deleterious to fuel stability.

The role of alkylindoles in reactions leading to sediment formation was initially deduced from the results of sediment pyrolysis experiments (ch. 2.1.9 and ch. 2.1.10). Subsequent analysis of the unblended CC and SR fuel components, showed that these compounds were present only in the CC portion of the fuel blend (ch. 2.2.2). Derivatives of alkylindoles containing the phenalene ring system were detected in a discrete fraction of the CC fuel (ch. 2.2.6, ch. 2.2.7). These compounds, later confirmed by synthesis to be alkyl derivatives of indolylphenalene and bis(indolyl)phenalene, (ch. 2.3.2 and ch. 2.3.3), were found to react with acid to form strongly coloured material, insoluble in hydrocarbon solvents (ch. 2.2.4). The analytical characteristics of this material were shown to be very similar to those of the major component of the sediment formed during storage of the unstable diesel fuel. The concentration of indolylphenalenes and bis(indolyl)phenalenes was observed to increase during fuel storage (ch. 2.2.8). It was concluded that this increase in concentration resulted from reactions of alkylindoles with phenalene, alkylphenalenes or derivatives thereof.

Phenalene and alkylphenalenes were detected in the CC portion of the unstable fuel (ch. 2.2.10). These compounds were observed to autooxidise to form the corresponding phenalenone derivatives (ch. 2.2.10 and ch. 2.4.2). Two different classes of alkylphenalenones were detected in the CC fuel, differing in their fluorescence and normal phase TLC characteristics and in their reactivity towards indoles (ch. 2.3.5). It was suggested that these differences arose from the presence or absence of alkyl substitution in the "peri" ring (ch. 2.2.9), although this explanantion has neither been confirmed or rationalised.

The results and conclusions of experiments described in this thesis have been used to formulate a theory to account for sediment formation during storage of the unstable diesel fuel (ch. 2.4.1). This theory suggests that sediment formation resulted from acid promoted reactions of alkylindoles with autooxidation products of phenalene and alkylphenalenes.

3.2 Recommendations for further work

It was stated in ch. 1.3 that the work described in this thesis was carried out in order to provide a chemical understanding of the processes leading to sediment formation, which could be used in the future both to develop tests to predict diesel fuel storage stability characteristics and to develop additives to stabilise diesel fuel during storage.

However before further studies towards meeting these practical objectives are undertaken, it will be necessary to prove the general applicability of the conclusions, since they refer only to the stability of one diesel fuel produced from a single UK oil refinery. To this end, quantitative analysis of a wide spectrum of fuels should be carried out in order to correlate their storage stability characteristics with the presence or absence of indoles, phenalenes, phenalenones and acids. Comparative analysis of sediments from other unstable fuels could be used to assess the general applicability of the proposed theory of sediment formation. The results of such studies would also provide an indication of the viability of a test method to predict diesel fuel storage stability characteristics based on the principle of quantitative determination of certain species known to be involved in sediment formation. For such a test method to be of practical value, it would be essential that the quantitative measurements were made using relatively simple analytical techniques which could be carried out routinely within a few hours in a quality control laboratory.

Selection of an appropriate fuel stabilising additive will require a thorough mechanistic understanding of the reactions leading to sediment formation. There are several subjects arising directly from this study which require further investigation. These include the following;

(i) elucidation of the mechanism of reaction 2 (2-methylindole with phenalenone), both in pure solvents and in diesel fuel (ch. 2.3.3 and ch. 2.4.2).

(ii) structural determination of the alkylphenalenones detected in CC fuel fractions 4(2), 4(3) and 4(4), 4(5) in order to account for the observed differences in their fluorescence, polarity and reactivity (ch. 2.2.9 and ch. 2.3.5).

(iii) identification of the acids in diesel fuel which contribute to sediment formation.

CHAPTER FOUR

EXPERIMENTAL

4.1 Spectroscopic analysis

4.1.1 Mass spectrometry

GC/MS and pyrolysis/MS experiments were carried out using a Kratos MS25 mass spectrometer. A Data General Eclipse S/120 mini-computer, running Kratos DS90 software, was used for data processing. Typical MS operating conditions are given in table 4.1.1-1.

Table 4.1.1-1 Kratos MS25 operating conditions

	GC/MS	Py/MS
ionisation	EI, 70eV	EI, 70eV or 10eV
resolution	600	600
mass range	30-600 at 2kV	30-600 at 2kV or 30-900 at 1.33kV
scan speed	1 second/decade	4 seconds/decade
source temperature	250°C	250°C or 350°C

High resolution EI spectra of CC fuel fractions 3(b) and 3(c) (ch. 2.2.7) and low resolution FAB spectra of sediment (ch. 2.1.8), were obtained by PCMU, Harwell, UK using a VG ZAB-1F instrument. Other high resolution EI and FAB spectra were obtained by the School of Pharmacy, London, UK using a VG ZAB-SE instrument.

4.1.2 **Infrared spectroscopy**

All infrared spectra, except that of phenalanone (ch. 2.3.2), were obtained using a Perkin Elmer 683 spectrophotometer linked to a Perkin Elmer 3500 data station. Samples were analysed in the form of KBr disks. The spectrum of phenalanone was obtained at Royal Holloway and Bedford New College, Egham, UK, using a Perkin Elmer 1710 FTIR instrument. The sample was analysed in CCl_4 solution.

4.1.3 **Proton nuclear magnetic resonance spectroscopy**

All spectra were recorded at Royal Holloway and Bedford New College, Egham, UK, using a Nicolet 200MHz instrument. Samples were analysed in deuterochloroform solution.

4.1.4 **Atomic absorption spectroscopy**

The concentrations of iron, copper, nickel and vanadium in the fuel sediment (ch. 2.1.5) were determined using a Varian AA 875 with a GTA 95 graphite furnace attachment.

4.2 Chromatographic analysis

4.2.1 **Thin layer chromatography**

Normal phase TLC was carried out on plates coated with silica gel, 10-12μm particle size, 15nm pore size. Analytical separations used 5cm × 20cm plates with 250μm layer thickness (Whatman LK5DF) whilst preparative separations used 20cm × 20cm plates with 1000μm layer thickness (Whatman PLKF).

Reversed phase TLC was carried out on plates coated with C_{18}

bonded silica gel, 10-12μm particle size, 6nm pore size. Analytical separations used 5cm × 20cm plates with 200μm layer thickness (Whatman LKC_{18}F) whilst preparative separations used 20cm × 20cm plates with 1000μm layer thickness (Whatman PLKC_{18}F)

Two dimensional TLC was carried out on 20cm × 20cm plates (Whatman SC5 multi K, K5F/KC_{18}F) coated with a 3cm × 20cm, 250μm thickness normal phase layer of silica gel 10-12μm particle size, 15nm pore size and a 17cm × 20cm 250μm thickness reversed phase layer of C_{18} bonded silica gel, 10-12μm particle size, 6nm pore size.

All solvents used were BDH HPLC grade.

4.2.2 **Gas chromatography**

GC analysis was carried out using a Perkin Elmer Sigma 2 gas chromatograph fitted with FID, NPD and FPD detectors, a split/splitless capillary column injector and a 25m 0.22mm ID WCOT vitreous silica capillary column, coated with 0.25μm BP1 stationary phase (Scientific Glass Engineering, UK, Ltd.)

GC/MS analysis was carried out using a Perkin Elmer Sigma 3 gas chromatograph, directly coupled to the Kratos MS25 mass spectrometer described in ch. 4.1.1, fitted with a split/splittless capillary injector and a 25m 0.22mm ID WCOT vitreous silica capillary column, coated with 0.25μm BP1 stationary phase (Scientific Glass Engineering, UK, Ltd.). A 12m 0.22mm ID WCOT vitreous silica capillary column, coated with 0.10μm BP1 stationary phase (Scientific Glass Engineering, UK, Ltd.) was used for pyrolysis/GC/MS experiments. Pyrolysis conditions are described in ch. 4.3.4.

4.2.3 **Liquid chromatography**

The separation of fuel sediment into fractions 1, 2 and 3+4 (ch. 2.1.6) was carried out by applying the sediment (500mg) to a 15cm × 1.8cm column of Florisil, 100-200 mesh (Aldrich). Fraction 1 (48mg) was eluted with dichloromethane, fraction 2 (128mg) was eluted with 3% methanol in dichloromethane and fractions 3+4 (258mg) were eluted together by inverting the column and backflushing it with a mixture of 10% water and 40% methanol in dichloromethane.

The separation of CC fuel into fractions 1, 2 and 3 (ch. 2.2.3) was carried out by passing the fuel (150cm^3) through a 25cm × 2.5cm column of silica gel 60, particle size 0.063mm-0.200mm (Merck), under gravity flow. Fraction 1 was eluted with n-hexane (200cm^3) and fraction 2, collected in 20cm^3 aliquots, was eluted with 50% n-hexane in dichloromethane (200cm^3). The aliquots of fraction 2 were analysed by normal phase TLC (mobile phase 40% toluene in n-hexane) and those found to contain compounds sensitive to Ehrlich´s reagent[12,40,41] and with Rf´s between 0.43 and 0.57, were combined to form fraction 3.

CC fuel fraction 3(b) was extracted from CC fuel fraction 3 (prepared as described above from 150cm^3 of fuel) using normal phase followed by reversed phase liquid chromatography. Fraction 3 (400mg) was dissolved in 40% n-hexane in toluene (3cm^3). This was injected onto a normal phase Lobar (Merck) size B column, 31cm × 2.5cm, packed with silical gel 60, particle size 40-63μm. This was eluted with 40% n-hexane in toluene followed by 50% toluene in dichloromethane. The mobile phase flow of $7cm^3$/minute was maintained using a positive displacement piston pump. The chromatographic separation was monitored using a UV detector tuned to 300nm and $10cm^3$ aliquots were collected over regions of maximum absorbance. These were analysed by normal phase TLC (mobile phase 40% n-hexane in toluene). The plates were sprayed after elution with 25% concentrated HCl in methanol. The aliquots containing compounds with TLC Rf´s of 0.27-0.31, which also immediately reacted with the spray reagent producing a green colouration, were combined and the solvent removed by rotary evaporation. The solid extract was dissolved in 10% water in methanol ($1cm^3$) and injected onto a reversed phase Lobar (Merck) size A column, 24cm × 1cm, packed with C_8 bonded silica gel, particle size 43-60μm. This was eluted at $4cm^3$/minute with 10% water in methanol. $5cm^3$ aliquots were collected throughout the elution. These were analysed by reversed phase TLC (mobile phase 10% water in methanol). Aliquots containing compounds which reacted with the acidic spray reagent as described above, were combined. After addition of excess water, the organics (CC fuel fraction 3(b)) were extracted into dichloromethane.

<u>CC fuel fraction 3(c)</u> was prepared by passing the CC fuel ($150cm^3$) through a 25cm × 2.5cm column of silica gel 60, particle size 0.063-0.200mm (Merck) under gravity flow. The column was eluted with n-hexane ($200cm^3$) followed by 50% n-hexane in dichloromethane ($100cm^3$) and finally dichloromethane ($100cm^3$). $20cm^3$ aliquots were collected during elution with n-hexane/dichloromethane and dichloromethane moblile phases. The

aliquots were analysed using normal phase TLC (mobile phase toluene). The plates were sprayed with 25% concentrated HCl in methanol. Aliquots containing compounds with an Rf of 0.53 which also reacted with the spray reagent to immediately produce a green colouration, were combined and concentrated by rotary evaporation. CC fuel fraction 3(c) was prepared directly from this extract using the reversed phase liquid chromatography procedure described above for the preparation of CC fuel fraction 3(b).

<u>CC fuel fraction 4</u> was prepared by passing 200cm^3 of CC fuel through a normal phase liquid chromatography column, 15cm × 1.8cm, packed with silica gel 60, particle size 0.063-0.200mm (Merck). Compounds eluted with n-hexane (200cm^3) were discarded whilst those subsequently eluted with 5% isopropanol in dichloromethane (100cm^3) were collected and concentrated, to form CC fuel fraction 4.

<u>CC fuel fractions 4(1) to 4(7)</u> inclusive, were prepared from CC fuel fraction 4, by a second normal phase liquid chromatography separation followed by preparative reversed phase TLC. CC fuel fraction 4 prepared from 200cm^3 of CC fuel was injected onto a normal phase Lobar (Merck) size B column, 31cm × 2.5cm packed with silica gel 60, particle size 40-63μm. This was eluted with 1% methanol in dichloromethane. The first 25cm^3 of eluent were discarded. The remaining eluent was collected successively in 20cm^3, 25cm^3 and 150cm^3 aliquots. Analysis of each of these by two dimensional TLC, normal phase (mobile phase toluene) followed by reversed phase (mobile phase 10% water in methanol) showed that the first aliquot contained CC fuel fractions 4(1), 4(2)

and 4(3), the second aliquot contained CC fuel fractions 4(4) and 4(5) and the third aliquot contained CC fuel fractions 4(6) and 4(7). In order to obtain pure samples of each of these fractions, the aliquots were applied in turn to preparative reversed phase TLC plates and eluted with 10% water in methanol. The discretely separated CC fuel fractions 4(1) to 4(7) were located using UV light (365nm) and then removed from the TLC plate.

All solvents used were BDH HPLC grade.

4.2.4 High pressure liquid chromatography

A discrete fraction of the CC fuel, containing polycyclic aromatic hydrocarbons including phenalene (ch. 2.2.10), was prepared using an HPLC system consisting of two 25cm × 0.49cm columns connected in series, the first packed with Spherisorb S5NH amino-silica and the second packed with Spherisorb S5W plain silica. The CC fuel (20μl) was injected and eluted with n-pentane at a flow rate of 1cm^3/minute. Refractive index detection was used to monitor the progress of the separation.

4.3 Miscellaneous analysis

4.3.1 Fuel properties

The fuel properties, discussed in ch. 2.1.2, were determined as indicated in table 4.3.1-1.

Table 4.3.1-1 Methods used to determine fuel properties

Property	Method of determination
Colour	ASTM D1500*
Density	ASTM D1298*
Distillation	ASTM D86*
Total acidity	ASTM D974*
Total nitrogen content	Chemiluminescene
Basic nitrogen content	Colorimetric titration
Total sulphur content	X-ray fluorescence spectrometry
Hydrogen content	ASTM D3701*
Aromatic content	HPLC

*Standardised test method for petroleum products[74].

4.3.2 Scanning electron microscopy

Sediment particles were viewed using a CAMSCAN series 4 electron microscope (ch. 2.1.3).

4.3.3 Elemental analysis

Quantitative carbon, hydrogen, nitrogen and sulphur determinations were carried out by Butterworth Laboratories Ltd, Teddington, UK.

4.3.4 **Pyrolytic analysis**

Pyrolysis/GC/MS experiments were carried out using a Pyrojector (Scientific Glass Engineering Ltd., UK) constant temperature furnace operated at 700°C for sediment pyrolysis (ch. 2.1.9) and 350°C for all other experiments. The Pyrojector was directly coupled to the injector of the GC/MS system described in ch. 4.2.2. Samples were applied to a solids injection syringe from solution and the solvent allowed to evaporate before injection into the furnace.

Pyrolysis/MS experiments were carried out using a Kratos Desorption Chemical Ionisation probe with the Kratos MS25 mass spectrometer, described in ch. 4.1.1. The probe tip consisted of a platinum/iridium filament which was inserted, via the conventional direct insertion probe vacuum lock, into the MS source and located in or near the electron beam. The probe was designed, as its name implies, for use under chemical ionisation conditions. However in this work it was used entirely for pyrolysis under electron impact ionisation conditions. Pyrolysis of the sample was achieved by heating the filament from source temperature to 800°C at 5°C/second.

Pyrolysis of the sediment followed by TLC (ch. 2.1.9) was carried out by heating a few milligrammes of the sediment in a pyrex tube. Products which condensed in the cooler parts of the tube were taken into dichloromethane solution and concentrated prior to TLC analysis.

4.4 Storage tests

4.4.1 Storage tests 1, 2 and 3

Test 1 contained CC fuel fraction 3 (extracted from 150cm^3 of CC fuel), dissolved in 25% toluene in decane (150cm^3). This solution was stored in a vented pyrex flask for 30 days, in a dark oven held at 25°C. At the end of the storage period, the solution was subjected to ultrasonic agitation to resuspend insolubles and then filtered through a pre-weighed glass fibre filter (Whatman grade GF/C). The filter and sediment collected on it were washed with 60/80 petroleum spirit (previously filtered through glass fibre, Whatman grade GF/C), dried for 30 minutes at 90°C and then weighed.

Tests 2 and 3 each contained CC fuel fraction 3 (extracted from two 150cm^3 portions of CC fuel) which had been treated with 40% aqueous NaOH to remove acidic species. The NaOH treatment of CC fuel fraction 3 was carried out by dissolving the fuel components in SR fuel (50cm^3, previously passed through a column of silica gel 60 to remove polar fuel components) and shaking this with 40% aqueous NaOH (25cm^3), followed by dilute HCl (25cm^3) to neutralise any entrained NaOH and finally washing the solution with de-ionised H_2O (25cm^3). The solution was then dried, made up to 300cm^3 with silica treated SR fuel, filtered through a glass fibre filter (Whatman grade GF/C) and divided equally into two pyrex containers for storage. One of these aliquots, test 2, was stored with no further treatment. However 3mg of 2-naphthalenesulphonic acid (Aldrich Chemical Co. Ltd.) dissolved in propan-2-ol ($3cm^3$) was added to the second aliquot, test 3. These tests were stored, vented to air, in a dark oven held at 43°C for 40 days. At the end of the storage period the test mixtures were worked up as described above for test 1.

4.4.2 **Storage tests 4, 5, 6 and 7**

Storage test 4 consisted of SR fuel ($200cm^3$), previously filtered through a glass fibre filter (Whatman grade GF/C). Tests 5, 6 and 7 also contained filtered SR fuel ($200cm^3$), together with, in the case of test 5, phenalene (20mg, synthesised according to the method of Boudjouk and Johnson[68]) and in the case of test 6, 2-methylindole (20mg, Aldrich Chemical Co. Ltd.). Test 7 contained both phenalene (20mg) and 2-methylindole (20mg). These compounds were dissolved in toluene ($1cm^3$) before addition to the fuel. All the test solutions were stored in vented pyrex bottles in a dark oven held at 25°C for 27 weeks. At the end of the storage period, the test solutions were vigorously shaken, subjected to ultrasonic agitation for 20 seconds and then filtered through glass fibre filters (Whatman grade GF/A). Insoluble sediments collected on the filters were washed with filtered 60/80 petroleum spirit and then dried for 30 minutes at 90°C.

An extract of test solution 7 containing 2-methylindolylphenalene, bis(2-methylindolyl)phenalene, phenalenone, phenalene and 2-methylindole was prepared by passing the test solution ($10cm^3$) through silica gel ($2cm^3$), followed by n-hexane ($10cm^3$). Subsequent elution with 5% propan-2-ol ($5cm^3$) in dichloromethane yielded a concentrate containing the above compounds which were identified by normal phase TLC analysis (mobile phase toluene). The presence of phenalenone in test 5 was also established using this method.

4.5 Synthesis

4.5.1 Reaction 1

Phenalanone, (0.66mmol, synthesised using the method of Boudjouk and Johnson[68]), 2-methylindole, (0.66mmol, Aldrich Chemical Co. Ltd.) and p-toluenesulphonic acid, (0.66mmol, Aldrich Chemical Co. Ltd.) were dissolved in methanol ($15cm^3$) and left to stand at room temperature in the dark for 24 hours. The coloured products were treated with a saturated solution of aqueous potassium hydrogen carbonate. Organic products were extracted from the resulting suspension with diethylether to yield a brown solution which was dried over sodium sulphate and concentrated by rotary evaporation. The product mixture was separated by flash chromatography, according to the method of Still et al[71], using a 15cm × 2cm column of silica gel 60 (Merck), particle size 0.040-0.063mm, with 50% n-hexane in dichloromethane mobile phase.

4.5.2 Reaction 2

Phenalenone, (2mmol, Aldrich Chemical Co. Ltd.), 2-methylindole, (4 mmol, Aldrich Chemical Co. Ltd.) and p-toluenesulphonic acid, (2mmol, Aldrich Chemical Co. Ltd.) were dissolved in methanol ($30cm^3$) and left to stand for 24 hours in the dark. The product mixture was treated as described for reaction 1.

4.5.3 **Reaction 3**

Indole, (10mg,Aldrich Chemical Co. Ltd.) and p-toluenesulphonic acid, (5mg, Aldrich Chemical Co. Ltd.) were added to methanol ($1cm^3$) containing CC fuel fraction 4(1) (2mg). This was repeated in turn for CC fuel fractions 4(2) to 4(7) inclusive. The CC fuel fractions were prepared as described in ch. 4.2.3. The solutions were left at room temperature in the dark for 18 hours and then analysed directly by normal phase TLC (mobile phase toluene).

REFERENCES

1. **Stockil P.A.** (Editor)
"Our Industry Petroleum"
The British Petroleum Company Ltd. 1977.

2. **British Technical Council**
"Diesel fuel trends: The UK and Western Europe to 1990"
BTC/F1/82 1982

3. **Ritchie J.**
"A study of the stability of some distillate diesel fuels"
J. Inst. Petrol., 1965, 51 (501), 296

4. **Pedley J.F., Hiley R.W.** and **Hancock R.A.**
"Storage stability of petroleum-derived diesel fuel.
1. Analysis of sediment produced during the ambient storage of diesel fuel."
Fuel, 1987, 66, 1646

5. **Hiley R.W.**
"Diesel fuel for the Royal Navy - present and future"
I. Mech. E. Paper C264/83 1983

6. **Nixon A.C.**
"Autoxidation and antioxidants of petroleum"
Ch. 17 in Autoxidation and Antioxidants, 1962, Vol. II
W.O. Lundberg, Ed., Interscience, New York.

7. **Nixon A.C.** and **Thorpe R.E.**
"The effect of compsition on the stability and inhibitor response of Jet fuel"
Am. Chem. Soc., Div. Petrol. Chem., Preprints,
1956, 1 (3), 265

8. **Thompson R.B., Chenicek J.A., Druge L.W.** and **Symon T.**
"Stability of fuel oils in storage. 2. Effect of nitrogen compounds"
Ind. Eng. Chem., 1951, 43 (4), 935

9. **Thompson R.B., Druge L.W.** and **Chenicek J.A.**
"Stability of fuel oils in storage. 1. Effect of sulphur compounds"
Ind. Eng. Chem., 1949, 41 (12), 2715

10. **Offenhauer R.D., Brennan J.A.** and **Miller R.C.**
"Sediment formation in catalytically cracked distillate fuel oils"
Ind. Eng. Chem., 1957, 49 (8), 1265

11. **Sauer R.W., Weed A.F.** and **Headington C.E.**
"A mechanism for organic sediment formation in heating oils"
Am. Chem. Soc., Div. Petrol. Chem., Preprints, 1958, 3 (3), 95

12. **Thompson R.B., Symon T** and **Wankat C.**
"Estimation of pyrrole nitrogen in petroleum distillates"
Anal. Chem., 1952, 24, 1465

13. **Durham L.J., Wurster C.F.** and **Mosher H.S.**
"Peroxides VIII. The mechanism for the thermal decomposition of n-butylhydroperoxide and n-butyl-1-hydroxybutylperoxide"
J. Amer. Chem. Soc., 1958, 80 332

14. **Oswald A.A.**
"Organic sulphur compounds. 1. Hydroperoxide intermediates in the co-oxidation of mercaptans and olefins"
J. Org. Chem., 1959, 24 443

15. **Oswald A.A.** and **Noel F.**
"Role of pyrroles in fuel instability"
J. Chem. and Eng. Data, 1961, 6 (2), 294

16. **WPRA-Bureau of Mines Cooperative Distillate Fuel Storage Stability Programme**
"Summary report no. 1. Storage data - fuels and blends"
Bureau of Mines, Petroleum Experiment Station,
Bartlesville, Okla., USA. 1958

17. **LePera M.E.** and **Sonnenburg J.G.**
"How stable is diesel in storage?"
Hydrocarbon Processing, 1973, 52 (9), 111

18. **Stavinoha L.L** and **Westbrook S.R**
"Accelerated stability test techniques for middle distillate fuels"
Distillate fuel stability and cleanliness, ASTM Special Technical Publication, 1981, 751, 3

19. **Garner M.Q.** and **White E.W.**
"Correlation of long-term storage and accelerated stability tests"
Distillate fuel stability and cleanliness, ASTM Special Technical Publication, 1981, 751, 34

20. **Brinkman D.W., Bowden J.N.** and **Giles H.N.**
"Crude oil and finished fuel storage stability. An annotated review"
DOE/BETC/RI-79/13, 1980

21. **Goetzinger J.W., Thompson C.J.** and **Brinkman D.W.**
"A review of storage stabilty characteristics of hydrocarbon fuels, 1952-1982"
DOE/BETC/IC-83/3, 1983

22. **Brown F.R.** and **Karn F.S.**

"Stability studies of coal-derived liquids"

Fuel, 1980, 59, 431

23. **Dahlin K.E.**, **Daniel S.R.** and **Worstell J.H.**

"Deposit formation in liquid fuels. 1. Effect of coal-derived Lewis bases on storage stability of Jet A turbine fuel"

Fuel, 1981, 60, 477

24. **Brinkman D.W.** and **Bowden J.N.**

"Stability of some coal and tar sands syncrude fractions"

Fuel, 1982, 61, 1141

25. **Jones L.** and **Li N.C.**

"Aging of SRC-II middle distillate from Illinois No.6 coal. 1. In presence of copper and oxygen"

Fuel, 1983, 62, 1156

26. **White C.M.**, **Jones L.** and **Li N.C.**

"Aging of SRC-II middle distillate from Illinois No.6 coal. 2. Further evidence of phenolic oxidative coupling in coal-derived liquids"

Fuel, 1983, 62, 1397

27. **Frankenfeld J.W.** and **Taylor W.F.**

"Storage stability of synfuels from oil shale. 1. General features of sediment formation in model fuel systems"

Ind. Eng. Chem. Prod. Res. Dev., 1983, 22, 608

28. **Frankenfeld J.W.** and **Taylor W.F.**

"Storage stability of synfuels from oil shale. 2. Effects of nitrogen compound type and the influence of other non-hydrocarbons on sediment formation in model fuel systems"

Ind. Eng. Chem. Prod. Res. Dev., 1983, 22, 615

29. **Frankenfeld J.W.** and **Taylor W.F.**
"Storage stability of synfuels from oil shale. 3. Studies with actual shale-derived middle distillates"
Ind. Eng. Chem. Prod. Res. Dev., 1983, 22, 622

30. **Cooney J.V., Beal E.J** and **Hazlett R.N.**
"Mechanisms of synfuel degradation. 1. The effects of organic nitrogen compounds on the stability of a shale derived diesel fuel"
Liquid Fuels Technology, 1984, 2 (4), 395

31. **Jones L., Hazlett R.N., Li N.C.** and **Ge J.**
"Storage stability studies of fuels derived from shale and petroleum"
Fuel, 1984, 63, 1152

32. **Malhotra R.** and **St John G.A.**
"Pyrolysis/field ionisation mass spectrometric analysis of fuel sediments"
Conference Proceedings. 2nd International Conference on Long Term Storage Stabilites of Liquid Fuels. San Antonio, Texas, USA. 29th July-1st August 1986.

33. **Wright B.W., Kalinoski H.T., Udseth H.R.** and **Smith R.D.**
"Chemical characterisation of fuel sediments using supercritical fluid methodologies"
Conference Proceedings. 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels. San Antonio, Texas, USA. 29th July-1st August 1986.

34. **Power A.J.**
"Accelerated oxidation of diesel distillate"
Fuel, 1986, 65, 133

35. **Hazlett R.N.** and **Power A.J.**
"The role of phenols in distillate fuel stability"
Conference Proceedings. 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels. San Antonio, Texas, USA. 29th July-1st August 1986.

36. **Hazlett R.N., Power A.J., Kelso A.G.** and **Solly R.K.**
"The chemistry of deposit formation in distillate fuels"
Materials Research Laboratories, Melbourne, Australia.
Report no. MRL-R-986, 1986.

37. **Bahn O.K., Green J.B., Brinkman D.W.** and **Carley W.**
"Causes of colour change and sediment formation in Navy distillate fuels"
Conference Proceedings. 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels. San Antonio, Texas, USA. 29th July-1st August 1986.

38. **Bahn O.K., Brinkman D.W., Green J.B.** and **Carley w.**
"Storage stability of marine diesel fuels"
Fuel, 1987, 66, 1200

39. **Loeffler M.C.** and **Li N.C.**
"Role of nitrogen- and sulphur-containing compounds in the aging of liquid fuels"
Fuel, 1985, 64, 1047

40. **Kupfer D.**
"Qualitative method for partial characterisation of indole derivatives"
Anal. Biochem., 1964, 8, 75

41. **Fiegel F.**
Spot Tests, Vol. 2. Organic Applications, 4th Edition, Elsevier, 1954

42. **Miller R.G.** and **Willis H.A.** (editors)
IRSCOT Infrared structural correlation tables.
Table 7-A24 and Table 7-A24a
Published by Heyden and Sons Ltd. 1966

43. NBS/NIH/EPA Mass Spectrum Library

44. **Beynon J.H.** and **Williams A.E.**
"The mass spectra of alkylindoles"
Applied Spectroscopy, 1959, 13 (4), 101

45. **Powers J.C.**
"The mass spectrometry of simple indoles"
J. Org. Chem., 1968, 33 (5), 2044

46. **Williams P.T.**, **Bartle K.D**, **Mills D.G.** and **Andrews G.E.**
"Capillary GC analysis of diesel fuels using simultaneous parallel triple detection"
J. of High Resolution Chromatography and Chromatography Communications, 1986, 9, 39

47. **Whitehead E.V.**
"Geochemistry of natural products in petroleum prospecting"
Petroanalysis ´81 (Edited by G. Crump), Ch.6., p.31
John Wiley and Sons, 1982.

48. **Wenzel B.** and **Aiken R.A**
"Thiophenic sulphur distribution in petroleum fractions by gas chromatography with a flame photometric detector"
J. of Chromatographic Science, 1979, 17, 503

49. **Powers E.J.** and **Wotring W.T.**
"Stabilisation of No. 2 fuel oils with caustic treating and with additives"
Distillate fuel stability and cleanliness, ASTM Special Technical Publication, 1981, 751, 92

50. **Hiley R.W.** and **Pedley J.F.**
"Storage stability of petroleum-drived diesel fuel.
2. The effect of sulphonic acids on the stability of
diesel fuels and a diesel fuel extract"
Fuel, 1988, 67 (4), 469

51. **Reid D.H.**
"The chemistry of the phenalenes"
Chem. Soc. Quart. Rev., 1965, XIX, 274

52. **Boekelheide V.** and **Larrabee C.E.**
"An investigation of the preparation and some
properties of perinaphthene"
J. Amer. Chem. Soc., 1950, 72, 1245

53. **Stehling F.C.** and **Bartz K.W.**
"Identification of perinaphthene radical in
petroleum products"
J. Chem. Phys., 1961, 34, 1076

54. **Bennett J.E.**
"The detection of the phenalenyl radical in
pyrolysed hydrocarbons by electron-spin resonance"
Proc. Chem. Soc., 1961, 144

55. **Pettit R.**
"The synthesis and properties of the perinaphthenylium cation"
J. Amer. Chem. Soc., 1960, 82, 1972

56. **Houlihan W. J.** (editor)
"The chemistry of heterocyclic compounds. Indoles. Part 1"
Wiley-Interscience 1972

57. **Albert A.**
"Heterocyclic chemistry, essential books"
Fairlawn, New Jersey, 1959

58. **Houlihan W.J.** (editor)
"The chemistry of heterocyclic compounds. Indoles. Part 2"
Wiley-Interscience 1972

59. **Kamal A.** and **Qureshi A.A**
"Syntheses of some substituted di-indolylmethanes in aqueous media at room temperature"
Tetrahedron, 1963, 19, 513

60. **Treibs A.** and **Herrmann E.**
Leibigs Ann. Chem., 1954, 589, 207

61. **Treibs A.** and **Herrmann E.**
"Pyrroletrimethine and indoletrimethine dyes"
Leibigs Ann. Chem., 1955, 592, 1

62. **Treibs A.** and **Hintermeier K.**
"Pyrroletrimethine dyes"
Liebigs Ann. Chem., 1955, 592, 11

63. **Treibs A., Herrmann E.** and **Meissner E.**
"Pyrrole-blue dyestuffs"
Liebigs Ann. Chem., 1958, 612, 229

64. **Fieser L.F.** and **Gates M.D.**
"Synthetic experiments utilizing perinaphthanone-7"
J. Amer. Chem. Soc., 1940, 62, 2335

65. **Simpson J.E.** and **Daub G.H.**
"Convenient synthesis of perinaphthane via chloroaluminium hydride reduction of perinaphthanone"
J. Org. Chem., 1979, 44 (8), 1340

66. **Fieser L.F.** and **Newton L.W.**
"Reactions of perinaphthane derivatives"
J. Amer. Chem. Soc., 1942, 64, 917

67. **Fieser L.F.** and **Hershberg E.B.**

J. Amer. Chem. Soc., 1938, 60, 1658

68. **Boudjouk P.** and **Johnson P.D.**

"Improved routes to phenalene and phenalanone. Alane, borane and silane reductions of phenalenone"

J. Org. Chem., 1978, 43 (20), 3979

69. **Campbell R.D** and **Cromwell N.H.**

"Endocyclic $\alpha\beta$-unsaturated ketones. VI. Ultraviolet and infrared absorption spectra and resonance studies"

J. Amer. Chem. Soc., 1957, 79, 3456

70. **Prinzbach H.**, **Freudenberger V.** and **Scheidegger U.**

"Cyclic, cross-conjugated systems. XIII. NMR studies of the phenafulvene system"

Helv. Chim. Acta., 1967, 50, 1087

71. **Still W.C.**, **Kahn M.** and **Mitra A.**

"Rapid chromatographic technique for preparative separations with moderate resolution"

J. Org. Chem., 1978, 43 (14), 2923

72. **Cohen L.A.**, **Daly J.W.**, **Kny H** and **Witkop B.**

"Nuclear magnetic resonance spectra of indoles"

J. Amer. Chem. Soc., 1960, 82, 2184

73. **Lock G.** and **Gergley G.**

Ber., 1944, 77B, 461

74. "Annual Book of ASTM Standards"

American Society for Testing of Materials, Philadelphia, USA, 1984, Volume 05.02.