STUDIES IN MOLECULAR POLARISATION.

A Thesis submitted to the
University of London
for the Degree of
Doctor of Philosophy,
by
Jean Macqueen.

November, 1954.

ABSTRACT.

A number of inner-complex compounds of beryllium, aluminium, iron, copper and nickel have been prepared, and measurements of the molecular polarisation have been made on those which were sufficiently soluble in either benzene or dioxan. A heterodyne beat apparatus was used for dielectric constant measurements. The appropriate molecular refractions have been either measured or calculated, and, on the assumption that the molecules are symmetrical, the atomic polarisations have been estimated. These values of the atomic polarisations are discussed in relation to the force constants for the bending vibrations of the chelate rings and the effective dipole moments of the rings.

It was found that the large atomic polarisations observed by previous workers for the acetylacetonates are apparently general for all inner-complex compounds in which the chelate ring contains six atoms. Exceptions may occur when the ring is held rigidly by some means, as in the salicylaldoxime complexes, where hydrogen bonding between the two oxime residues has been postulated to explain their unusually low atomic polarisations. For the other six-membered ring complexes, atomic polarisation values of between 29 and 67 c.c. were found for complexes containing two chelate rings in the molecule, and between 45 and 94 c.c. when three chelate rings are present, the variations being due to changes in the ring moment and the force constant. It was found that the force constants were considerably affected by changes in the strain of the chelate ring, since an increase in the strain of the ring increased its rigidity. Complexes of copper and nickel which contained five-membered rings have quite

small atomic polarisations, this being attributed to the large force constants for the vibration of the rings, which in these compounds are greatly strained.

PREFACE.

The work described in this Thesis was carried out in the laboratories of the Chemistry Department, Bedford College, under the supervision of Dr. J.W. Smith.

The writer wishes to express her sincere appreciation of the help and encouragement given by Dr. Smith during the course of this work. Grateful thanks are also due to the Department of Scientific and Industrial Research for the award of a Maintenance Grant, during the tenure of which this work was carried out.

CONTENTS.

Chapter I. Methods of Research.

Chapter II. Experimental Results.

Chapter III. Discussion of Results.

List of Illustrations.

INTRODUCTION.

It has been realised for many years that, in the measurement of electric dipole moments, serious errors may arise if the orientation polarisation of the molecule is taken as the difference between the polarisations measured at radio and at visible frequencies. When any molecule which contains polar bonds, so that the nuclei carry unequal effective charges, is subjected to an electric field, it undergoes deformation, the positive charges tending to move towards the negative end of the field, and vice versa. A dipole is thus created, which is superimposed upon any permanent dipole which the undisturbed molecule may possess. The deformations which occur can be divided into those which involve the movements of electrons relative to the positions of the nuclei, which take place even when the bonds of the molecule are non-polar, and those involving the movements of the nuclei relative to each other. The former type give rise to the effect known as electron polarisation and the latter to atomic polarisation. All molecules containing polar bonds, that is, all molecules except those of the elements, may be expected to show atomic polarisation to some extent, but it will obviously be most marked in those molecules which contain very highly polar bonds, together with a flexible structure.

The atomic polarisation of a compound may be determined by measuring the molecular refraction of the compound in the infra-red region of the spectrum, and also at visible frequencies. The molecular refraction in the infra-red gives the total distortion polarisation of the molecule, since the frequency of the vibrations is too high to allow the molecule to orientate itself in the field, but both nuclei and electrons may undergo displacements. In the visible region of the spectrum, the alternations of the field are so rapid that only the electrons are displaced, and the electron polarisation of the compound is therefore given by the molecular refraction measured at optical frequencies, and extrapolated to infinite wavelength to eliminate the dispersion effect. The atomic polarisation is then given by the difference between these two quantities. Cartwright and Errera (1,2) have measured the atomic polarisations of a number of compounds by this method. The measurement of refractive indices at infra-red frequencies, however, presents considerable experimental difficulties; but for a non-polar compound, the square of the refractive index measured at infinite wavelength is equal to the dielectric constant, and the atomic polarisation may therefore be taken as the difference between the total polarisation and the electron polarisation.

For a polar compound the evaluation of the atomic polarisation is more difficult, but it may be estimated by measuring the molecular polarisation, P, of a compound in the vapour state over a range of different temperatures, and then plotting the graph of P against the reciprocal of the absolute temperature. The graph is extrapolated to $1/T = 0$, where the intercept on the P axis should represent the total distortion polarisation, from which the atomic polarisation may be calculated by subtracting the electron polarisation. This method has a number of disadvantages as compared with the former, including the length of the extrapolation, the uncertainty of the manner in which

P varies with temperature, and its restriction to compounds which are stable in the vapour state: however, values obtained by this method by Groves and Sugden (3) and by Watson and Ramaswamy (4) are of a similar order to those found by Cartwright and Errera.

Where direct measurement of atomic polarisations has been possible, it has been found that they are usually of the order of 5 to 15% of the electron polarisation of the compound. Accordingly, it is usual, in the measurements of dipole moments, to make a small, arbitrary allowance for the atomic polarisation of 5% of the molecular refraction measured at the sodium D line, although no simple systematic relationship can be shown to hold good: indeed, no such relationship can be expected on theoretical grounds. Over the past thirty years, however, a number of cases have been noted in which anomalous dipole moments have been found for compounds having symmetrical molecules, for which a zero moment would have been expected. These "moments" have since been interpreted as large atomic polarisations.

The first cases noted of this kind were the polynitrobenzenes. Højendahl (5) found small apparent moments for p-dinitrobenzene and 1:3:5-trinitrobenzene, and later measurements by Jenkins (6) confirmed this work and also showed that other symmetrical di- and tri- nitrobenzenes possessed small apparent moments. Symmetrical diketones were found to have "moments" of about 0.7 D, as shown by measurements on p-benzoquinone by Hassel and Naeshagen, which were confirmed by Le Fèvre and Le Fèvre (8), who also found a nearly equal moment for carbon suboxide. Hammick, Hampson and Jenkins (9) extended the measurements to a number of 2:5- disubstituted p-benzoquinones, and to 2:2:4:4-tetramethylcyclobutane-1:3-dione. In all these cases, instead of finding $[R_D]$ to be almost equal to the total polarisation, which would have been expected for a planar symmetrical molecule, there was a discrepancy of between 8 and 11 c.c.

Symmetrical dicyano compounds were also found to show anomalies. Cyanogen had been shown, by measurements made at various temperatures by Watson and Ramaswamy (loc. cit.), to possess a rather high atomic polarisation; and Coop and Sutton (10) found that for p-dicyanobenzene, the difference between $P_{2\infty}$ and $[R_D]$ was 8 c.c., approximately equal to the value for cyanogen.

Smith and Angus (11) were the first to postulate high atomic polarisations in metallic complexes, when they found apparent moments of 1.07 and 1.35 D. for beryllium acetylacetonate and basic beryllium acetate respectively. Both these compounds were believed to possess molecular symmetry. Thereafter, a number of metallic compounds were found to have anomalous moments. Jensen (12) investigated several phosphine complexes of the type $[PtA_2(PR_3)_2]$, where A represents a halogen atom and R either the ethyl, n-propyl or iso-propyl group. Most of these complexes can be prepared in two forms, and the measurements were carried out in order to distinguish between cis and trans isomers. The α-forms were undoubtedly cis isomers, possessing large dipole moments of about 11 D. In the case of the β-compounds, or trans isomers, however, a moment of about 1 D. was found, corresponding to an atomic polarisation of about 23 c.c., or approximately 20% of $[R_D]$. A similar result was found for the complexes of substituted arsines and stibines, and Mann and Purdie (13) found very nearly equal apparent moments for similar complexes of palladium.

Apparent moments of about 1.3 D. were found by Cavell and Sugden (14) for the nickel complexes of various glyoximes, which they examined for <u>cis-trans</u> isomerism. Measurements were also made by Hampson on diphenylmercury, di-<u>p</u>-chlorophenyl mercury and related compounds (15); by Curran and Wenzke (16) on the mercuric halides, and by Coop and Sutton (loc. cit.) on the tetrahalides of titanium, germanium and tin: all of which compounds were found to have small anomalous "moments".

Finn, Hampson and Sutton (17) extended the measurements of Smith and Angus to the series of metallic complexes of acetylacetone, and in every case found unusually high values of the atomic polarisation. A rough additivity was apparent in their results, since the P_A values fell into three groups having roughly the ratios 2:3:4; these groups comprised compounds with two, three and four chelate rings respectively, although considerable variations occurred within each group.

Smith and Angus pointed out that the difference between the total and the electron polarisations of the beryllium complexes could not be due to a permanent moment, since there was no variation in P with temperature. They suggested therefore that the differences observed could be attributed to the existence of large atomic polarisations, which might be expected to be large in a molecule containing bonds as highly polar as the Be ← O partial coordinate link. Since at that time the existence of large atomic polarisations had not been conclusively demonstrated, this suggestion was not generally accepted, particularly as the measurements in question had been made in solution, so that the possibility of a solvent effect could not be ruled out.

Jenkins (6) proposed a theory to account for certain of the anomalous moments, in particular those of the polynitrobenzenes and mercury compounds, based on the assumption that a given bond moment is not constant, but is subject to fluctuations about a most probable value, caused by the variations in solvent-solute forces. An alternative theory was put forward by Frank and Sutton (18), explaining the anomalies on the basis of moments induced in the molecules of the solvent by the balanced dipoles in the molecules of the solute. Finn, Hampson and Sutton (loc. cit.) were, however, able to show that the molecular polarisation of beryllium acetylacetonate, measured in a number of different solvents, was practically constant, within the limits of experimental error. The values obtained from measurements made on solutions in carbon disulphide were no exception, whereas both the Jenkins and the Sutton-Frank solvent theories predicted a higher value for the molecular polarisation in this solvent. Moreover, Coop and Sutton (loc. cit.) were able to demonstrate that the anomalies persisted when the measurements were made on the acetylacetonates, p-benzoquinones, p-dinitrobenzene and the tetrahalides of titanium, germanium and tin in the vapour state, thus proving that a solvent effect could not be wholly responsible. They also showed that there was no variation in the molecular polarisation in the vapour state with temperature, which ruled out the possibility of the presence of a permanent dipole. An explanation based on incomplete chelation of the acetylacetonate ring was also eliminated, since in such a case variations with temperature would be expected; also, the stability of the compounds makes this unlikely. The symmetry of the chelate rings is indicated by the resonance theory. It was shown that slow bending, caused by thermal collisions, as postulated by Hampson to account for the anomalies found for diphenylmercury and the related compounds, could not explain the effects observed for the acetylacetonates, since the frequency of bending can be shown to be too high to allow the molecules to orientate themselves while bent. The only other possible explanation was that of large atomic polarisations, as originally put forward by Smith and Angus. Atomic polarisations can be expected to be independent of solvent or temperature, and may be expected to show the additivity exhibited by the acetylacetonates: moreover, all the compounds for which anomalies have been observed are of the type containing two or more large balanced dipoles in the molecule, so that, while in the unperturbed state the molecules are non-polar, they become highly polar if a small displacement from the symmetrical arrangement occurs.

The expression

$$P_A = \frac{4\pi N \mu^2}{9 V_o}$$

which expresses the contribution made to the polarisation of a flexible molecule of a vibrating system, either bond or group, of moment μ, the force constant for the vibration being V_o, was applied by Finn, Hampson and Sutton to the acetylacetonates, quinones and tetrahalides in order to gain information about the force constants of the vibrations. For most molecules, μ is not large for any bond, and P_A will not usually exceed about 5 c.c.: but where μ is greater than about 2.5 D. for any bond, the effect of atomic polarisation must be taken into account.

This treatment also explains the almost exactly equal atomic polarisations of the symmetrical diketones, including the various substituted quinones, carbon suboxide and 2:2:4:4-tetramethyl<u>cyclo</u>butane-1:3-dione. Each of these compounds possesses the same vibrating system of two collinear carbonyl groups, which make a large contribution to the atomic polarisation of the molecule on account of the large C=O bond moment; the contributions from the remainder of the molecule, whatever that may be in each case, are much smaller in comparison. Similar considerations apply to the dicyano compounds, and the additivity of the atomic polarisations of the acetylacetonates is explained on the same basis. It is surprising that nickel carbonyl was found by Sutton, New and Bentley (19) to have an atomic polarisation of only 2 c.c., since spectroscopic measurements (20) show that the force constant is of the same order as those calculated for the acetylacetonates, i.e., about 3×10^{-12} ergs/radian^2/molecule, and the moment of the C ⟶ Ni bonds would have been expected to be very high. Repeat measurements might be of advantage in this case, since only two solutions were used.

The initial treatment along these lines assumed that two distinct factors were involved, i.e., the bending of the molecules, followed by the orientation of the bent molecules in the electric field. It was suggested, therefore, that if the natural period of the bending vibrations were less than the time required for orientation (assumed to be about 5×10^{-12} sec.) then the only effect involved would be that of bending, whereas if it were larger, contributions would be made both by bending and by orientation. Davidson and Sutton, however, (21) were able to show by statistical methods that the two factors do not make independent contributions to the total polarisation, and it is not possible to distinguish between them.

In the present work, the aim has been to extend measurements of atomic polarisation to as wide a range of chelate complexes as possible. The number of compounds on which measurements can be made is greatly restricted by the limited solubility of most metallic complexes in non-polar solvents: this expecially applies to compounds in whose molecules the chelate ring contains five atoms, and only two compounds of this type have been found to be sufficiently soluble for measurements to be made. A fairly wide range of six-membered rings, including a number of complexes of the salicylaldehyde series, is available, in which either oxygen or nitrogen atoms are coordinated to the central atom, which is generally copper or nickel in the soluble complexes.

In certain cases thesymmetry of the molecules has been established by crystallographic analysis: this applies to the salicylaldoxime complexes of nickel and copper, which have been shown by Cox, Webster et al. (22,23) to be planar, and to possess a centre of symmetry. In the case of the nickel complex the planarity was confirmed by magneto-chemical measurements. Symmetry of the molecules of the acetylacetone and dibenzoylmethane complexes is required by the resonance theory, and, in the case of copper acetylacetonate, this has been confirmed by X-ray examination by Cox and Webster. The remaining compounds have been confirmed by theresults obtained. No value of the molecular polarisation has been found for these complexes greater than 250 c.c., except in the case of copper salicylideneaniline, which appears to be exceptional: Jensen (loc. cit.), on the other hand, obtained values for the molecular polarisations of the cis planar complexes of platinum of approximately 2500 c.c. No measurements of the moment of a tetrahedral complex of this type appear to have been made, but it is probable that it would be large, and intermediate between the moments of the cis and trans complexes.

CHAPTER I.

METHODS OF RESEARCH.

Section 1. Apparatus.

It was pointed out by Debye (1) that the Clausius-Mosotti-Debye equation for the molecular polarisation of a polar compound in the gaseous state could be applied to the case of a polar compound in dilute solution in a non-polar solvent. For the calculation of the molecular and electronic polarisations of a compound by this method it is necessary to determine the densities, dielectric constants and refractive indices of a series of solutions of graded concentrations. The apparatus which was used for the determination of these quantities will be described in this section.

Determination of the Dielectric Constants.

It was desired to measure dielectric constants between 2.2 and 2.5, with, if possible, an accuracy of ±0.0001, and for this purpose an apparatus based on the heterodyne beat principle is the most satisfactory. The apparatus which was used was that designed by Few, Smith and Witten, (2), and built by Few (3). It was designed in such a way that one side of the tuned circuit in each of the two oscillators was earthed: this enabled the adjustment of the tuning condensers to be made without any changes in the frequency due to hand capacity. Screen-grid and anode potentials were supplied from a single high-tension unit to reduce variations in frequency: the beat frequency was found to be insensitive to deliberately imposed variations of the screen-grid or anode potentials. The two oscillators were connected to the same low-tension source. All the anode leads and screen-grid leads were decoupled to prevent interaction, and the use of electron coupling to mix the two high-frequency oscillations completely eliminated all tendency to "locking-in" (vide Groves (4)). High quality short-wave tuning condensers were employed. The inductances consisted of 24 S.W.G. enamelled copper wire, closely wound on Paxolin formers. By the use of a substitution technique, it was possible to introduce either the dielectric cell or the precision condenser into the tuned circuit, while the other was earthed on both sides. By this means, a very rapid matching of the capacity of the precision condenser to the capacity of the dielectric cell was possible, which minimised errors arising from a possible frequency drift in either of the oscillators. The oscillators were housed in metal boxes, and all interconnections were made by screened cable.

List of Components.

V_1 - Cossor V.9.

V_2 - Marconi S.24.

V_3 - Raytheon 6.SA.7.

V_4 - Osram Z.21.

L_1 - 30 turns of 24 S.W.G., 2 in. diameter, close wound.

L_2 - 7 " " " " " " " "

L_3 - 34 " " " " " " " "

C_1 {
250 μμF short-wave variable.
7 μμF trimmer.
200 μμF fixed, switched in or out.
Dielectric cell and precision condenser.

C_2 {
75 μμF short-wave variable.
300 μμF fixed.

C_3 - 200 μμF fixed.

C_4, C_5, C_6 - 2μF - 1000 volts.

C_7, C_9, C_{11}, C_{12}, C_{13} - 1 μF - 350 volts.

C_8 - 1 μF - 800 volts.

C_{10} - 0.25 μF - 450 volts.

C_{14}, C_{15} - 2 μμF trimmers.

R_1, R_2 - 1 megohm.

R_3, R_4 - 0.1 megohm.

R_5 - 150 ohms.

R_6 - 2 megohms.

R_7 - 10,000 ohms + 50,000 ohms variable.

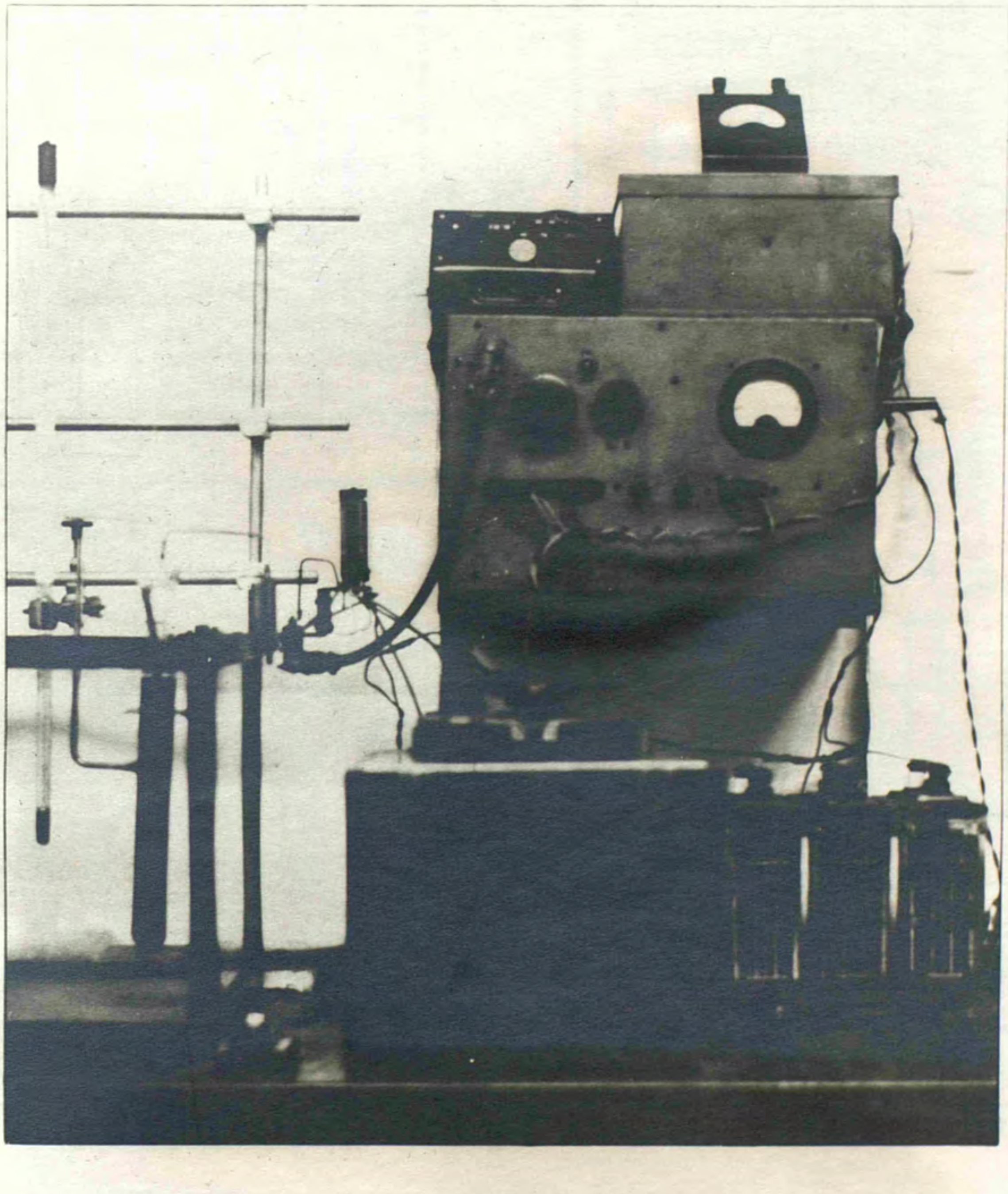
A_1 - 0-10 moving coil milliammeter.

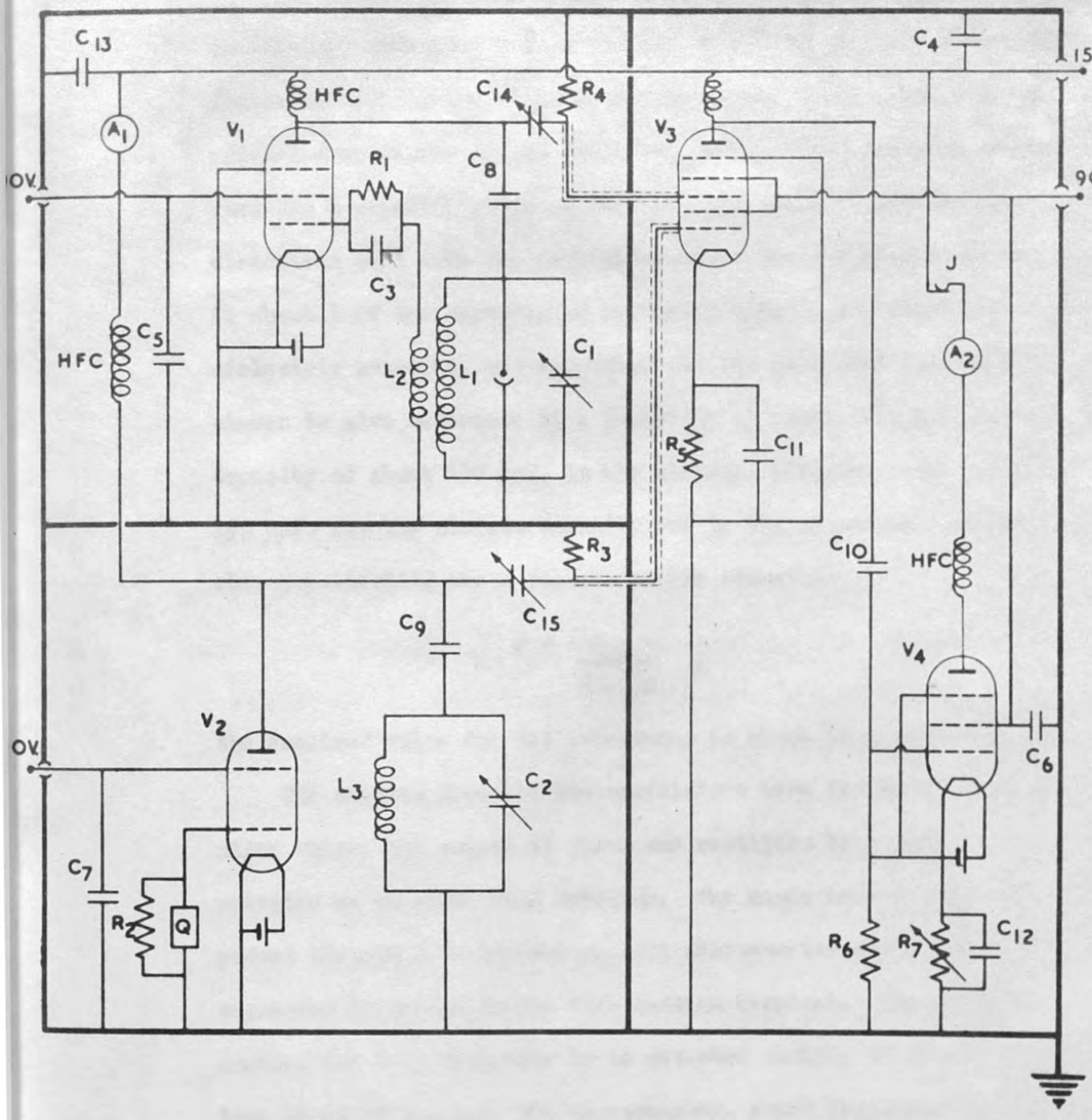
A_2 - 0-200 moving coil microammeter.

J - jack for earphones.

Q - quartz crystal, approximately 1 megacycle.

P - socket for screened cable.





CIRCUIT DIAGRAM OF HETERODYNE BEAT APPARATUS

The heterodyne beat apparatus consisted of a crystal-controlled oscillator, operating at a frequency of 10^6 c.p.s., and a variable frequency oscillator, which contained in the tuned circuit either the precision condenser or the dielectric cell. The precision condenser used had a capacity range of 300 μμF, and could be matched against the dielectric cell with the maximum accuracy for dielectric constants up to about 3 if the capacity of the cell, when it contained air as the dielectric material, was approximately 100 μμF. The inductance was chosen to give resonance at a frequency of about 10^6 c.p.s. with a total capacity of about 450 μμF. in the circuit, allowing about 100 to 150 μμF. for the minimum capacity due to the adjustment condensers, leads, etc. Substituting these figures in the equation

$$f = \frac{1}{2\pi\sqrt{LC}} ,$$

the required value for the inductance is about 50 microhenries.

The outputs from the two oscillators were fed on to the grids of a mixer valve, the output of which was rectified by a pentode valve, which operated as an anode bend detector. The anode lead of this detector passed through a 0—200 moving-coil microammeter and a pair of earphones, connected in series to the high tension terminal. The earphones enabled the beat frequency to be detected audibly at frequencies greater than about 30 c.p.s.: The microammeter, which responded to frequencies between approximately 20 c.p.s. and zero, provided detection within this range.

High Tension Supply.

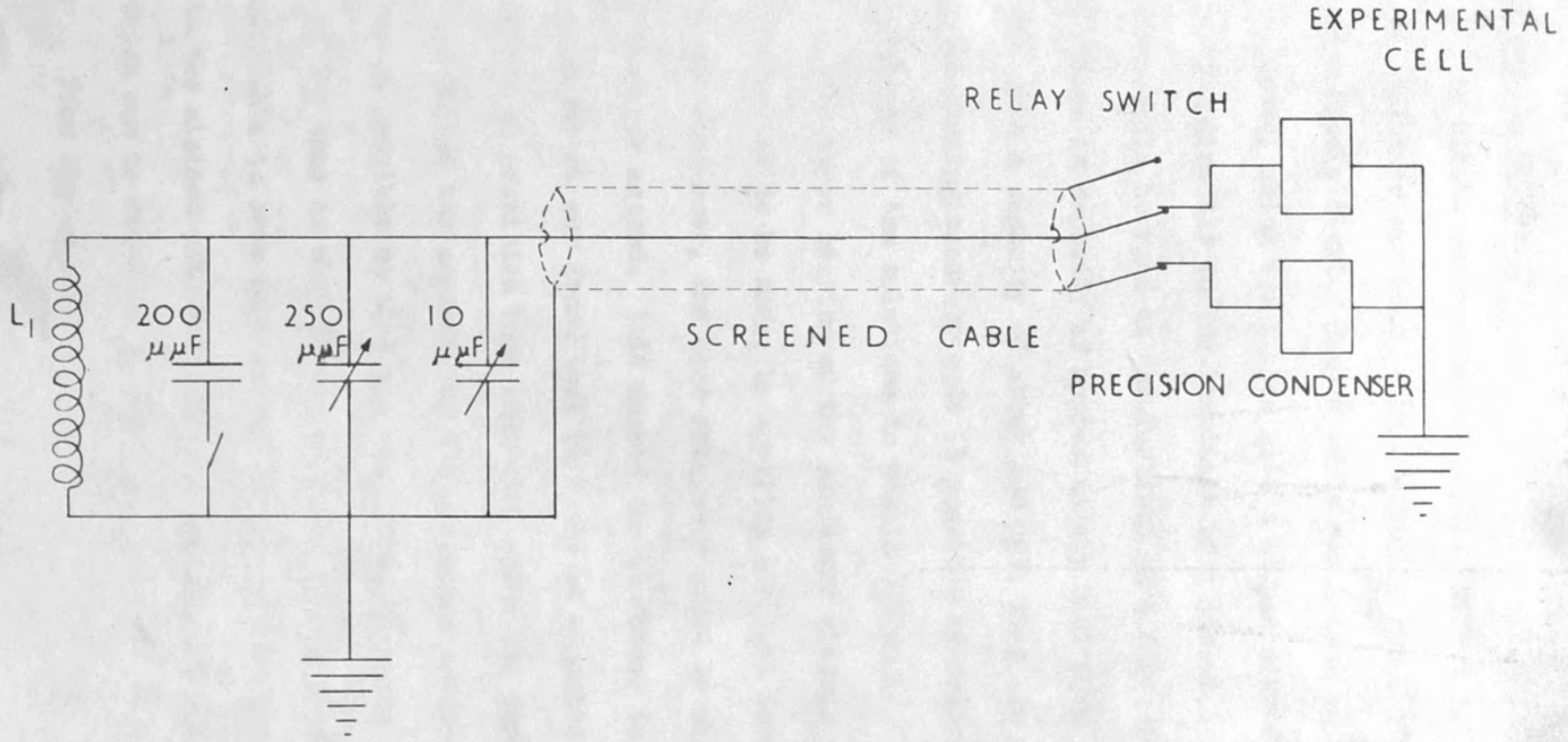
The high tension supply was drawn from the A.C. mains using a

Clarke's "Atlas" eliminator from which certain set values of the potential could be chosen. The most satisfactory combination of the available values was found to be given by a potential of 150 volts on the anodes and of 90 volts on the screen-grids of the valves. The anodes and screen-grids were decoupled to earth by the condensers $C_4, C_5 C_6, C_7$ and C_{13}.

Relay unit.

The relay unit used was of the Post Office switch type, and was used in preference to the mercury cup type because it can be operated by a bell-push situated at a distance from the dielectric cell and the precision condenser. The relay itself was placed near to the dielectric cell platform and the precision condenser, which made possible the use of short leads, thereby reducing stray capacities. The connections between the oscillator compartment and the relay were made by low capacity screened cable. The leads from the relay to the dielectric cell and to the precision condenser were of rigid 12 S.W.G. brass rods, arranged so that the earthed lead adequately screened the radio frequency lead. The relay connections were arranged to earth both sides of the precision condenser when the dielectric cell was in the oscillator circuit, and to earth both plates of the cell when the precision condenser was in the oscillator circuit.

In practice it was found that the capacity associated with the relay unit remained constant during use, but to ensure trouble-free operation the contacts were always cleaned with fine emery paper, and finally polished with silk, before the apparatus was used.



VARIABLE FREQUENCY OSCILLATOR TUNED CIRCUIT

Precision Condenser.

An N.P.L. certificated, Sullivan direct drive precision variable air condenser was used, with a capacity range of 65 to 365 μμF. It had a finely divided degree scale consisting of 720 directly engraved divisions, which was fitted with a simple microscope and a vernier reading directly to one-twentieth of a division. By estimation the scale could be read to one-fortieth of a division: this corresponded to a change in capacity of approximately 0.01 μμF. Using a dielectric cell with a capacity of about 100 μμF. when air was the dielectric, this scale reading accuracy made it possible to determine the dielectric constants of the solutions to within ±0.0001.

The taper bearing of the condenser allowed very small increments of capacity to be made: by applying a slight torque to the capstan head of the condenser, the beat frequency could be altered by one or two cycles per second. This showed the condenser to be entirely free from backlash: it was found that it could be adjusted with a far higher degree of precision than that with which the scale could be read.

Whilst the capacity of the precision condenser was adjusted as far as possible so that the beat frequency when it was in the circuit was the same as when it was replaced by the precision condenser, it is desirable to know what is the change in the beat frequency corresponding to the minimum alteration in the capacity of the precision condenser which can be detected on the scale.

From the equation

$$f = \frac{1}{2\pi\sqrt{LC}} \quad . \quad . \quad . \quad 1.$$

differentiation with respect to C, L remaining constant, gives

$$\frac{df}{dC} = - \frac{1}{4\pi C\sqrt{LC}} \quad . \quad . \quad . \quad . \quad . \qquad 2.$$

Dividing equation 2 by equation 1,

$$\frac{df}{f} = - \frac{dC}{2C} \quad . \quad . \quad . \quad . \quad . \qquad 3.$$

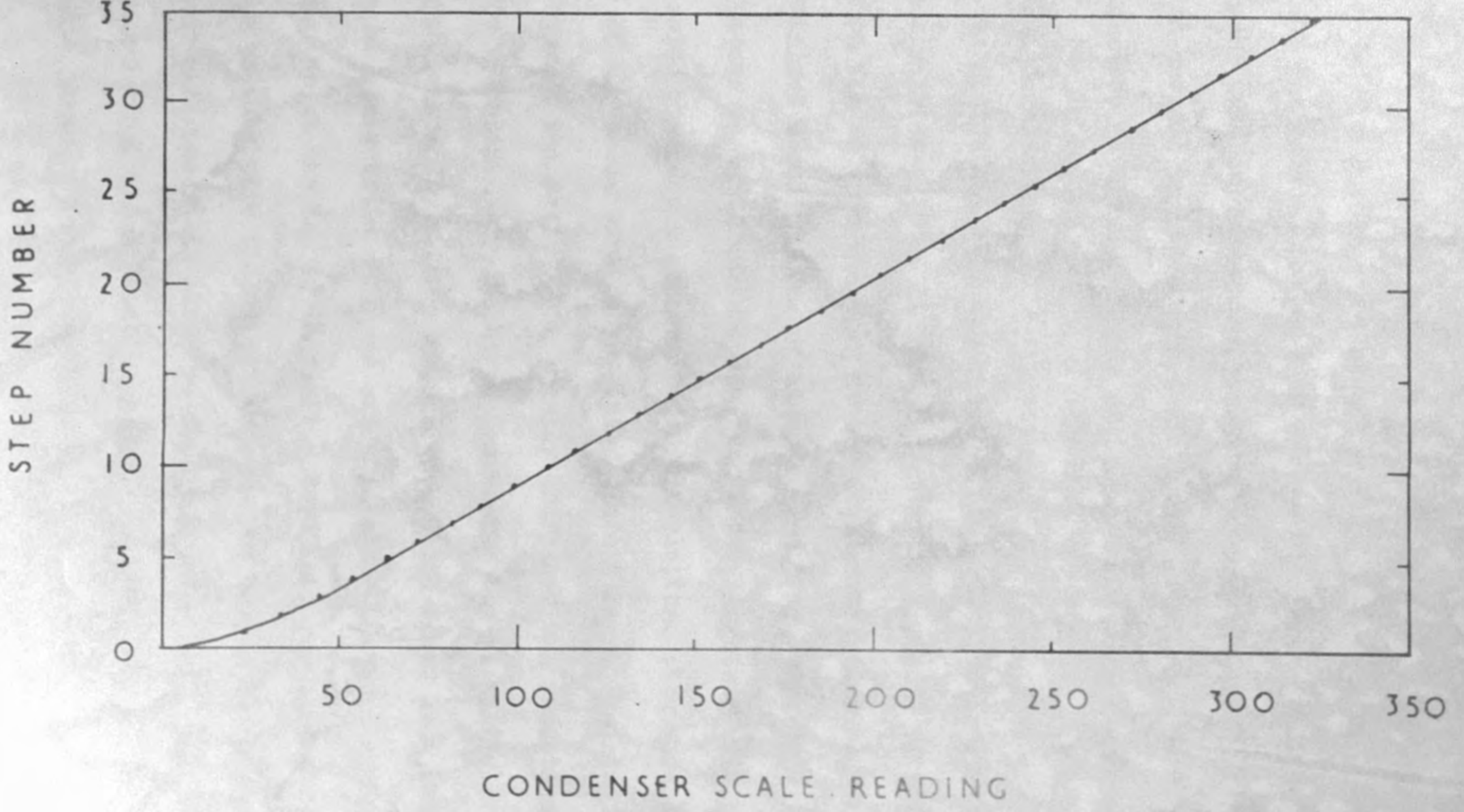
Since $f = 10^6$ c.p.s., and C is of the order of 500 µµF., then for the smallest detectable capacity change of 0.01 µµF.,

$$\frac{df}{10^6} = - \frac{0.01}{2 \times 500} \,,$$

whence $df = 10$ c.p.s.

Thus it was actually necessary only to match the capacity of the precision condenser to that of the dielectric cell to within a beat frequency difference of five cycles per second, ensuring at the same time that the beats were occurring on the same side of the zero beat position.

The calibration of the condenser was carried out by the "step" method, using the heterodyne beat apparatus. The precision condenser was first adjusted to the zero of the scale, andthen by operation of the relay a small fixed condenser was introduced into the circuit. This fixed condenser was in fact the capacity associated with the rigid brass leads from the relay to the dielectric cell platform. The oscillators were then matched to zero beats by adjustment of the tuning condensers in the variable frequency oscillator. The fixed condenser was then removed from thecircuit by operation of the relay, and the oscillators were again matched by adjustment of the precision condenser. The new reading on the condenser was noted and it was then readjusted to the



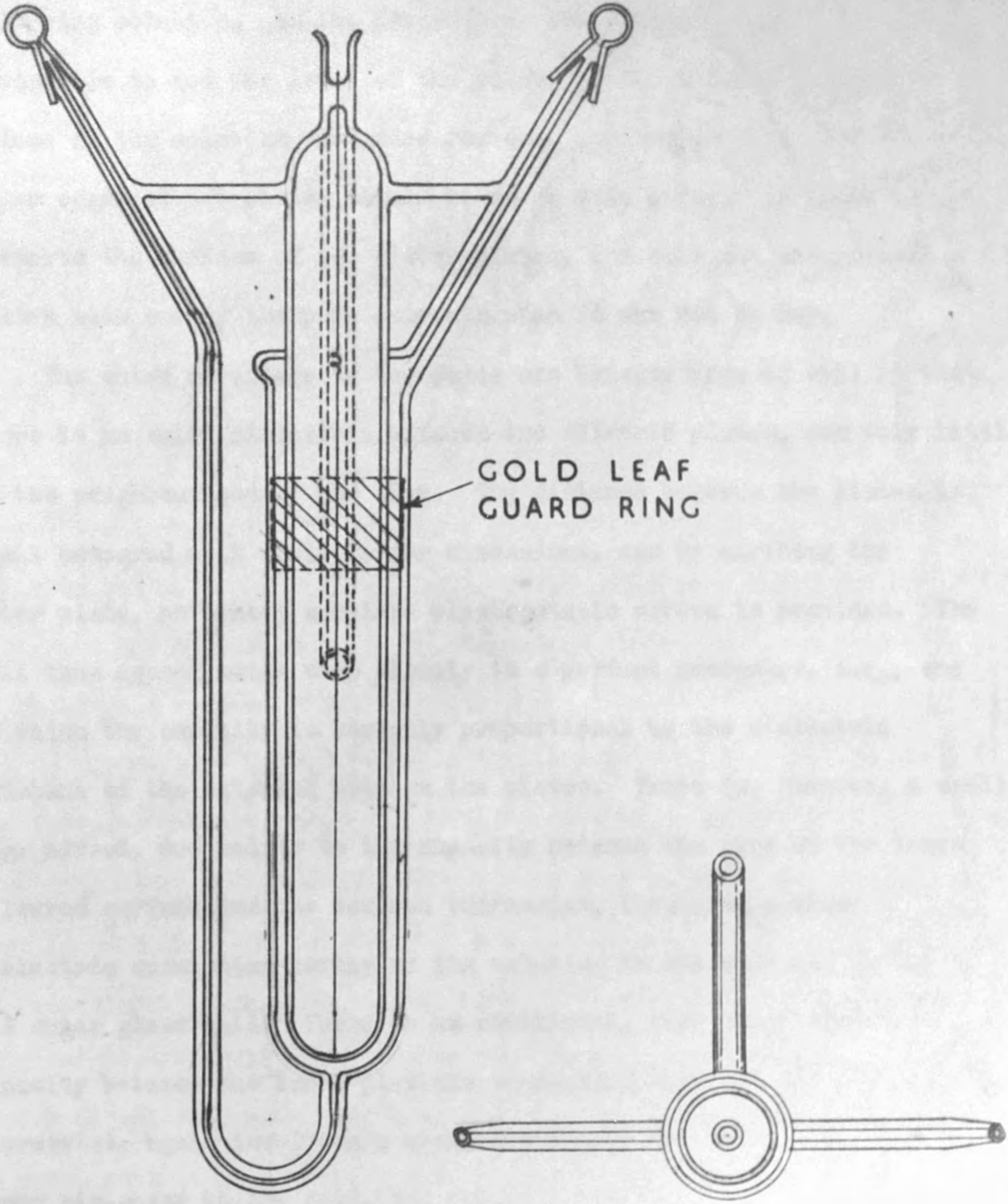
CALIBRATION OF PRECISION CONDENSER SCALE zero of the scale, and the procedure was repeated. The mean of two or three such readings was taken as the correct capacity increment.

The precision condenser was then adjusted to this mean reading and the whole procedure was repeated for the second "step".

By this method, the part of the scale of the precision condenser which was used in these measurements was calibrated. Checking repeats, made at several points of the scale, showed that the calibration was satisfactory within the limits of the scale reading accuracy.

Dielectric Cell.

The dielectric cell was based on the principle introduced by Sayce and Briscoe (5). It had an electrical capacity of about 100 μμF when filled with nitrogen as the dielectric material, and when full it contained about 30 c.c. of liquid. Two 3 mm. bore capillary tubes gave access to the annular space, and these, together with the elbow-tube which provided a connection to the platinum electrode of the outer plate of the cell, were supported by glass tie-arms joining them to the main body of the cell. This greatly increased the resistance of the cell to mechanical strain, hence increasing the stability of its electrical capacity. The platinum wire which acted as a connection to the inner plate ofthe cell was extended along the axis and fused into a glass cup at the top of the cell. Both this cup, and the outer plate connection tube were filled with mercury to ensure that proper contact was made with the rigid leads to the cell. The cell incorporated a gold-leaf guard-ring, which greatly reduced the small edge-effect which otherwise occurs in this type of cell.



DIELECTRIC CELL

The silvering of the cell was carried out by the method described by Sugden (6), using four applications of the specified silvering solution. As the presence of the guard-ring made it impossible to see the level of the silvering solution, a constant volume of the solution was added for each application, so that the upper edges of the plates should be on an even level. In order to preserve the surface of the silver plates, the cell was always left filled with one of the pure solvents when it was not in use.

The chief advantage of the Sayce and Briscoe type of cell is that there is no solid dielectric between the silvered plates, and very little in the neighbourhood of the edge. The distance between the plates is small compared with their linear dimensions, and by earthing the outer plate, an almost complete electrostatic screen is provided. The cell thus approximates very closely to a perfect condenser, i.e., one in which the capacity is strictly proportional to the dielectric constant of the material between the plates. There is, however, a small edge effect, due mainly to the capacity between the edge of the inner silvered surface and the earthed thermostat, involving a mixed dielectric consisting partly of the solution in the cell and partly of its outer glass wall. There is an additional, very small effect due to the capacity between the inner platinum connecting wire and the earthed thermostat, again involving a mixed dielectric consisting of the inner air-space in the cell, the solution contained in the cell and the two glass walls. This effect is much smaller than the former and can be considered negligible.

The edge effect of the Sayce and Briscoe type of cell has been studied in detail by Sugden (loc. cit.) and Ball (7) in investigations of the dielectric constants of liquids up to a dielectric constant of about 30. If the edge effect is ignored, the experimentally determined values of the dielectric constants were slightly lower than the absolute values, the largest discrepancies being for the highest dielectric constants. Sugden showed that for a mixed dielectric of the type described above, the edge capacity C varied according to the following relationship:

$$C \quad \propto \quad \frac{1}{\frac{d_1}{\epsilon_1} + \frac{d_2}{\epsilon_2}}$$

where ϵ_1 and ϵ_2 are the dielectric constants respectively of the liquid in the cell, and of the glass of the outer cell wall, and d_1 and d_2 are the thicknesses of the dielectric layers of the liquid and the glass wall respectively.

In the present work, the measurements were of dielectric constants of solutions, which varied only slightly from those of the pure solvents, which themselves were approximately 2. The edge correction in these cases is therefore small. However, the measurement of its magnitude was made by the general method of Sugden, by determining the capacity of the dielectric cell when it contained nitrogen, or liquids of varying dielectric constants, both when it was remote from, and when it was near, earthed conductors. The change in capacity under these conditions is then a measure of the edge correction.

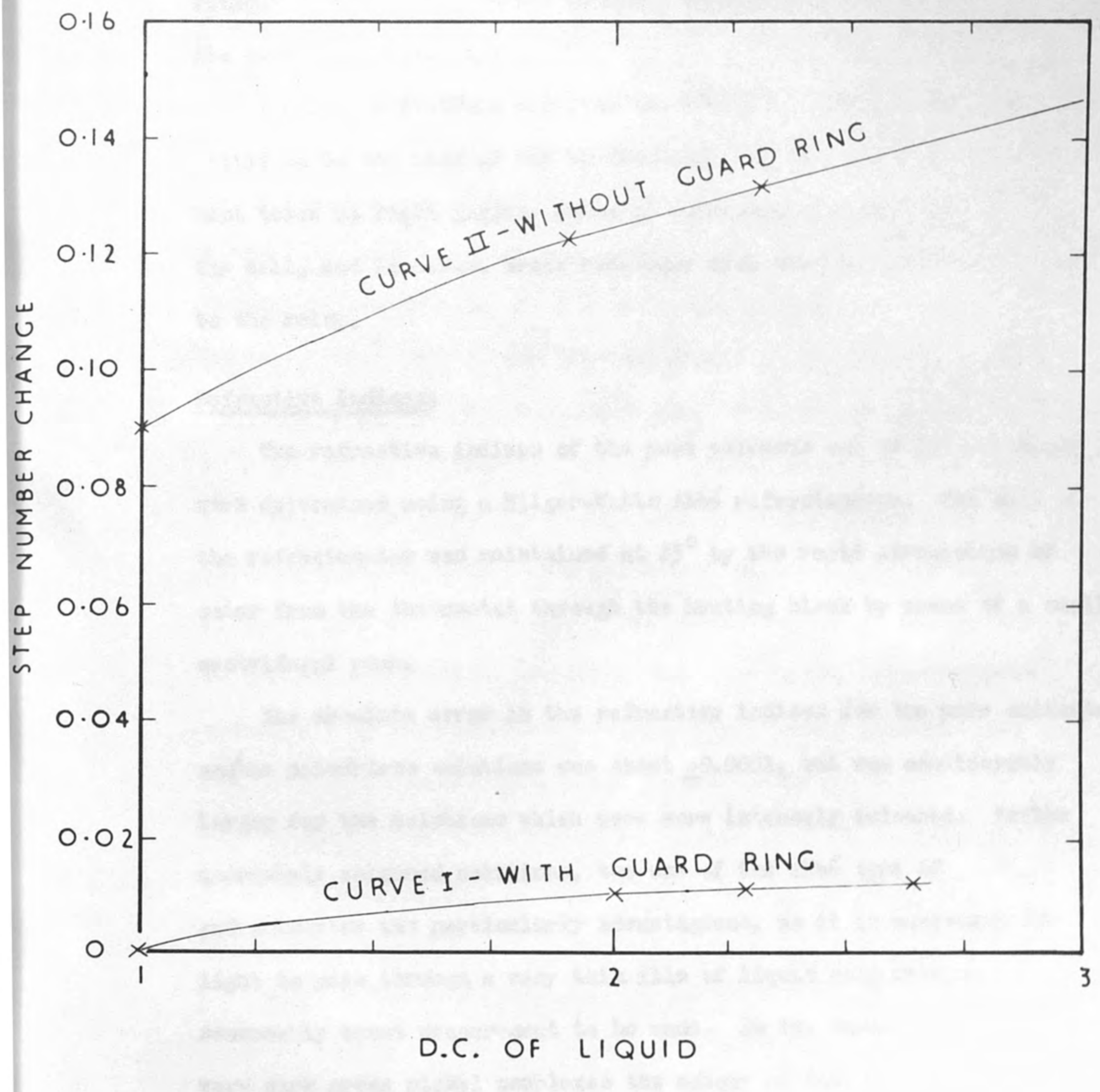
A copper collar, about 3 cm. long, which closely fitted the outer glass wall of the cell, was used. The collar, which was earthed, could be moved up and down the cell so that it was either below the level of the edge of the silvered surfaces, or above this level, thus simulating the absence and presence of the earthed thermostat water.

The dielectric cell was supported in the empty thermostat at 20°, remote from earthed conductors. The collar was adjusted to a position below the level of the silvered surfaces, and the cell was filled with nitrogen. The capacity was then determined in the usual way. The collar was then moved up so that its lower edge was a few mm. below the edge of the silvered surfaces, and the capacity again determined. This reading was found to be slightly higher than the first, the difference corresponding to the edge capacity. This procedure was repeated with cyclohexane, benzene and carbon disulphide successively as dielectrics, giving a range of dielectric constants between 1 and 2.6, thus completely covering the full range of the dielectric constants of the solutions used. A graph was plotted, showing the variation of the edge correction, expressed in terms of step numbers, with the dielectric constant of the liquid. On the same diagram is shown the curve of edge correction plotted against step number which was obtained by Few (loc. cit.) using the same technique, but for a cell which did not include the gold-leaf guard-ring, and which therefore had a considerably higher edge effect.

Cell Edge Correction.

Dielectric material.	Nitrogen.	Cyclohexane.	Benzene.	Carbon disulphide.
D.c. of dielectric.	1.0	2.01	2.27	2.63
Step number change.	0.0028	0.0090	0.0109	0.0120

In practice, this correction is found to be cancelled by another correction (cf. Method of Calculation of Dielectric Constants).



DIELECTRIC CELL EDGE CORRECTION

When in the thermostat, the dielectric cell was supported by a brass stand, constructed so that the cell could be easily inserted and removed, without involving any strain upon it, which would result in changes in its electrical capacity.

A Distrene platform carrying two stainless steel mercury cups was bolted on to the side of the thermostat. Two rods of 12 S. W.G. brass, bent twice at right angles, acted as connections between the cups and the cell, and 12 S.W.G. brass rods were also used to connect the cups to the relay.

Refractive Indices.

The refractive indices of the pure solvents and of the solutions were determined using a Hilger-Watts Abbé refractometer. The cell of the refractometer was maintained at 25° by the rapid circulation of water from the thermostat through the heating block by means of a small centrifugal pump.

The absolute error in the refractive indices for the pure solvents and the colourless solutions was about ±0.0001, but was considerably larger for the solutions which were more intensely coloured. For the moderately coloured solutions, the use of the Abbé type of refractometer was particularly advantageous, as it is necessary for light to pass through a very thin film of liquid only, enabling a reasonably exact measurement to be made. In the cases of some of the very dark green nickel complexes the colour of the solutions was too intense for any refractive index measurements to be made, since, even if solutions were prepared sufficiently dilute to allow light to pass through them, the change in refractive index from that of the pure solvent was too small to be measured at such high dilution.

Densities.

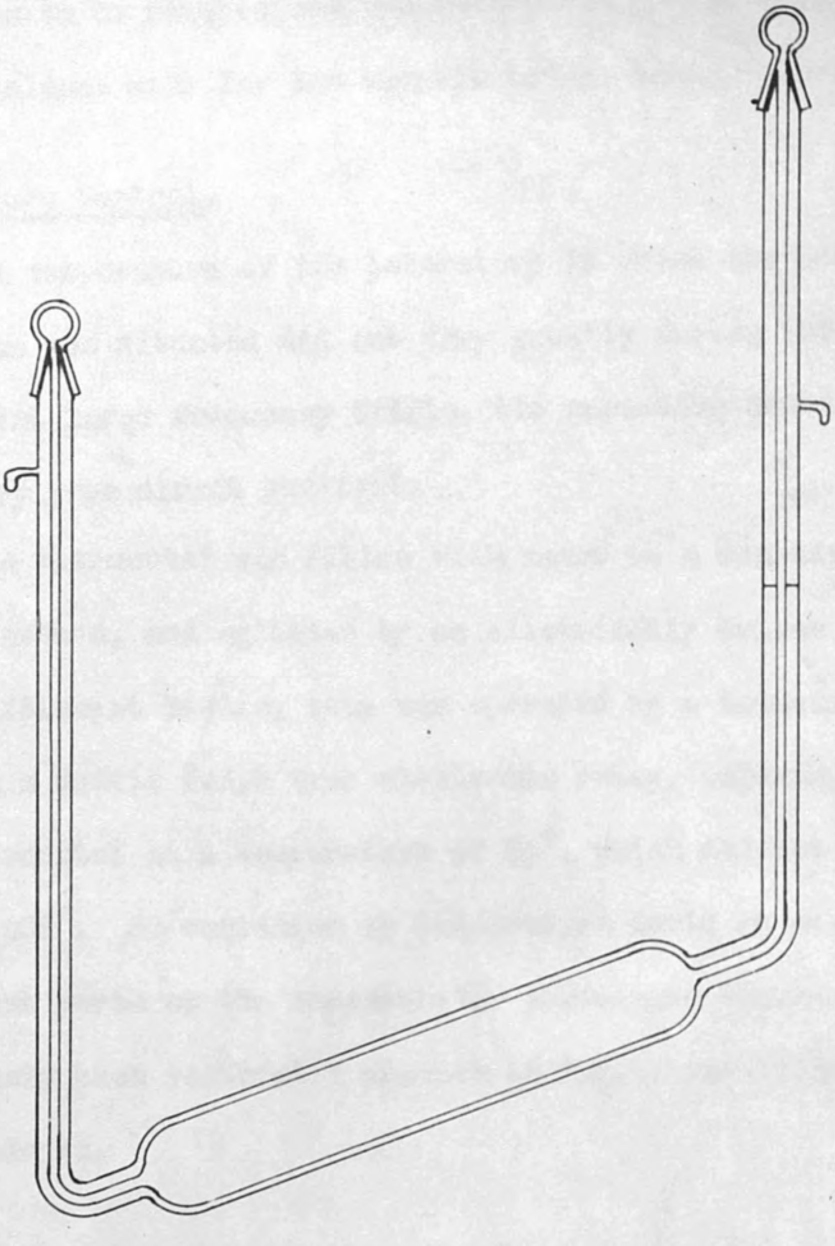
The densities of the pure solvents and the solutions were determined, relative to the density of water at 4° = 1, by means of a Sprengel type of pyknometer with a capacity of about 10 c.c. The pyknometer had two fine-bore capillary side-arms, fitted with ground-glass caps to reduce losses by evaporation. It was provided with a removable stirrup made of stainless steel wire for attachment to the balance. When in the thermostat it rested in a brass holder.

The pyknometer was calibrated with boiled-out distilled water at 25°, and several repetitions of the calibration showed that the accuracy of a density measurement depended chiefly on the accuracy of the weighings, rather than on the adjustment of the liquid in the pyknometer to constant volume. The absolute error in the densities in most cases was about ±0.00002. For some of the most intensely coloured solutions the error was probably slightly greater since in some cases it became difficult or impossible to see clearly the exact position of the meniscus in the capillary tube, which had then to be estimated.

Weighings.

All the weighings were carried out on a Stanton Model C.B.3 balance, having a sensitivity of 2.3 divisions per milligram throughout the range used, thus enabling the weighings to be made with an accuracy of ±0.1 mg.

B.T.L. analytical gold-plated weights were used, after



PYKNOMETER

calibration against an N.P.L. certificated 5 mg. rider. All glass apparatus to be weighed was handled with silk throughout, and was left in the balance case for ten minutes before being weighed.

Temperature Control.

The temperature of the laboratory in which the heterodyne beat apparatus was situated did not vary greatly during the day, but in order to prevent large frequency drifts, the apparatus could be screened when necessary from direct sunlight.

The thermostat was filled with water to a constant level, the water being earthed, and agitated by an electrically driven stirrer. The carbon filament heating lamp was operated by a toluene-mercury spiral through a Sunvic E.A.2 type electronic relay, adjusted to maintain the thermostat at a temperatore of 25°, which did not vary by more than 0.002°. No variation in temperature could be detected between different parts of the thermostat. A Beckmann thermometer, which had previously been calibrated against an N.P.L. certificated thermometer, was employed.

Section 2. Method of Calculation of the Dielectric Constants.

In this work no attempt has been made to determine dielectric constants absolutely, but consideration has been given to the accurate determination of relative dielectric constants of solutions differing only slightly from that of the pure solvent.

Two reference substances were used in the determination: pure dry benzene, the dielectric constant of which was taken as 2.2725 at 25° , the value obtained by Hartshorn and Oliver (8), and dry nitrogen, which has a dielectric constant of 1.0005 at 25°, the value given in the "International Critical Tables".

All condenser readings were converted into step numbers, and the dielectric constants were calculated as follows:

If the capacity of the cell in vacuo is C_o,

then the capacity of the cell filled with nitrogen = $C_o \epsilon_N$,
" " " " " " " benzene = $C_o \epsilon_B$,
" " " " " " " solution = $C_o \epsilon_S$,

where ϵ_N, ϵ_B and ϵ_S are the respective dielectric constants.

Then if R_N, R_B and R_S are the step numbers corresponding to the precision condenser readings when the cell is filled with nitrogen, benzene and solution respectively, and if C_L is the capacity which remains constant during the course of the run, due to the leads between the cell and the relay, etc., and where k is a constant:

$$C_o \epsilon_N + C_L = kR_N \quad . \quad . \quad . \quad . \quad . \quad 1.$$

$$C_o \epsilon_B + C_L = kR_B \quad . \quad . \quad . \quad . \quad . \quad 2.$$

$$C_o \epsilon_S + C_L = kR_S \quad . \quad . \quad . \quad . \quad . \quad 3.$$

Subtracting equation 1 from equation 2,

$$C_o(\epsilon_B - \epsilon_N) = k(R_B - R_N) \quad . \quad . \quad . \quad . \quad 4.$$

Subtracting equation 1 from equation 3,

$$C_o(\epsilon_S - \epsilon_N) = k(R_S - R_N) \quad . \quad . \quad . \quad 5.$$

Then, dividing equation 5 by equation 4,

$$\frac{\epsilon_S - \epsilon_B}{\epsilon_B - \epsilon_N} = \frac{R_S - R_B}{R_B - R_N},$$

that is,

$$\epsilon_S = \epsilon_B + \frac{(R_S - R_B)}{(R_B - R_N)} \cdot (\epsilon_B - \epsilon_N) \quad . \quad . \quad 6.$$

Thus, with a knowledge of the values of ϵ_B and ϵ_N, and of the step numbers R_S, R_B and R_N, the dielectric constants can be calculated from equation 6.

If the term $\dfrac{R_S - R_B}{R_B - R_N} = K$,

then when K = 0, 0.1 and 0.2, the values of ϵ_S are respectively

$2.2725 \qquad 2.3997_0 \qquad 2.5269_0$.

However, if the dielectric constant of nitrogen is assumed to be unity, the corresponding values of ϵ_S, calculated from equation 6, are

$2.2725 \qquad 2.3997_5 \qquad 2.5270_0$.

The errors introduced by making this assumption are then

zero $\qquad + 0.0000_5 \qquad +0.0001_0$.

This small positive error is of the same order as the negative error introduced by the edge effect.

Evaluation of the Edge Correction.

Tabulated below are some typical condenser step numbers, both uncorrected. and with a correction applied for the edge effect, the magnitude of which was read off from the graph:

	Uncorrected.	Corrected.
R_N.	5.2974	5.2946
R_B.	31.9094	31.8985
R_{S1}.	34.5589	34.5478
R_{S2}.	37.2193	37.2077

From equation 6, the uncorrected dielectric constants are:

$$\epsilon_{S1} = 2.3991 \; ; \qquad \epsilon_{S2} = 2.5262.$$

The dielectric constants, corrected for the edge effect, are:

$$\epsilon_{S1} = 2.3992; \qquad \epsilon_{S2} = 2.5264.$$

The correction is zero for the calibrating liquid, benzene.

The total errors are then as follows:

Dielectric constant.	Nitrogen error.	Edge error.	Total error
2.40	$+\,0.0000_5$	-0.0001	-0.0000_5
2.53	$+\,0.0001_0$	-0.0002	-0.0001

Therefore, if the dielectric constant of nitrogen is assumed to be unity, and at the same time the edge effect is ignored, the total error introduced is less than the experimental error of ±0.0001 for liquids with dielectric constants within the range measured, since this lies between 2.2 and 2.4, and it may accordingly be neglected.

Section 3. Calculation ofthe Molecular Polarisations.

The molecular polarisation of a polar compound consists of two terms, namely, the orientation polarisation, P_μ, due to the presence of the permanent dipole in the molecule, and the distortion polarisation, P_D, which is itself composed of two terms: the atomic polarisation, P_A, resulting from the displacement of the atomic nuclei in the applied electric field, and the electronic polarisation, P_E, due to the displacement of the electrons.

Debye (9) first showed that the Clausius-Mosotti equation required a further polarisation term, to allow for the presence of a permanent dipole, and deduced, for a low-frequency field, the equation

$$P = P_A + P_E + P\mu = \frac{4}{3}\pi N\alpha + \frac{4\pi N\mu^2}{9kT} \quad . \quad . \quad . \quad 1.$$

For the derivation of this equation, however, it was necessary to assume that the molecules are sufficiently far apart to prevent any interaction between them. This assumption restricts the strict application of the equation to gases at low pressures; but it was pointed out by Debye (1) that, since the kinetic behaviour of a solute in dilute solution is analogous to that of a gas, the equation derived for the molecular polarisation of an ideal gas should be equally applicable to the case of a solute in low concentration in a non-polar solvent, always with the provision that there is no interaction between the molecules of the solute andthose of the solvent. The polarisation of a given solution P_{12}, will then be equal to the sum of the polarisation contributions of the solute and solvent, i.e.,

$$P_{12} = P_1f_1 + P_2f_2 = \frac{(\epsilon_{12} - 1)}{(\epsilon_{12} + 2)} \cdot \frac{M_1f_1 + M_2f_2}{d_{12}} \quad . \quad . \quad 2.$$

where f denotes the molar fraction of the component concerned, and the subscripts 1, 2 and 12 refer to the solvent, solute and solution respectively. From this equation, P_2, the molecular polarisation of the solute, can be calculated, assuming that P_1 remains constant over the concentration range studied.

The value of P_2, when calculated in this way, varies in many cases with the concentration of the solution, in a manner which cannot at present be predicted on any theoretical basis. Two methods are available for the determination of the molecular polarisation at infinite dilution.

The first method involves the calculation of P_2 for each solution, followed by the plotting of the graph of P_2 against the weight-fraction of the solute, and extrapolation to zero concentration. It has been shown by Sugden (10) that the calculation of P_2 from equation 2 is considerably simplified by the use of specific polarisations. The molecular polarisation is equal to the product of the specific polarisation, p_2, and the molecular weight, M_2, of the solute, and therefore it follows that, since

$$P_{12} = P_1 f_1 + P_2 f_2,$$

$$p_{12} = p_1 w_1 + p_2 w_2, \quad . \quad . \quad . \quad . \quad . \quad 3.$$

where w_1 and w_2 are the weight fractions of the solvent and the solute respectively.

Now $w_1 = 1 - w_2$, so that, from equation 3,

$$p_{12} = p_1 (1 - w_2) + p_2 w_2,$$

it follows that $p_2 = p_1 + \dfrac{p_{12} - p_1}{w_2}$ . . . 4.

and thence that $P_2 = M_2 p_2 + M_2 \left(p_1 + \dfrac{p_{12} - p_1}{w_2}\right)$. 5.

Therefore, since $p_{12} = \dfrac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot v_{12}$ . . 6.

where v_{12} is the specific volume of the solution, the value of P_2 can be calculated.

The values of the molecular polarisation calculated in this way are always subject to a considerable uncertainty, especially for solutions of low concentration, since the expression involves the term $(p_{12} - p_1)$, that is, a difference between two terms which may be very nearly equal: the percentage error in P_2 thus increases as w_2 decreases. In the present work, most of the measurements had to be made on very dilute solutions, on account of the limited solubility of the compounds. In certain cases, therefore, the values of P_2 were subject to a rather large error, which was increased by the fact that the apparent dipole moments of the compounds were quite small so that the changes in dielectric constant were also small. Reasonably accurate extrapolation to infinite dilution was therefore difficult. In all the cases considered in this work, P_2 was found to vary in a random manner about a mean figure which approximated to the value obtained by using the second method of calculation.

The second method used was that due to Smith and Cleverdon (11). This method makes two assumptions: firstly, that the dielectric constants of the solutions vary with the weight-fractions of the solute according to the relation:

$$\epsilon_{12} = \epsilon_1 + \alpha w_2 + \alpha' w_2^2 \quad . \quad . \quad . \quad . \quad . \quad 7.$$

where α and α' are constants ; and secondly, that there is a linear relationship between the specific volumes of the solutions and the weight fractions of the solute, which may be written

$$v_{12} = v_1 + \beta w_2 \quad . \quad . \quad . \quad . \quad . \quad 8.$$

where β is a constant.

The constant α may be determined by plotting the graph of $(\epsilon_{12} - \epsilon_1)/w_2$ ~~$/w_2$~~ against w_2, and extrapolating linearly to $w_2 = 0$, the intercept on the w_2 axis giving α. In fact, in all the cases studied in this work, it was found that there was no variation in $(\epsilon_{12} - \epsilon_1)/w_2$ with w_2 greater than that due to experimental error. It was then possible to determine α by finding the slope of the graph of ϵ_{12} plotted against w_2; alternatively, the value was taken as $\frac{\sum(\epsilon_{12} - {}_1)}{\sum w_2}$ The latter method has the merit that less weight is placed on the measurements on the very dilute solutions, where the percentage experimental error is likely to be large.

The value of β was determined in a similar way, using the relationship $\beta = \frac{\sum(v_{12} - v_1)}{\sum w_2}$. The value of β calculated at each concentration was found to be approximately constant.

From the values of the parameters α and β determined in this way, the molecular polarisation at infinite dilution was calculated using the equation derived by Halverstadt and Kumler (12):

$$P_{2\infty} = M_2p_2 = M_2\left[\frac{3\alpha v_1}{(\epsilon_1 + 2)^2} + (v_1 + \beta)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}\right]. \qquad 9.$$

which is derived by differentiation of equation 6, followed by combination with equations 4, 7 and 8.

The advantage of this method over the former is that individual errors in the experimentally determined values of ϵ_{12} and v_{12} are evident before combination into polarisation terms, where they may become masked.

In practice, it was found that the values of P_2 obtained by the first method did not differ greatly from the value of $P_{2\infty}$ calculated by the Smith and Cleverdon method, although the first method involved rather more uncertainty than the second. $P_{2\infty}$ was therefore always calculated from the experimental results in both ways, the value obtained using the first method acting as a check on the result calculated by the second.

Section 4. Calculation of the Electronic Polarisations.

For a compound which does not contain a permanent dipole in the molecule, the molecular polarisation is equal to the distortion polarisation that is, the polarisation resulting from the displacement of the atomic nuclei and the electrons in the applied electric field. Maxwell (13) showed that, for a non-polar substance, the dielectric constant was equal to the square of the refractive index of the substance, measured for light of infinitely long wave-length. If this value, n_{∞}^{2}, is substituted in the Lorentz-Lorenz equation for molecular refraction, a value for the molecular refraction is obtained which is identical with the molecular polarisation of the substance calculated by the Clausius-Mosotti equation. Thus

$$[R_{\infty}] = P_D = P_A + P_E.$$

Observations of refractive indices in the infra-red region of the spectrum will therefore indicate the total distortion polarisation of the substance. Such observations are experimentally difficult: and the measurement of refractive indices for light in the visible spectrum gives a different figure for the molecular refraction, since, at the lower frequencies in the infra-red region, both atomic nuclei and electrons will be displaced, but, at the frequency of visible light, alternations are so rapid that only displacements of the electrons occur. It is usual to measure refractive indices at the frequency of the sodium D line, and from this to calculate the molecular refraction $[R_D]$, which may be used as an approximation for the electronic polarisation, from which it normally differs by only a small amount, provided that the measurements are not made in the region of an absorption band. Since the molecules of the coordination compounds dealt with in this work are symmetrical, and possess no permanent dipole moment, the difference between the molecular polarisation calculated from the dielectric constants and the electronic polarisation either determined in this way, or calculated from bond refractions, will be equal to the atomic polarisation.

The molecular refractions were calculated by a method analogous to that used for the molecular polarisations. From the equation

$$[R_D] = M_2 r_2 = M_2 \left[r_1 + \frac{r_{12} - r_1}{w_2} \right],$$

where $r_1 = \dfrac{n_1^2 - 1}{n_1^2 + 2} \cdot v_1$

and $r_{12} = \dfrac{n_{12}^2 - 1}{n_{12}^2 + 2} \cdot v_{12}$,

values of $[R_D]$ were calculated for each solution. These were found to vary very little outside the limits of experimental error, and the mean of these values was taken as an approximate $[R_D]$, which was used as a check on the figure obtained from an equation of the same form as that derived by Halverstadt and Kumler for the molecular polarisations:

$$[R_D] = M_2 \left[\frac{3 \gamma v_1}{(n_1^2 + 2)^2} + (v_1 + \beta) \frac{(n_1^2 - 1)}{(n_1^2 + 2)} \right]. \quad . \quad 10.$$

The parameter γ in this equation is given by the slope of the graph of n^2 against w_2, or the mean of the values of $(n_{12}^2 - n_1^2)/w_2$ for each solution. The weighted mean, $\Sigma(n_{12}^2 - n_1^2)/\Sigma w_2$, was not employed except in the cases where the solute was colourless or nearly so. When the solutions were very deeply coloured, the refractive indices of the more concentrated solutions were subject to nearly as large a percentage error as those at lower concentrations, since the error introduced in setting the refractomenter was considerably increased.

Section 5. Observational Errors.

The accuracy with which P_2 can be measured depends not only upon the accuracy of the measurements of the dielectric constants and the specific volumes, but also upon the concentration of the solution. As the concentration diminishes, the quantity $(p_{12} - p_1)$ is decreased, and the errors which arise in p_2, and hence in P_2, may become considerable. The error in p_2 due to these variables can be calculated as follows:

From the equation:

$$p_2 = p_1 + \frac{p_{12} - p_1}{w_2},$$

p_1 being constant,

$$\Delta p_2 = \frac{\Delta p_{12}}{w_2} \quad . \quad . \quad . \qquad 11.$$

From the relationship

$$p_{12} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot v_{12},$$

partial differentiation with respect to ϵ_{12} gives

$$\frac{\partial p_{12}}{\partial \epsilon_{12}} = \frac{3v_{12}}{(\epsilon_{12} + 2)^2} \quad . \quad . \quad . \quad . \quad . \qquad 12.$$

and partial differentiation with respect to v_{12} gives

$$\frac{\partial p_{12}}{\partial v_{12}} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \quad . \quad . \quad . \quad . \quad . \qquad 13.$$

Then, from equations 11, 12 and 13,

$$\Delta p_2 = \frac{1}{w_2}\left[\frac{3v_{12}\Delta\epsilon_{12}}{(\epsilon_{12}+2)^2} + \frac{\epsilon_{12}-1}{\epsilon_{12}+2}\cdot\Delta v_{12}\right].$$

If the error in the measurement of the dielectric constants is ± 0.0001, and the error in the specific volumes is ± 0.00002, then taking ϵ_{12} as 2.3, and v_{12} as 1.0, as average values of these quantities, the errors in p_2 are as follows:

When $w_2 = 0.01, \Delta p_2 = \pm\ 0.2\%$.

When $w_2 = 0.001, \Delta p_2 = \pm 2\%$.

The error in the value of the molecular polarisation at infinite dilution cannot be ascertained with such certainty, but since, in the cases considered in the present work, p_2 did not vary greatly with w_2, the error in $P_{2\infty}$ is probably not more than $\pm$ 2%, and in some cases may be much less.

The accuracy with which the measurements of $[R_D]$ can be carried out depends also on the concentration of the solution, as well as on the accuracy of the measurements of the refractive indices and the specific volumes. By a procedure analogous to that used to calculate the error in p_2, the following equation can be derived forthe calculation of the error in $[R_D]$:

$$\Delta r_2 = \frac{1}{w_2}\left[\frac{6nv_{12}\Delta n}{(n^2+2)^2} + \frac{n^2-1}{n^2+2}\cdot\Delta v_{12}\right].$$

If Δv_{12} is taken as $\pm$ 0.00002 as before, and Δn is taken as ± 0.0001 then for the average values of $n = 1.45$ and $v_{12} = 1.0$, the error in $[R_D]$ is as follows:

When $w_2 = 0.01, \Delta r = 0.6\%$.

When $w_2 = 0.001, \Delta r = 6\%$.

For a coloured solution, the error in the measurement of the refractive index is greater, and Δr may be almost twice as large. The value of $[R_D]$ calculated by an equation of the Halverstadt and Kumler type, however, is probably not in error by more than ±2% or less for the colourless solutions, or ±5% for the more intensely coloured solutions.

The errors considered here are due to the limitations of the measuring instruments used: they do not take into account systematic errors, or errors introduced by the absorption of moisture or by the evaporation of the solvent during measurements on a series of solutions; nor, in the case of the molecular refractions, possible errors due to anamalous dispersion through the measurements being made at frequencies near the absorption bands. The use of the procedure described in the following section tends to minimise errors of the first type; errors introduced by anomalous dispersion are discussed fully in Chapter III.

Section 6. Experimental Procedure.

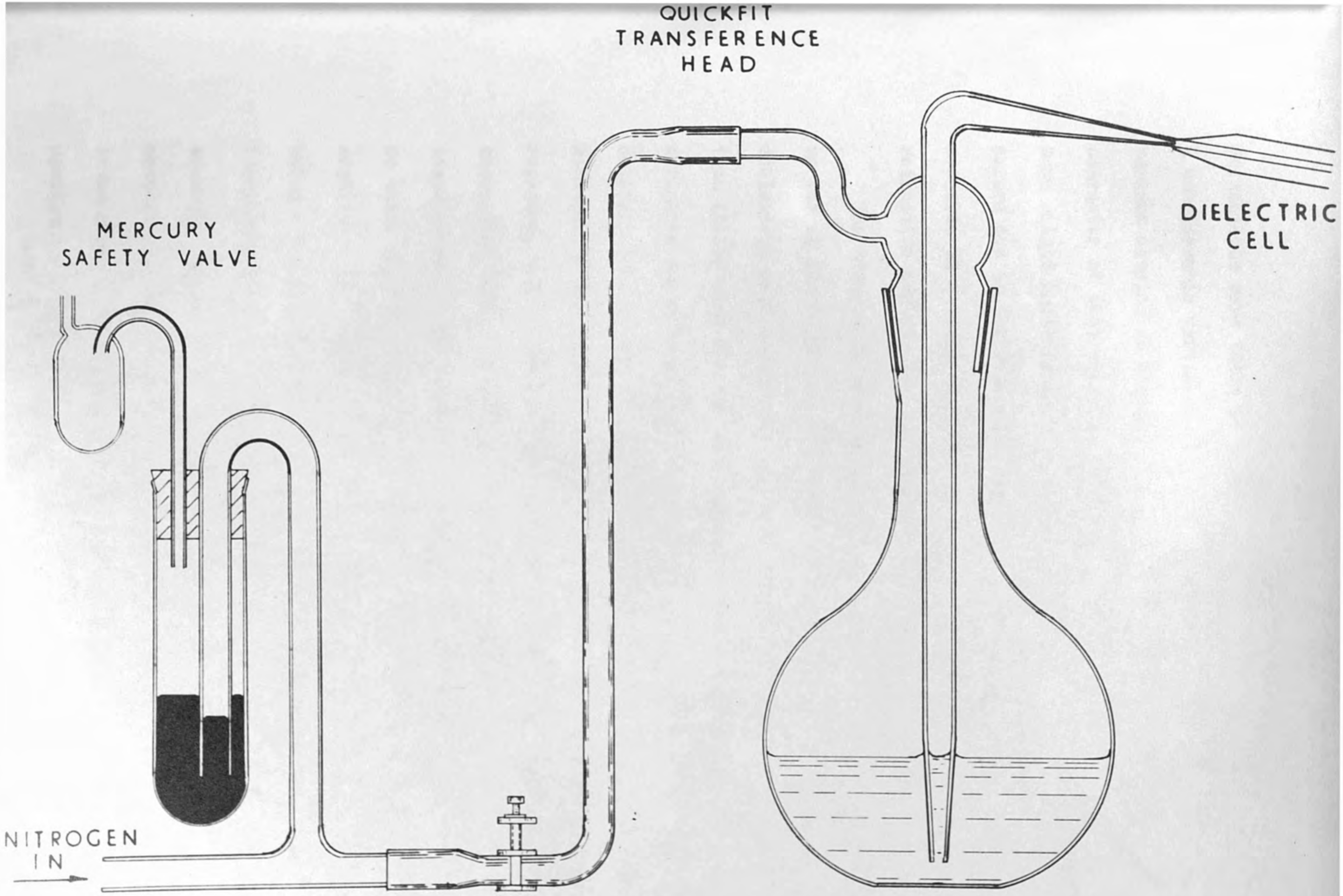
For reasonably accurate measurements of the molecular polarisation, it is desirable to use about six solutions of graded concentrations, usually up to about 5%. The use of a more restricted range of concentrations considerably increases the error in the measured molecular polarisation, but owing to the very limited solubility of many coordination compounds, the use of very dilute solutions was unavoidable except in a few cases.

Preparation of the Solutions.

The solutions were prepared in 200 c.c. flasks fitted with ground-glass stoppers, and graduated in 10 c.c. increments, so that an approximately known volume of solvent could be rapidly introduced. Before each series of measurements they were cleaned with alcohol-nitric acid cleaning mixture, thoroughly washed with distilled water, and dried overnight in an electric oven at 120°. Dry nitrogen from a cylinder was then passed into them, the outsides of the flasks were cleaned with silk, and they were placed in the balance-case for ten minutes. They were weighed accurately to 0.0001 g. The solute, which until now was kept in a vacuum desiccator, was introduced in a finely powdered form, and the flasks were reweighed. The solvent was introduced by the use of the transference apparatus, using the screw-clip to control the exact amount of solvent added; at the same time, a sample of the pure solvent was transferred to another flask which had been prepared in the same way as the solution flasks; thus, any slight contamination of the solutions by atmospheric moisture during the period between preparation and use also affected the pure solvent. The solution flasks were then weighed accurately to 0.0001 g. Throughout the time between the removal of the flasks from the oven and the use of the solutions, the flasks were kept in a large desiccator.

Determination of the Dielectric Constants.

Owing to the high dielectric constant of water, the dielectric constants of the solvents and the solutions were affected to an appreciable degree even by minute traces of moisture. All possible



APPARATUS FOR TRANSFERENCE OF LIQUIDS

precautions were taken to exclude atmospheric water vapour, but even so, a considerable variation was found in the dielectric constants of the various samples of dioxan, possibly due in part to the hygroscopic character of this solvent. Benzene was less affected in this way, although some slight contamination probably occurred. In order to minimise errors due to the absorption of water, the dielectric constants were measured as quickly as possible, before the determination of the refractive indices and the specific volumes, which were less affected.

The heterodyne beat apparatus was switched on and allowed to warm up for at least half an hour before any measurements were made. The dielectric cell was rinsed out three times with the pure solvent, and then filled with the solvent, using the transference apparatus, which minimised exposure of the liquid to air and moisture, since the delivery-tube of the transference apparatus fitted just inside the side-arm of the dielectric cell. The ground-glass caps of the cell were replaced, and it was put into position in the brass stand in the thermostat bath. It was left for twenty minutes to reach the temperature of the thermostat. The tuning condensers were then adjusted so that, with the cell in the circuit, the frequency of the variable oscillator was equal to that of the crystal-controlled oscillator, using the earphones for rapid approximate matching, and finally visual observation of the beat frequency on the microammeter for an accurate setting. The capacity of the precision condenser was then matched as accurately as possible to that of the cell. Care was taken always to match on the high-capacity side of the zero-beat position. It was occasionally found to be necessary to switch off the thermostat motor during the final matching, as the rotation of the stirrer and the variations in the level of the water were found to have a slight effect on the stray capacities. It was then ascertained that the cell and leads were in the correct position, by slightly lifting the cell and then replacing it in the holder, and checking that the setting of the precision condenser still corresponded to an exact match of the capacities. Normally, no discrepancy in the setting was apparent: if any change of capacity was noticed, a new reading was taken, and the procedure was repeated until a constant reading was obtained.

The cell was removed from the thermostat, the solvent was poured out, and the cell was rinsed out three times with the first of the solutions, before filling with this solution. Readings were taken in this manner for each of the solutions. After measurements had been made on the most concentrated of the solutions, the cell was rinsed out three times with the pure solvent, and dried by passing dry nitrogen from a cylinder through it for thirty minutes: the ground-glass caps were then replaced, the cell was allowed to come to the temperature of the thermostat, and a reading was then taken for the cell filled with nitrogen. Finally, the cell was refilled with the pure solvent, and a repeat measurement was made. If there had been any shift in the capacity of the dielectric cell, or of the stray capacities associated with it, or if the solvent had absorbed an appreciable amount of water vapour during the time taken to carry out the measurements on the solutions, there was a discrepancy between this repeat reading and the initial reading: in calculating the dielectric constants of the solutions the mean of these two readings was used.

Determination of the Specific Volumes.

The pyknometer was dried by passing nitrogen through it for thirty minutes: the outside was cleaned with silk and the wire stirrup and the ground-glass caps were fitted to it. It was placed in the balance case for ten minutes, and then weighed accurately to 0.0001 g. It was rinsed three times with the pure solvent, and then filled with the solvent, by applying gentle suction to one arm by means of a water pump. It was placed in its holder in the thermostat for fifteen minutes, and then, while still in the thermostat, the liquid in it was adjusted to constant volume by holding a piece of filter paper over the end of the unmarked arm until the meniscus, moving down the other arm, touched the calibration mark. The pyknometer was cleaned and dried with silk, the stirrup and the caps were attached, and it was placed in the balance case for weighing. This procedure was repeated for each solution.

Determination of Refractive Indices.

The pump circulating water from the thermostat at 25° through the heating block of the Abbé refractometer was allowed to run for ten minutes to preheat the cell. A small quantity of the pure solvent was poured into the cell, and allowed to remain there for one minute to reach the temperature of the cell. The refractometer was adjusted, and the reading noted. At least two repeat readings were made, and the mean of the three readings was taken as the refractive index of the solvent.

The refractometer cell was cleaned with lens tissue, washed with acetone, and wiped dry with a clean tissue, and the procedure was repeated for each solution.

CHAPTER II.

EXPERIMENTAL RESULTS.

Section 1. Preparation and Purification of Materials.

Care was taken in all cases to ensure that the solvents and solutes used were perfectly free from moisture when the measurements were made. Benzene was stored over phosphorus pentoxide until immediately before use, and dioxan was fractionated directly from sodium. All solutes were stored in a desiccator, and dried in vacuo for several hours just before use.

Methods of Analysis.

Where the melting-point of a complex was too high to be used as a reliable test of purity, the metallic content of the compound was estimated. A weighed quantity was digested with a mixture of concentrated sulphuric and nitric acids in the proportion 3: 1, until all the organic matter was destroyed and the solution became clear. It was then carefully diluted. Copper was estimated iodimetrically, and iron by reduction to the ferrous state with stannous chloride, excess of which was removed with mercuric chloride solution, followed by titration with potassium permanganate solution. Calcium was estimated by precipitation of the oxalate, which was filtered off and decomposed with dilute sulphuric acid, the oxalic acid being then determined with potassium permanganate solution. Aluminium was estimated gravimetrically as the 8-hydroxyquinoline complex, and nickel with dimethylglyoxime. Micro-analyses for carbon, hydrogen and nitrogen were carried out by Drs. Weiler and Strauss, of Oxford.

BENZENE.

Benzene of the commercial "crystallisable" grade was purified by the method of Few and Smith (1). It was shaken for thirty minutes with concentrated sulphuric acid, and then washed twice with distilled water, twice with 10% aqueous potassium hydroxide, and finally four times more with distilled water. After drying over phosphorus pentoxide for at least a fortnight it was fractionally crystallised four or five times, until it formed a glassy mass on freezing. It was stored over phosphorus pentoxide, and immediately before use it was distilled from this reagent, and the middle fraction, of constant boiling-point to within 0.02°, was collected.

B.p. 79.7°/760 mm.

Few and Smith give b.p. 79.7°/760 mm.

DIOXAN.

The commercial product was purified by boiling with sodium for one or two days, until the sodium remained bright. It was distilled, and immediately before use it was distilled from fresh sodium, collecting the middle fraction, of constant boiling-point to within 0.02°.

B.p. 101.1°/760 mm.

Few and Smith (loc. cit.) give b.p. 100.9°/760 mm.

CYCLOHEXANE.

Cyclo hexane was purified by shaking for two hours with concentrated sul~~l~~phuric acid, and then washing twice with distilled water, twice with 10% potassium hydroxide solution, twice more with water, once with dilute potassium permanganate solution, and finally four times with water. It was dried first with calcium chloride and then with phosphorus pentoxide, and fractionated from phosphorus pentoxide. The middle fraction was collected.

B.p. 80.7°/765 mm.

Broughton (2) gives b.p. 80.9°.

CARBON DISULPHIDE.

A sample of carbon disulphide was kindly provided by Dr. J.W. Smith, which had previously been purified by shaking with solid potassium permanganate and with mercury. It was dried over phosphorus pentoxide, and fractionated, the middle fraction being collected.

B.p. 46.2°/765 mm.

Smith and Witten (3) give b.p. 46.2°.

ALUMINIUM ACETYLACETONATE.

Aluminium acetylacetonate was prepared by the method described in "Inorganic Syntheses" (4). Acetylacetone (3 mols.) in suspension in water was treated with dilute ammonium hydroxide until it just dissolved. This solution was added to a 10% aqueous solution of ammonium alum (1 mol.). The complex was precipitated immediately as small, pale yellow crystals, which were purified by precipitation from benzene solution with petroleum ether, b.p. 80-100°. The pure substance was obtained as small, colourless prisms, m.p. 192-3°.

Finn, Hampson and Sutton (5) give m.p. 192-3°.

FERRIC ACETYLACETONATE.

Ferric acetylacetonate was prepared analogously, adding the neutral solution of acetylacetone to a concentrated aqueous solution of ferric chloride. The addition of a little more ammonia was required to complete the precipitation. The complex separated as bright red crystals, which were purified by recrystallisation from benzene; m.p. 182°.

Finn, Hampson and Sutton (loc.cit.) give m.p. 181.3-182.3°.

BERYLLIUM DIBENZOYLMETHANE.

Beryllium dibenzoylmethane was obtained on the gradual addition of an aqueous solution of beryllium sulphate in slight excess of the theoretical quantity to an alcoholic solution of dibenzoylmethane. The complex was purified by precipitation with alcohol from benzene solution, which gave long, pure white needles, melting sharply at 214°.

Booth and Pierce (6) give m.p. 214-5°.

FERRIC DIBENZOYLMETHANE.

Ferric dibenzoylmethane was prepared from ferric chloride and dibenzoylmethane by the method used for the beryllium complex. It was purified by precipitation with alcohol from benzene solution, giving very small, dark red needles. This compound has not previously been described.

(Found: Fe, 7.60; required for $Fe(C_{15}H_{11}O_2)_3$: Fe, 7.70%.)

ALUMINIUM DIBENZOYLMETHANE.

Aluminium dibenzoylmethane was prepared by the same method from ammonium alum and dibenzoylmethane. The product was a cream-coloured, microcrystalline powder, which was not sufficiently soluble in any solvent to permit recrystallisation, or for polarisation measurements to be made. This compound has not previously been described.

(Found : Al, 3.76%; required for $Al(C_{15}H_{11}O_2)_3$: Al, 3.87%)

NICKEL SALICYLALDOXIME.

Salicyladoxime[1] was prepared from salicylaldehyde and hydroxylamine hydrochloride in equimolecular proportions in alkaline solution. Unconverted aldehyde was removed by steam distillation, and the product which crystallised out on cooling the solution was used without further purification.

Nickel salicylaldoxime was precipitated as a bright green powder on the addition of a dilute solution of salicylaldoxime in aqueous alcohol to a solution containing a slight excess of nickel chloride. The product was crystallised once from chloroform, forming shining, dark green needles.

COPPER SALICYLALDOXIME.

Copper salicylaldoxime was prepared analogously from salicylaldoxime and cupric sulphate. The complex was precipitated as a yellow-green powder, which was crystallised once from dioxan, forming dark olive-green platelets.

NICKEL BENZENEAZO-p-CRESOL.

Benzeneazo-p-cresol was prepared by the addition of a solution of benzenediazonium chloride (1 mol.) to a cold alkaline solution of p-cresol (1 mol.). The red-brown precipitate was crystallised once from alcohol.

M.p. 108°.

Nickel benzeneazo-p-cresol was prepared as described by Elkins and Hunter (7), by adding a solution of nickel acetate (1.2 mols.) in 50% aqueous acetone to a solution of benzeneazo-p-cresol in hot acetone containing a little ammonia. On careful dilution of the solution with water, the nickel complex was precipitated in an impure form, which was purified by repeated precipitation from chloroform solution with petroleum ether, b.p. 80-100°. It was obtained pure as small shining green-black crystals, m.p. 216°.

Elkins and Hunter give m.p. 216°.

COPPER BENZENEAZO-p-CRESOL.

Copper benzeneazo-p-cresol was prepared as described by Elkins and Hunter (loc.cit.), by the addition of cupric acetate dissolved in 50% aqueous alcohol to a hot, concentrated alcoholic solution of benzeneazo-p-cresol. The complex separated out as a brown powder, which was obtained pure by precipitation from hot benzene solution with petroleum ether. It was found to be too insoluble for polarisation measurements.

NICKEL BENZENEAZO-2-NAPHTHYLAMINE.

Benzeneazo-2-naphthylamine was prepared by the general method given by Hodgson and Foster (8). A solution of benzenediazonium chloride (1 mol.) was added slowly, with stirring, to a solution of 2-naphthylamine (1 mol.) in alcohol, containing fused sodium acetate, at 0°. Stirring was continued at 0° for one hour, and the solution was then warmed to 50° for fifteen minutes, and allowed to stand overnight. The azo-compound crystallised out in small, scarlet needles, m.p. 117°, which were used without further purification.

Nickel benzeneazo-2-naphthylamine was prepared by the method given by Charrier and Beretta (9). A hot solution of benzeneazo-2-naphthylamine in alcohol was added slowly to a hot, concentrated solution of nickel chloride in large excess, in 20% ammonia, and the mixture was boiled for thirty minutes. The complex was precipitated as a deep green powder, only slightly soluble in benzene or dioxan.

COPPER BENZENEAZO-2-NAPHTHYLAMINE.

Copper benzeneazo-2-naphthylamine was prepared by the method of Charrier and Beretta, from cupric sulphate and benzeneazo-2-naphthylamine. It was precipitated as a fine, violet-brown powder, which crystallised from benzene as shining, very dark brown crystals, m.p. 170°.

Charrier and Beretta give m.p. 130°, not sharp.

This compound was soluble in benzene with a deep red colour, but appeared always to undergo some decomposition in solution, so that it could not be obtained uncontaminated by some of the free azo-compound. The instability of a copper complex in which the copper atom is bonded to four nitrogen atoms was observed also in copper pyrrole-2-aldimine, which was prepared after Pfeiffer (10) and obtained as light copper-coloured crystals with a metallic appearance from chloroform; these decomposed slowly on keeping, and could not be obtained pure enough for polarisation measurements. An attempt to prepare copper benzeneazo-2-pyrrole produced shining black crystals, soluble in benzene with a deep blue colour, which could not be obtained pure.

NICKEL BENZENEAZO-2-NAPHTHOL.

Benzeneazo-2-naphthol, prepared from 2-naphthol and benzenediazonium chloride by the method described for benzeneazo-p-cresol, was obtained as a red, microcrystalline powder, m.p. 133°, which was used without further purification.

The nickel complex, which was prepared in the same way as the complex of benzeneazo-2-naphthylamine, was precipitated as a grey-green powder, which was purified by recrystallisation from toluene, forming small, dark green needles.

COPPER BENZENEAZO-2-NAPHTHOL

Copper benzeneazo-2-naphthol was prepared analogously. It was precipitated as a brown powder which was crystallised from toluene, forming a small, dark red-brown crystals.

Both the nickel and the copper complexes of benzeneazo-2-naphthol were found to be insufficiently soluble for polarisation measurements.

NICKEL BENZENEAZO-2-PYRROLE.

Benzeneazo-2-pyrrole was prepared as described by O. Fischer (11), by a method analogous to that described for benzeneazo-2-naphthylamine. It was found that unless cooling was carried out with extreme care, tar formation occurred, and the azo-compound was not obtained. It separated out as a dark yellow sticky solid, which was crystallised once from dilute alcohol and used without further purification.

The nickel complex was prepared by the method given by

Pfeiffer (loc. cit.). Nickel chloride (3 mols.) was dissolved in concentrated ammonia, and the solution was added slowly to a boiling alcoholic solution of benzeneazo-2-pyrrole. After warming for an hour, the green-black crystalline precipitate was filtered off and recrystallised from a mixture of three parts of alcohol to one part of chloroform. It was obtained pure as shining, very dark green needles, soluble in benzene with an intense red-brown colour.

(Found: C, 59.9, H, 4.06, N, 21.1%. Required for $Ni(C_{10}H_8N_3)_2$: C, 60.2, H, 4.04, N, 21.1%.)

COPPER SALICYLALDEHYDE.

Copper salicylaldehyde was prepared by adding an alcoholic solution of the aldehyde dropwise, with stirring, to a solution of cupric sulphate. The complex was precipitated immediately as small green crystals, which were filtered off and thoroughly washed with alcohol and water.

COPPER SALICYLALDIMINE.

Copper salicylaldimine was obtained as a light-green, crystalline powder on allowing copper salicylaldehyde to stand for some days in contact with a concentrated solution of ammonia. It was found to be too insoluble for use in polarisation measurements.

COPPER SALICYLIDENEMETHYLIMINE.

Copper salicylidenemethylimine was prepared as described by Pfeiffer and Glaser (12). To a warm solution of salicylaldehyde in methyl alcohol was added the theoretical quantity of methylamine in aqueous solution. An excess of cupric acetate solution was then added slowly with stirring. On cooling, the complex separated out as long, sage-green needles, which were recrystallised from alcohol. The pure compound had m.p. 158°.

Pfeiffer and Glaser give m.p. 158°.

(Found : Cu, 19.13%; required for $Cu(C_8H_8ON)_2$: Cu, 19.16%)

COPPER SALICYLIDENEANILINE.

Copper salicylideneaniline was prepared by adding copper sulphate solution in excess to an alcoholic solution of the anil. The complex separated out at once, and was obtained pure, by precipitation from benzene solution with alcohol, as very deep brown, star-shaped crystals.

(Found : Cu, 14.0%; required for $Cu(C_{13}H_{10}ON)_2$: Cu, 13.9%)

Nickel salicylideneaniline was prepared similarly, but was not used for polarisation measurements on account of its limited solubility in benzene and dioxan. It formed a microcrystalline powder, which was too insoluble to be purified.

COPPER SALICYLIDENE-p-CHLORANILINE.

Copper salicylidene-*p*-chloraniline was prepared similarly. It was obtained as coppery-brown plates from benzene.

(Found : Cu, 12.0%; required for $Cu(C_{13}H_9ONCl)_2$: 12.1%)

COPPER SALICYLIDENE-p-BROMANILINE.

Copper salicylidene-*p*-bromaniline was prepared similarly. It was purified by precipitation from benzene solution with alcohol, forming dark golden-brown rhombic platelets.

(Found : Cu, 10.2%; required for $Cu(C_{13}H_9ONBr)_2$: Cu, 10.3%)

COPPER SALICYLIDENE-p-IODOANILINE.

Copper salicylidene-p-iodoaniline was prepared similarly. It was purified by precipitation from benzene solution with alcohol, forming shining copper-coloured platelets.

(Found : Cu 9.0%; required for $Cu(C_{13}H_9ONI)_2$: Cu 9.0%)

COPPER 1:3-DIPHENYL-3-HYDROXYTRIAZENE.

1:3-Diphenyl-3-hydroxytriazene was prepared by the method described by Bamberger and Rising (13). A solution of benzenediazonium chloride was added, at 0°, to a 10% alcoholic solution of phenylhydroxylamine, freshly prepared by the reduction of nitrobenzene with zinc and ammonium chloride. A pale yellow, crystalline precipitate separated at once, and was filtered off and used for the synthesis of the complexes without further purification. For the refractivity measurements, it was purified by recrystallisation from alcohol. The pure substance had m.p. 126-7°.

Bamberger and Rising give m.p. 126-7°.

Copper 1:3-diphenyl-3-hydroxytriazene was prepared by the same general method that was used for the complexes of the anils. It separated as deep red-brown needles, which were purified by precipitation from chloroform solution by petroleum ether, b.p. 80-100°. The pure substance had m.p. 191-2°.

Elkins and Hunter (14) give m.p. 190-2°.

NICKEL 1:3-DIPHENYL-3-HYDROXYTRIAZENE.

The nickel complex was obtained by the same method. It separated as a bright yellow powder, almost insoluble in benzene and dioxan, and therefore could not be used for polarisation measurements.

COPPER 1-HYDROXY-1-PHENYL-3-p-CHLORPHENYLTRIAZENE.

1-Hydroxy-1-phenyl-3-p-chlorphenyltriazene was prepared from phenyl#hydroxylamine and p-chloraniline by the method of Bamberger and Rising (loc. cit.). It separated as a buff-coloured powder, which formed lemon-yellow needles from alcohol, m.p. 154°, decomposing at the melting-point.

The copper complex was prepared by the same method used for the unsubstituted compound. It was obtained as fine, light-brown needles with a silvery lustre, m.p. 200°. It was too insoluble for measurements of polarisation.

Neither the triazene nor the copper complex have previously been described.

NICKEL α-BENZILDIOXIME.

α-Benzildioxime was prepared as described by Auwers and V.Meyer (15). A hot, concentrated alcoholic solution of benzil containing a trace of hydrochloric acid was treated with the theoretical quantity of powdered hydroxylamine hydrochloride. The mixture was boiled under reflux for two hours, during which time a heavy white crystalline precipitate appeared, which was filtered off. A little more hydroxylamine hydrochloride was added to the filtrate, and the digestion was repeated for a further two hours, at the end of which time, a further crop of the dioxime was obtained. The two portions were combined, and used without further purification.

The nickel complex of α-benzildioxime was prepared from the dioxime and nickel acetate in the theoretical proportions, which were boiled together in suspension in 50% aqueous alcohol, containing a little ammonia, for two hours. The complex separated as a bright orange-red amorphous powder, which was filtered, washed and dried, and freed from excess dioxime by washing with benzene.

COPPER α-BENZILDIOXIME.

Copper α-benzildioxime was prepared from α-benzildioxime and cupric acetate by the method used for the nickel complex, and was purified in the same way. It was obtained as a dark brown, crystalline powder.

The copper and the nickel complexes of α-benzildioxime were both too insoluble in benzene and dioxan for polarisation measurements to be made.

COPPER GLYCINE.

Copper glycine was prepared by adding freshly precipitated cupric hydroxide to a hot concentrated aqueous solution of glycine until no more of the hydroxide would dissolve. The hot solution was filtered, and allowed to cool; the complex crystallised out as brilliant blue leaflets. It was too insoluble for polarisation measurements to be made.

NICKEL o-AMINOPHENOL.

o-Aminophenol was prepared by the method of Galatis (16). o-Nitrophenol was powdered, and mixed to a paste with just sufficient sodium hydroxide solution to convert it to the sodium salt, and this was added gradually, with stirring, to an excess of molten sodium sulphide, in a porcelain dish. When the addition was complete, the melt was heated a little longer, and then poured into a large volume of water. The solution was filtered, and a rapid stream of carbon dioxide was passed through it to neutralise free alkali. The phenol began to separate after a time as small white crystals. A little sodium bisulphite was added to the solution as a precaution against oxidation. When no more *o*-aminophenol separated out, the crystals were filtered off, washed with water containing a little sodium bisulphite, and dried between filter-papers. The compound was used at once before oxidation could occur.

The nickel complex was precipitated as a grey-green powder when aqueous-alcoholic solutions of nickel acetate and o-aminophenol were warmed together.

COPPER o-AMINOPHENOL.

Copper *o*-aminophenol was obtained analogously from cupric acetate and the phenol. It was precipitated as a grey powder.

The nickel and copper complexes of *e*-aminophenol were both insufficiently soluble for polarisation measurements to be made.

COPPER N-NITROSOPHENYLHYDROXYLAMINE.

Copper *N*-nitrosophenylhydroxylamine was prepared by mixing aqueous solutions of cupric sulphate and "cupferron". It separated out as a very pale blue-grey powder, which was completely insoluble in benzene, but which dissolved in dioxan to the extent of about 16 g./litre, forming a bright blue solution. This marked difference in solubility indicated a possibility of interaction with the molecules of the solvent, and on this account, no measurements were carried out on this compound.

COPPER PHTHALIMIDE.

Copper phthalimide was prepared as described by Ley and Werner (17). An aqueous solution of cupric acetate (1 mol.) was added gradually to a solution of phthalimide (2 mols.) in the mimimum quantity of potassium hydroxide. A light blue, microcrystalline precipitate separated out, which was filtered off, washed with water and warm alcohol, and dried.

The compound was quite insoluble in both benzene and dioxan.

COPPER α-BENZOINOXIME.

α-Benzoinoxime was prepared as described by Vogel (18). An aqueous solution of hydroxylamine hydrochloride (1 mol.) was just neutralised with sodium hydroxide, and then boiled under reflux with an alcoholic solution of benzoin (1 mol.) for one hour. Addition of water to the solution precipitated the oxime, which crystallised on cooling in ice. It was used in the preparation of the copper complex without further purification.

Copper α-benzoinoxime was obtained as a finely crystalline, olive-green precipitate on the addition of a dilute, alcoholic solution of the oxime to an aqueous solution of cupric sulphate.

The solubility in benzene and dioxan was too low to allow polarisation measurements to be made.

NICKEL γ-BENZILDIOXIME.

γ-Benzildioxime was prepared by the method of Auwers and V. Meyer (19), from β-benzilmonoxime. This was prepared by the procedure described by Vogel (20). α-Benzilmonoxime was first prepared from benzil, by adding the theoretical quantity of hydroxylamine hydrochloride in concentrated aqueous solution to a paste of benzil with a little alcohol; sodium hydroxide solution was then added dropwise in slight excess, with rapid stirring and efficient cooling. After 1½ hours standing at 0°, the solution was diluted with water, and the unchanged benzil was removed by filtration. The filtrate was acidified with dilute acetic acid, and the crude α-benzilmonoxime was precipitated. It was filtered off, washed and dried, and dissolved in the minimum quantity of boiling benzene, and 10% of its weight of animal charcoal was added. After boiling under reflux for fifteen minutes, the solution was filtered and allowed to crystallise. β-Benzilmonoxime separated as colourless crystals.

β-Benzilmonoxime (1 mol.) was treated with a very large excess of sodium hydroxide (20 mols.) in aqueous solution, and hydroxylamine hydrochloride (6 mols.), and the mixture was allowed to stand for two days. It was then diluted with water, and acidified with very dilute hydrochloric acid, avoiding a large rise in temperature. A pale pink, crystalline precipitate separated, consisting mainly of γ-benzildioxime, together with much smaller quantities of α- and β-dioximes. α-Benzildioxime was removed by shaking the precipitate with ten times its weight of cold alcohol, in which the α-dioxime is almost completely insoluble. This alcoholic solution was used directly in the preparation of the nickel complex, since the presence of small quantities of the β-dioxime was immaterial, as this compound is not capable of forming a complex with nickel.

Nickel γ-benzildioxime was prepared as described by Atack (21). The alcoholic solution of the dioxime was added to excess of nickel chloride in aqueous solution, and the compound was precipitated, by the dropwise addition of ammonia, as a buff-coloured powder. It was crystallised from chloroform, and was obtained as dark brown crystals containing one molecule of chloroform of crystallisation, which was removed by heating the crystals at 120° for one hour.

The compound was slightly soluble in benzene, but not sufficiently for polarisation measurements to be made on the solutions : in dioxan the solubility was much higher, approximately 90 g./litre. On account of this large difference, it was concluded that association occurred in dioxan solutions; no measurements were therefore made on this compound.

COPPER MONOSALICYLALDOXIME.

Copper monosalicylaldoxime was prepared as described by Feigl and Bondi (22). Copper disalicylaldoxime was warmed with a large excess of sodium hydroxide in 50% aqueous alcohol, and the mixture was allowed to stand overnight. Copper monosalicylaldoxime was obtained as a finely-divided, deep blue-green powder, which was filtered off, washed with water and alcohol, and dried.

Copper monosalicylaldoxime was found to be too insoluble in benzene and dioxan for polarisation measurements to be made.

NICKEL MONOSALICYLALDOXIME.

An attempt was made to prepare nickel monosalicylaldoxime, which has not been previously described, by an analogous procedure. A finely-divided, brown powder was obtained, which, although it was stable to strong alkalis, was very rapidly decomposed by acids or by water, with formation of the disalicylaldoxime complex. It could not be obtained pure.

ALUMINIUM DIETHYL MALONATE.

Aluminium diethyl malonate was prepared by the method of Titschenko (23). Aluminum powder (1 mol.) and diethyl malonate (3 mols.) were heated together with a trace of mercuric chloride in xylene solution for six hours. At the end of this time, the liquid had turned yellow-green, with a strong peacock-blue fluorescence. The undissolved aluminium was filtered off, and the xylene was distilled off until a temperature of 150° was reached. On cooling, a sticky mass of fine, greenish-white needles was formed.

The complex could not be recrystallised in the ordinary way on account of its exceptionally high solubility in all solvents. It was recrystallised several times by dissolving it in dry ether, boiling for ten minutes with active charcoal, filtering, and then concentrating the solution by passing dry air over it until a thick mass of crystals had formed in the remaining ether. These were then filtered off. The complex was obtained pure in this way as long white needles, highly soluble in all solvents except light petroleum, in which it was quite insoluble, and rapidly decomposed by water; m.p. 95°.

Titschenko gives m.p. 94-5°.

CALCIUM DIETHYL MALONATE.

Several attempts were made to prepare the calcium complex of diethyl malonate, as described by Erdmann and van der Smissen (24). Calcium turnings were heated with an excess of diethyl malonate at the boiling-point for several hours. Some hydrogen was evolved, and an orange solution was produced which showed an intense blue-green fluorescence, closely resembling that which appeared during the preparation of the aluminium complex. The addition of ether or light petroleum to this solution precipitated an amorphous yellow powder, which could not be crystallised on account of its extremely high solubility in all organic solvents except ether or light petroleum, in which it was quite insoluble. This substance resembled that described by Erdmann and van der Smissen, but it was found on analysis that the calcium content was lower than that required by theory, whereas they obtained a higher value.

Required for $Ca(C_7H_{11}O_4)_2$: Ca 11.2, C 46.9, H 6.19 %.

Found : Ca 9.3, C 46.7, H 5.14 %.

Found by Erdmann and van der Smissen: Ca 13.8%.

The orange solution obtained from a second preparation was concentrated by distillation under reduced pressure, as it was found that the temperature reached during distillation at atmospheric pressure was sufficient to decompose the complex. This procedure gave a thick, syrupy solution, which could not be made to crystallise. Removal of all the diethyl malonate gave a hard, yellow glassy mass, which was found to resemble the first product in its extreme solubility, and in being readily decomposed by water, but it was very soluble in ether. It was quite insoluble, however, in light petroleum, and the addition of light petroleum to the ether solution precipitated an ether-insoluble powder, resembling the first product in appearance. The ether-soluble product was found to contain a higher proportion of calcium than the other, but the proportion was still lower than the theoretical figure.

(Found: Ca 10.2, C 47.5, H 5.70%.)

The investigation was not continued.

Section 2.

Tables of Experimental Results.

Table No.	Compound.	Solvent.
1.	Aluminium acetylacetonate.	Benzene.
2.	Aluminium acetylacetonate (Series I).	Dioxan.
3.	Aluminium acetylacetonate (Series II).	Dioxan.
4.	Ferric acetylacetonate.	Benzene.
5.	Ferric acetylacetonate.	Dioxan.
6.	Ferric dibenzoylmethane.	Benzene.
7.	Ferric dibenzoylmethane.	Dioxan.
8.	Beryllium dibenzoylmethane.	Benzene.
9.	Beryllium dibenzoylmethane.	Dioxan.
10.	Copper 1:3-diphenyl-3-hydroxytriazene.	Dioxan.
11.	Copper salicylaldehyde.	Dioxan.
12.	Copper salicylidenemethylimine.	Dioxan.
13.	Copper salicylideneaniline (Series I).	Dioxan.
14.	Copper salicylideneaniline (Series II).	Dioxan.
15.	Copper salicylidene-p-chloraniline.	Dioxan.
16.	Copper salicylidene-p-bromaniline.	Dioxan.
17.	Copper salicylidene-p-iodoaniline.	Dioxan.
18.	Copper salicylaldoxime.	Dioxan.
19.	Nickel salicylaldoxime.	Dioxan.
20.	Nickel benzeneazo-p-cresol.	Benzene.
21.	Nickel benzeneazo-2-pyrrole.	Benzene.
22.	Aluminium diethyl malonate.	Benzene.
23.	Refractivity of 1:3-diphenyl-3-hydroxytriazene.	Dioxan.

1. Aluminium acetylacetonate in benzene.

$100\,w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2725	1.14479	1.4977	2.2431
0.6028	2.2777	1.14291	1.4980	2.2440
1.3448	2.2840	1.14056	1.4983	2.2449
1.9036	2.2890	1.13895	1.4986	2.2458
2.7889	2.2962	1.13618	1.4990	2.2470
3.4396	2.3018	1.13412	1.4993	2.2479
4.9313	2.3157	1.12957	1.5000	2.2500

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
0.86	0.312	0.149	132.9	88.3
0.854	0.315	0.134	132.0	87.1
0.867	0.307	0.142	133.3	88.3
0.849	0.309	0.140	131.9	88.0
0.851	0.310	0.140	131.7	87.8
0.876	0.309	0.140	133.0	88.0

$\alpha = 0.861$; $\beta = -0.3098$; $\gamma = 0.140$.

$P_{2_\infty} = 133.2$ c.c.; $[R_D] = 88.0$ c.c.

$P_A = 45.2$ c.c.

2. Aluminium acetylacetonate in dioxan (Series I).

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2123	0.97312	1.4200	2.0164
0.7470	2.2203	0.97225	1.4208	2.0187
1.5269	2.2281	0.97132	1.4217	2.0212
2.1998	2.2365	0.97034	1.4224	2.0232
2.8771	2.2436	0.96954	1.4232	2.0255
3.4787	2.2515	0.96887	1.4239	2.0275
5.6832	2.2754	0.96614	1.4264	2.0346

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.08	0.117	0.308	136.9	88.4
1.03	0.118	0.314	136.1	88.6
1.10	0.126	0.309	137.3	87.6
1.09	0.124	0.316	136.6	88.1
1.13	0.122	0.319	138.7	88.4
1.11	0.123	0.320	137.3	88.4

$\alpha = 1.100$; $\beta = -0.1227$; $\gamma = 0.317$.

$P_{2_\infty} = 138.1$ c.c.; $[R_D] = 88.4$ c.c.

$P_A = 49.7$ c.c.

3. Aluminium acetylacetonate in dioxan (Series II).

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2086	0.97292	1.4198	2.0158
0.5235	2.2146	0.97231	1.4203	2.0173
1.1188	2.2209	0.97190	1.4209	2.0189
1.4906	2.2258	0.97122	1.4214	2.0204
2.5070	2.2367	0.96990	1.4226	2.0238
3.4811	2.2478	0.96865	1.4238	2.0272
3.6839	2.2504	0.96848	1.4239	2.0275

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
–	–	–	–	–
1.15	0.117	0.29	140.9	87.1
1.10	(0.091)	0.28	140.6	88.6
1.15	0.114	0.31	141.3	88.5
1.12	0.120	0.32	138.7	88.6
1.13	0.123	0.327	138.5	88.8
1.13	0.120	0.318	139.1	88.4

$\alpha = 1.121$; $\beta = -0.1201$; $\gamma = 0.315$.

$P_{2_\infty} = 139.3$ c.c.; $[R_D] = 88.4$ c.c.

$P_A = 50.9$ c.c.

4. Ferric acetylacetonate in benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2725	1.14468	1.4980	2.2440
0.7485	2.2805	1.14202	1.4987	2.2461
1.6940	2.2902	1.13832	1.4996	2.2488
3.2196	2.3064	1.13252	1.5010	2.2530
3.6454	2.3112	1.13099	1.5014	2.2542
4.2257	2.3172	1.12913	-	-
4.9819	2.3248	1.12608	-	-

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.07	0.355	0.28	153.7	100.6
1.04	0.375	0.28	149.7	98.6
1.05	0.378	0.28	149.3	98.0
1.06	0.376	0.28	150.0	98.7
1.06	0.368	-	150.3	-
1.05	0.373	-	148.9	-

$\alpha = 1.056$; $\beta = -0.3727$; $\gamma = 0.281$.

$P_{2\infty} = 151.4$ c.c.; $[R_D] = 98.8$ c.c.

$P_A = 52.6$ c.c.

5. Ferric acetylacetonate in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2371	0.97402	1.4195	2.0150
1.1608	2.2526	0.97187	1.4213	2.0201
2.2020	2.2666	0.96982	1.4230	2.0249
2.9560	2.2762	0.96846	1.4241	2.0281
4.1337	2.2924	0.96605	1.4260	2.0335
4.8929	2.3026	0.96473	1.4272	2.0369
6.0658	2.3190	0.96250	1.4291	2.0423

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.33	0.185	0.45	157.6	98.8
1.34	0.191	0.45	156.9	98.5
1.32	0.188	0.44	155.9	98.5
1.34	0.193	0.448	155.8	98.0
1.34	0.190	0.448	155.9	98.2
1.35	0.190	0.450	156.1	98.3

$\alpha = 1.337$; $\beta = -0.1900$; $\gamma = 0.448$.

$P_{2_\infty} = 157.7$ c.c.; $[R_D] = 98.7$ c.c.

$P_A = 59.0$ c.c.

6. Ferric dibenzoylmethane in benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2725	1.14477	1.4980	2.2440
0.2230	2.2752	1.14389	1.4983	2.2449
0.3750	2.2764	1.14333	1.4985	2.2455
0.5158	2.2781	1.14280	1.4988	2.2464
0.7420	2.2810	1.14182	1.4993	2.2479
0.8507	2.2819	1.14147	1.4994	2.2482
1.1339	2.2857	1.14048	1.5000	2.2500

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.22	0.395	0.40	327.1	231.3
1.03	0.384	0.40	306.0	217.0
1.07	0.382	0.46	312.5	226.4
1.14	0.398	0.53	317.1	231.3
1.10	0.388	0.49	313.6	229.0
1.16	0.378	0.53	323.4	235.8

$\alpha = 1.12$; $\beta = -0.386$; $\gamma = 0.468$.

$P_{2_\infty} = 317.5$ c.c.; $[R_D] = 226.1$ c.c.

$P_A = 91.4$ c.c.

7. Ferric dibenzoylmethane in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2158	0.97338	1.4198	2.0158
0.1602	2.2179	0.97308	1.4202	2.0170
0.2680	2.2198	0.97288	1.4205	2.0178
0.4586	2.2224	0.97253	1.4210	2.0192
0.6242	2.2245	0.97220	1.4214	2.0204
0.7695	2.2271	0.97197	1.4218	2.0215
0.8731	2.2284	0.97173	1.4221	2.0224

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.31	0.187	0.75	321.0	243.0
1.49	0.187	0.75	342.3	242.3
1.44	0.185	0.74	336.1	241.9
1.39	0.189	0.74	329.8	240.6
1.47	0.183	0.74	339.8	242.1
1.44	0.189	0.76	335.4	243.0

$\alpha = 1.44$; $\beta = -0.1868$; $\gamma = 0.745$.

$P_{2_\infty} = 336.3$ c.c.; $[R_D] = 242.2$ c.c.

$P_A = 941$ c.c.

8. Beryllium dibenzoylmethane in benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2725	1.14479	1.4980	2.2440
0.4663	2.2765	1.14319	1.4989	2.2467
1.0531	2.2818	1.14119	1.5000	2.2500
1.6171	2.2873	1.13925	1.5010	2.2530
2.3078	2.2928	1.13690	1.5022	2.2566
2.7216	2.2968	1.13554	1.5029	2.2587
4.4103	2.3128	1.12959	1.5069	2.2707

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
0.86	0.343	0.58	181.4	156.5
0.89	0.342	0.57	183.4	155.8
0.915	0.343	0.56	185.8	154.5
0.878	0.342	0.55	182.6	153.5
0.892	0.340	0.540	183.9	153.2
0.913	0.345	0.605	184.3	157.7

$\alpha = 0.891$; $\beta = -0.3426$; $\gamma = 0.564$

$P_{2_\infty} = 185.1$ c.c.; $[R_D] = 156.0$ c.c.

$P_A = 29.1$ c.c.

9. Beryllium dibenzoylmethane in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2243	0.97356	1.4198	2.0158
0.3748	2.2284	0.97298	1.4208	2.0186
0.7977	2.2335	0.97229	1.4220	2.0221
0.9941	2.2350	0.97203	1.4226	2.0238
1.5394	2.2418	0.97119	1.4240	2.0278
2.0366	2.2477	0.97024	1.4256	2.0323
3.0400	2.2590	0.96871	1.4283	2.0400

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.09	0.155	0.75	189.4	155.8
1.15	0.159	0.79	192.2	158.7
1.08	0.154	0.80	187.6	160.6
1.14	0.154	0.78	192.3	158.3
1.15	0.163	0.710	191.8	159.6
1.14	0.160	0.796	191.3	158.6

$\alpha = 1.13$; $\beta = -0.1585$; $\gamma = 0.795$.

$P_{2_\infty} = 192.0$ c.c.; $[R_D] = 159.4$ c.c.

$P_A = 32.6$ c.c.

10. Copper 1:3-diphenyl-3-hydroxytriazene in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2120	0.97323	1.4200	2.0164
0.4551	2.2159	0.97222	1.4213	2.0201
0.9841	2.2205	0.97064	1.4225	2.0235
1.3678	2.2239	0.96953	1.4238	2.0272
1.8406	2.2272	0.96831	1.4248	2.0301
2.1956	2.2308	0.96642	1.4259	2.0332
2.6621	2.2354	0.96626	-	-

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
0.85	0.222	0.81	174.2	164.5
0.86	0.263	0.72	168.8	151.1
0.870	0.270	0.79	168.1	156.1
0.826	0.267	0.742	164.9	152.4
0.854	0.310	0.765	161.9	148.7
0.878	0.262	-	169.6	-

$\alpha = 0.850$; $\beta = -0.2700$; $\gamma = 0.770$.

$P_{2_\infty} = 167.0$ c.c.; $[R_D] = 154.9$ c.c.

$P_A = 121$ c.c.

11. Copper salicylaldehyde in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2098	0.97290	1.4200	2.0164
0.1407	2.2122	0.97237	1.4203	2.0173
0.2027	2.2138	0.97214	1.4205	2.0178
0.3662	2.2167	0.97162	1.4208	2.0187
0.4559	2.2191	0.97126	1.4210	2.0192
0.5847	2.2217	0.97081	1.4212	2.0198
0.6643	2.2230	0.97054	1.4215	2.0207

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.73	0.377	0.64	140.5	81.6
1.98	0.375	0.69	151.7	84.7
1.88	0.350	0.63	149.4	83.0
2.04	0.360	0.61	156.2	81.4
2.03	0.357	0.58	156.1	79.7
1.99	0.355	0.65	153.8	83.5

$\alpha = 1.98$; $\beta = -0.3587$; $\gamma = 0.625$.

$P_{2_\infty} = 153.7$ c.c.; $[R_D] = 82.1$ c.c.

$P_A = 71.6$ c.c.

12. Copper salicylidenemethylimine in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2115	0.97306	1.4200	2.0164
0.3761	2.2174	0.97197	1.4207	2.0184
0.6601	2.2257	0.97129	1.4212	2.0198
0.9913	2.2268	0.97031	1.4219	2.0218
1.4145	2.2333	0.96916	1.4227	2.0241
1.9027	2.2415	0.96790	1.4237	2.0269
2.2312	2.2465	0.96703	1.4243	2.0280

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.56	0.290	0.53	151.9	89.8
(2.15)	0.268	0.52	(185.3)	90.6
1.55	0.277	0.54	151.1	91.5
1.54	0.276	0.54	150.9	91.6
1.57	0.271	0.55	153.0	92.4
1.57	0.270	0.53	152.5	90.5

$\alpha = 1.562$; $\beta = -0.2732$; $\gamma = 0.534$.

$P_{2\infty} = 153.0$ c.c.; $[R_D] = 91.4$ c.c.

$P_A = 61.6$ c.c.

13. Copper salicylideneaniline in dioxan (Series I).

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2147	0.97315	1.4200	2.0164
0.2776	2.2214	0.97244	1.4206	2.0181
0.6530	2.2299	0.97145	1.4216	2.0209
0.7566	2.2322	0.97118	1.4219	2.0218
1.2924	2.2447	0.96977	1.4230	2.0249
1.4429	2.2484	0.96939	1.4234	2.0261
2.1199	2.2633	0.96776	1.4248	2.0301

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
2.41	0.256	0.61	274.7	133.2
2.33	0.260	0.69	267.2	139.0
2.31	0.260	0.71	266.0	140.9
2.32	0.261	0.66	265.7	136.1
2.34	0.261	0.67	269.8	137.4
2.29	0.254	0.62	263.4	135.8

$\alpha = 2.319$; $\beta = -0.2585$; $\gamma = 0.678$.

$P_{2\infty}$ = 267.7 c.c.; $[R_D]$ = 138.4 c.c.

P_A = 129.3 c.c.

14. Copper salicylideneaniline in dioxan (Series II).

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2147	0.97330	1.4198	2.0158
0.3413	2.2223	0.97246	1.4206	2.0181
0.7889	2.2326	0.97130	1.4217	2.0212
0.9757	2.2367	0.97083	1.4221	2.0224
1.6362	2.2517	0.96920	1.4236	2.0266
1.7557	2.2547	0.96877	1.4240	2.0278
2.7109	2.2764	0.96654	1.4261	2.0338

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
2.23	0.246	0.67	262.0	139.4
2.27	0.253	0.68	263.6	139.4
2.25	0.253	0.68	262.4	138.7
2.26	0.251	0.66	262.3	137.5
2.28	0.258	0.68	262.4	138.5
2.28	0.249	0.66	262.1	137.7

$\alpha = 2.260$; $\beta = -0.2522$; $\gamma = 0.671$.

$P_{2_\infty} = 264.2$ c.c.; $[R_D] = 138.6$ c.c.

$P_A = 125.6$ c.c.

15. Copper salicylidene-p-chloraniline in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2338	0.97355	1.4200	2.0164
0.3603	2.2380	0.97254	1.4207	2.0184
0.7397	2.2433	0.97146	1.4215	2.0207
1.0256	2.2461	0.97050	1.4221	2.0224
1.4306	2.2507	0.96915	1.4231	2.0252
1.4434	2.2520	0.96877	1.4238	2.0272
2.6154	2.2646	0.96577	1.4258	2.0329

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.19	0.280	0.56	204.3	144.8
1.28	0.282	0.58	215.1	146.8
1.20	0.297	0.59	205.4	145.1
1.18	0.308	0.62	202.0	146.5
1.26	0.331	(0.74)	205.1	(155.9)
1.18	0.298	0.63	202.6	146.5

$\alpha = 1.18$; $\beta = -0.2970$; $\gamma = 0.590$.

$P_{2_\infty} = 204.4$ c.c.; $[R_D] = 145.9$ c.c.

$P_A = 58.5$ c.c.

16. Copper salicylidene-p-bromaniline in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2071	0.97300	1.4200	2.0164
0.2583	2.2098	0.97198	1.4205	2.0178
0.7334	2.2146	0.97012	1.4214	2.0204
0.9616	2.2164	0.96928	1.4220	2.0221
1.1346	2.2176	0.96906	1.4223	2.0229
1.4042	2.2203	0.96826	1.4228	2.0243
1.9740	2.2265	0.96536	-	-

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.06	0.395	0.54	207.8	149.9
1.02	0.393	0.55	205.8	150.5
0.97	0.387	0.59	201.2	156.5
0.92	0.347	0.57	207.3	160.4
0.94	0.338	0.56	202.1	152.9
0.98	0.387	-	204.9	-

$\alpha = 0.994$; $\beta = -0.390$; $\gamma = 0.563$.

$P_{2\infty}$ = 203.4 c.c.; $[R_D]$ = 153.1 c.c.

P_A = 50.3 c.c.

17. Copper salicylidene-p-iodoaniline in dioxan.

$100w_{12}$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2174	0.97294	1.4200	2.0164
0.2139	2.2192	0.97208	1.4204	2.0175
0.4966	2.2213	0.97090	1.4210	2.0192
0.6636	2.2242	0.97006	1.4212	2.0201
1.1542	2.2291	0.96795	1.4222	2.0227
1.1890	2.2291	0.96793	1.4223	2.0229
1.4630	2.2315	0.96668	1.4230	2.0249

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
0.84	0.402	0.51	214.3	168.0
0.79	0.411	0.56	205.8	172.7
1.02	0.434	0.56	227.9	167.6
1.01	0.432	0.55	227.3	166.9
0.98	0.421	0.55	226.1	168.3
0.96	0.428	0.58	222.2	171.4

$\alpha = 0.965$; β -0.429; $\gamma = 0.552$.

$P_{2_\infty} = 222.2$ c.c.; $[R_D] = 168.1$ c.c.

$P_A = 54.1$ c.c.

18. Copper salicylaldoxime in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2097	0.97281	1.4200	2.0164
0.3091	2.2124	0.97177	1.4204	2.0175
0.4879	2.2141	0.97105	1.4206	2.0181
0.7585	2.2159	0.97021	1.4212	2.0198
1.0394	2.2182	0.96903	1.4218	2.0215
1.2677	2.2209	0.96848	1.4220	2.0221

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
0.87	0.336	0.37	109.6	75.6
0.90	0.361	0.35	108.8	73.1
0.82	0.343	0.45	103.7	81.4
0.82	0.364	0.49	106.1	80.7
0.88	0.342	0.45	109.4	80.8

α = 0.854; β = -0.350; γ = 0.441.

P_{2_∞} = 107.4 c.c.; $[R_D]$ = 79.7 c.c.

P_A = 27.7 c.c.

19. Nickel salicylaldoxime in dioxan.

$100w_2$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2071	0.97302	1.4204	2.0156
0.1866	2.2092	0.97217	1.4207	2.0184
0.3459	2.2110	0.97139	1.4210	2.0192
0.5057	2.2129	0.97115	1.4212	2.0198
0.6561	2.2144	0.97057	1.4214	2.0204

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
1.13	0.456	0.43	109.7	68.6
1.13	0.471	0.46	108.2	69.3
1.15	0.370	0.44	118.9	76.1
1.11	0.373	0.43	116.6	75.3

$\alpha = 1.127$; $\beta = -0.401$; $\gamma = 0.437$.

$P_{2_\infty} = 115.1$ c.c.; $[R_D] = 73.6$ c.c.

$P_A = 41.5$ c.c.

20. Nickel benzeneazo-p-cresol in benzene.

$100w_2$	ϵ_{12}	v_{12}
0	2.2725	1.14479
0.5086	2.2771	1.14258
1.0128	2.2810	1.14056
1.4821	2.2853	1.13860
2.0250	2.2903	1.13620
2.2213	2.2923	1.13570

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	P_2
-	-	-
0.90	0.434	174.2
0.86	0.418	170.7
0.88	0.418	172.6
0.88	0.424	172.8
0.89	0.409	175.4

Owing to the intense colour of the solutions, no refractive indices were measured.

$\alpha = 0.879$; $\beta = -0.4176$.

$P_{2_\infty} = 174.6$ c.c.

21. Nickel benzeneazo-2-pyrrole in benzene.

$100w_2$	ϵ_{12}	v_{12}
0	2.2725	1.14484
0.2756	2.2754	1.14354
0.5914	2.2772	1.14199
0.9517	2.2804	1.14000
1.2320	2.2820	1.13905
1.6891	2.2857	1.13635

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	P_2
-	-	-
(1.04)	0.472	(158.9)
0.80	0.482	138.3
0.83	0.509	137.6
0.77	0.470	137.9
0.78	0.503	134.4

Owing to the intense colour of the solutions, no refractive indices were measured.

$\alpha = 0.791$; $\beta = -0.4909$.

$P_{2\infty} = 137.1$ c.c.

22. Aluminium diethyl malonate in benzene.

$100w_{12}$	ϵ_{12}	v_{12}	n_D	n_D^2
0	2.2725	1.14500	1.4982	2.2446
0.8741	2.2794	1.14206	1.4980	2.2440
1.5905	2.2841	1.14032	1.4978	2.2434
1.9940	2.2878	1.13929	1.4977	2.2431
2.5179	2.2908	1.13773	1.4977	2.2431
3.0793	2.2962	1.13622	1.4977	2.2431

$\Delta\epsilon_{12}/w_2$	$-\Delta v_{12}/w_2$	$-\Delta n_D^2/w_2$	P_2	$[R_D]$
-	-	-	-	-
0.78	0.291	0.07	202.5	113.0
0.73	0.294	0.07	196.4	118.6
0.77	0.289	0.07	201.2	121.0
0.73	0.285	0.06	196.9	116.6
0.77	0.286	0.05	201.4	119.9

$$\alpha = 0.754; \quad \beta = -0.2882; \quad \gamma = -0.066.$$

$$P_{2\infty} = 200.3 \text{ c.c.}; \quad [R_D] = 120.4 \text{ c.c.}$$

$$P_A = 79.9 \text{ c.c.}$$

23. Refractivity of 1:3-diphenyl-3-hydroxytriazene in dioxan.

$100w_2$	v_{12}	n_D	n_D^2
0	0.97408	1.4197	2.0155
0.7813	0.97294	1.4217	2.0212
1.5380	0.97179	1.4237	2.0269
2.3475	0.97063	1.4258	2.0329
3.0544	0.96956	1.4277	2.0383
3.6023	0.96872	1.4291	2.0423
4.2263	0.96784	1.4309	2.0469

$-\Delta v_{12}/w_2$	$\Delta n_D^2/w_2$	$[R_D]$
-	-	-
0.147	0.73	72.92
0.149	0.741	72.99
0.147	0.741	73.02
0.148	0.746	73.10
0.149	0.744	72.91
0.148	0.743	72.87

$\beta = -0.1483$; $\gamma = 0.743$.

$[R_D] = 73.25$ c.c.

CHAPTER III.

DISCUSSION OF RESULTS.

Section 1. Evaluation of Electronic Polarisations.

The intense colour of the solutions yielded by many of the compounds studied, which necessitated the use of very dilute solutions, led to considerable possible errors in the refractivity measurements, and, in view of this, an attempt was made to check the experimental figures by calculating $[R_D]$ from the appropriate bond refractions. These calculations were, however, complicated by the fact that, in every case, the molecule of the organic compound entering into the formation of a complex contained a system of the conjugated single and double bonds. The presence of such a system in the molecule leads to an enhancement of the molecular refraction by an amount which is difficult to predict : in the case of salicylaldehyde, the difference between the observed value found by Curran (1) and that calculated from the bond refractions given by Vogel and his co-workers (2) is about 2 c.c., while for 1:3-diphenyl-3-hydroxytriazene, the discrepancy is about 10 c.c. As both these compounds are colourless, the differences cannot be caused by dispersion effects.

The value of the molecular refraction of pure salicylaldehyde obtained by Curran was used to calculate the molecular refractions of salicylaldoxime and salicylidenemethylimine, which possess similar conjugating systems, and de Gaouck and Le Fèvre's value for the molecular refraction of salicylideneaniline in benzene (3) was used to calculate the molecular refractions of the substituted anils. The refractivity of 1:3-diphenyl-3-hydroxytriazene was measured directly in solution in dioxan, since this was the solvent in which polarisation measurements were made on the complex.

No figures are available which indicate the contribution to the molecular refraction made by the four bonds to the central metal atom. In order to check the experimental figures, therefore, this contribution was calculated for each of the copper complexes. The results are given in Table I, together with Finn, Hampson and Sutton's results from measurements on two solutions of copper acetylacetonate in chloroform solution (4), the $[R_D]$ of acetylacetone being calculated from refractive index and density data given in the "International Critical Tables".

Table I.

Complex-forming compound.	Experimental $[R_D]$ of complex.	$[R_D]$ of complex-forming compounds	Contribution of 4 bonds to copper atom.
1:3-diphenyl-3-hydroxy-triazene.	154.9 c.c.	72.2 c.c.	13.8 c.c.
Salicylideneaniline.	138.5	66.4	9.1
Salicylidene-p-chloraniline.	145.9	71.2	6.9
Salicylidene-p-bromaniline.	153.1	74.1	8.3
Salicylidene-p-iodoaniline.	168.1	79.3	12.9
Salicylidenemethylimine.	91.4	41.5	11.9
Salicylaldehyde.	82.1	34.4	16.6
Salicylaldoxime.	79.7	38.9	3.2
Acetylacetone.	65.7	27.5	14.1

The variations in the values for the contribution to the molecular refraction of the four bonds to the copper atom are far outside the experimental error involved in the measurements. All the compounds mentioned in Table I are extremely intensely coloured, forming solutions which are either dark brown or dark green in colour. The wide variations are evidently due to the fact that refractive indices have anomalous values when the measurements are made in or near an absorption band, and normal methods of measuring $[R_D]$ are therefore not applicable in these cases. Accordingly, values of $[R_D]$ have been calculated for these complexes, using for the contribution made by the bonds to a copper atom the approximately median value of 12 c.c. The corresponding contribution made by four bonds to a nickel atom has been assumed to be of the same magnitude, since the nickel atom possesses only one less electron than the copper atom; and bonds between a metal atom and either an oxygen or a nitrogen atom have been assumed to make equal contributions. The value of 70.0 c.c. for the molecular refraction of benzeneazo-p-cresol has been calculated from de Gaouck and Le Fèvre's results for salicylidene-aniline, since the two compounds have closely similar systems of conjugated bonds in their molecules; benzeneazo-p-cresol itself is too highly coloured to give a satisfactory value by direct measurement. A much higher figure, 87.4 c.c., is obtained if the molecular refraction is calculated from Bergmann and Weizmann's measurements on p-methoxyazobenzene (5); this is obviously in error as the molecular refraction of the complex, calculated on this basis, is considerably greater than the measured value of the molecular polarisation. The error is probably due to the deep orange-red colour of the solutions of the azo-compound.

The molecular refraction of benzeneazo-2-pyrrole has been calculated from that of salicylideneaniline, using Cowley and Partington's value for the molecular refraction of pyrrole (6). This gives a value of 55.4 c.c. for the molecular refraction of the azo-compound; however, this includes no correction for the change in the number of bonds in the conjugated system. By analogy with salicylaldehyde, this correction will probably be rather less than 2 c.c., and a value of 1.5 c.c. has been assumed.

These results have been used in the compilation of the following table.

Table II.

Summary of results.

Compound.	$P_{2\infty}$	$[R_D]$.	P_A.
Aluminium acetylacetonate.	133.2 c.c.	88.0 c.c.	45.2 c.c.
Ferric acetylacetonate.	151.4	98.8	52.6
Ferric dibenzoylmethane.	317.5	226.1	91.4
Beryllium dibenzoylmethane.	185.1	156.0	29.1
Copper 1:3-diphenyl-3-hydroxytriazene.	167.0	153.0	14.0
Copper salicylaldehyde.	153.7	86.4	67.3
Copper salicylidenemethylimine.	153.0	91.6	61.4
Copper salicylideneaniline.	265.9	141.4	124.5
Copper salicylidene-p-chloraniline.	204.4	151.0	53.4
Copper salicylidene-p-bromaniline.	203.4	156.8	46.6
Copper salicylidene-p-iodoaniline.	222.2	169.2	53.0
Copper salicylaldoxime.	107.4	86.4	21.0

Nickel salicylaldoxime.	115.1	86.4	28.7
Nickel-benzeneazo-p-cresol.	174.6	148.6	26.0
Nickel benzeneazo-2-pyrrole.	137.1	116.4	20.7
Aluminium diethyl malonate.	200.3	120.4	79.9

Section 2. Theory of Atomic Polarisation.

It has been shown (7), both by classical methods and on the basis of the quantum theory, that the refractive index of a substance varies with the frequency according to a relationship of the Sellmeier type, which may be written in the form :

$$n^2 - 1 = \frac{N\,d}{M} \sum_e \left[\frac{e_{ei}^{\,2}}{m_{ei}\,\pi\,(\nu_i^{\,2} - \nu^2)} \right] + \sum_v \left[\frac{e_{ei}^{\,2}}{3\pi m_{ei}\,(\nu_i^{\,2} - \nu^2)} \right]$$

where n is the refractive index at frequency ν, the natural frequencies, electronic and vibrational, associated with the molecule, being represented by the terms ν_i, whilst e_{ei} and m_{ei} are, respectively, the effective charge and the effective mass of the vibrating system for a particular freauency ν_i, whilst e_{ei} and m_{ei} are, respectively, the effective charge and the effective mass of the vibrating system for a particular frequency ν_i. In this equation, the term Nd/M gives the number of molecules per unit volume of the refracting material. The first summation term represents the contributions from the electronic vibrations, and the second the molecular vibrational terms. In the first, three-dimensional vibrators are concerned, but in the second, the vibrators are one-dimensional; this accounts for the inclusion of the factor 3 in the denominator of the second term.

At optical wavelengths, ν is much larger than ν_i for a vibrational frequency, as these occur in the infra-red region of the spectrum, and the contribution made to $n^2 - 1$ by the vibrational frequency thus approximates to $-Nde_{ei}{}^2/3\pi Mm_{ei}\nu^2$. Since for these vibrations m_{ei} is large relative to the corresponding value for the electron, this term is negligible compared with the electronic terms at these wavelengths.

But
$$P_E + P_A = \frac{n^2 - 1}{3} \cdot \frac{M}{d}$$
$$= \left[\frac{n_e{}^2 - 1}{3} + \sum \frac{n_{vi}{}^2}{3}\right]\frac{M}{d},$$

where n is the refractive index at infra-red frequencies, n_e the refractive index at infinite wavelength, calculated from the Sellmeier equation, omitting infra-red terms, and $n_{vi}{}^2$ is the contribution made to $n^2 - 1$ by a particular vibrational term. Then

$$P_E + P_A = P_E + \sum \frac{n_{vi}{}^2 M}{3d},$$

and therefore
$$P_{A_i} = \frac{n_{vi}{}^2 M}{3d} = \frac{Nde_{ei}{}^2}{3\pi Mm_{ei}\nu_i{}^2} \cdot \frac{M}{3d} = \frac{Ne_{ei}{}^2}{9\pi m_{ei}\nu_i{}^2} \quad . \quad . \quad 1.$$

where P_{A_i} is the contribution made by this vibration to the atomic polarisation.

Now if the restoring force of the vibration in question obeys Hooke's Law, and is proportional to the displacement from the equilibrium position, i.e., if the vibration is harmonic, then for an independent linear oscillator, ν_i may be expressed as follows:

$$\nu_i = \frac{1}{2\pi}\sqrt{\frac{k_i}{m_{ei}}}$$

where k_i is the force constant for the vibration, that is, the proportionality constant relating the restoring force of the vibrating system to its displacement.

It follows, then, that

$$m_{ei}\nu_i^{\,2} = \frac{k_i}{4\pi^2},$$

whence, substituting in equation (1), we have

$$P_{A_i} = \frac{4\pi N e_{ei}^{\,2}}{9k_i}.$$

It has been pointed out by Van Vleck that for linear, or stretching, vibrations, even if e_{ei} is equivalent to a full electron charge, the force constant is so large that the contribution to the atomic polarisation from vibrations of this kind cannot be more than 0.5 c.c. per vibrational mode, at the most. The unusually high values of the atomic polarisation which have been observed must therefore be due almost entirely to the bending vibrations of the molecule, for which the force constants are much smaller.

Now the energy, u, of a harmonic oscillator is given by the expression

$$u = \tfrac{1}{2}\,k_i x^2,$$

x representing the amplitude of the vibration. For a bending vibration of small angular amplitude ψ, x may be replaced by r , where r is the effective length of the vibrator. Then

$$u = \tfrac{1}{2}\,k_i r^2 \psi^2 \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

If a bending force constant, V_i, is chosen, such that

$$u = \tfrac{1}{2}\,V_i \psi^2,$$

then, from equation (2),

$$V_i = k_i r^2,$$

and the contribution to the atomic polarisation is therefore

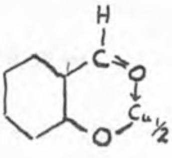
$$P_{A_i} = \frac{4\pi N e_{ei}^2 r^2}{9V_i}$$

But $e_{ei}r$ is equal to the dipole moment of the vibrating system, μ, so that

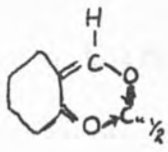
$$P_{A_i} = \frac{4\pi N \mu^2}{9V_i} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus, if the atomic polarisation of a molecule is known, and if it may be attributed entirely to one particular vibration or to several equal and independent vibrations of the same type, and if the group moment of the vibrating system is known, or may be estimated, the force constant of the vibrating system may be calculated.

In the discussion that follows, the chelate rings of the metal complexes have each been considered as vibrating as a whole, rather than as a group of vibrating systems, and it has been assumed in each case that the moment of the ring acts in a direction bisecting the angle between the two bonds to the metal atom. The former assumption is justifiable, since all the rings considered are resonating structures, and are therefore planar ; all are under a certain amount of strain and accordingly are more or less rigid. The second assumption is certainly true for the acetylacetone and dibenzoylmethane rings, which are symmetrical structures. It is probably equally justifiable in the case of copper salicylaldehyde, for which two resonance structures may be written:

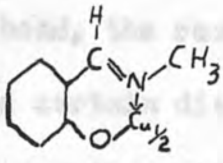


and

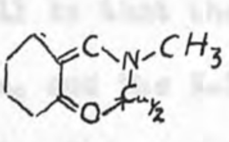


neglecting for this purpose resonance within the benzene nucleus. It is probable that the~~se~~ structures will make equal or nearly equal, contributions in the formation of the resonance hybrid, so that the two O-Cu bonds will be of nearly equal polarity, as will also the two C-O bonds.

For a ring such as that of copper salicylidenemethylimine, in which both oxygen and nitrogen are bonded to copper, similar considerations apply. The two relevent resonance structures are as follows :



(I.)



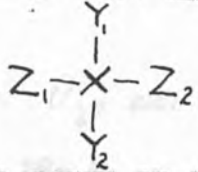
(II.)

Of these, (I) will make a somewhat larger contribution than (II) ; compounds containing a covalent bond between copper and nitrogen exist, for example copper benzeneazo-2-naphthylamine, and copper benzeneazo-2-pyrrole, but they are only moderately stable in comparison with compounds such as the acetylacetonates, most of which may be sublimed without decomposition. However, there will be a considerable contribution from (II), with the result that both the O-Cu and the N-Cu bonds will be highly polar; the moments of the C-O and the C-N bonds will be approximately the same, and the direction of the resultant ring moment will not differ greatly from that of a line bisecting the O-Cu-N valency angle.

Similar considerations apply to the other compounds on which measurements have been made.

A more precise justification of these assumptions may be made if the method originated by Barriol and Régnier, (8), for the derivation of an expression for the atomic polarisations of molecules of simple geometric shape, is applied to these molecules.

Consider first an imaginary, <u>trans</u> planar molecule,



$$Z_1-\overset{\displaystyle Y_1}{\underset{\displaystyle Y_2}{X}}-Z_2$$

in which the Y atoms each carry an effective charge of $+e_1$, and the Z atoms an effective charge of $+e_2$; the effective charge on the atom X is consequently $-2(e_1 + e_2)$.

If a field F is applied to this molecule in a direction parallel to the X-Y_1 bond, the result will be that the X-Y_1 bond will be extended by a certain distance a, and the X-Y_2 bond will be shortened by a smilar amount. The X-Z_1 and X-Z_2 bonds will, however, undergo no appreciable change in length, but the atoms Z_1 and Z_2 will be displaced towards Y_1, so that the angles Y_1-X-Z_1 and Y_1-X-Z_2 are each decreased by an equal amount θ_1, and the angles Y_2-X-Z_1 and Y_2-X-Z_2 are increased by the same amount. The potential energy, u, of the molecule in the field is therefore given by:

$$u = 2 \times \tfrac{1}{2}k_1 a^2 + 2\times\tfrac{1}{2}V\theta_1^{\,2} = k_1 a^2 + V\theta_1^{\,2},$$

where k_1 is the stretching force constant of the X-Y bond, and V is the bending force constant of the X-Z bonds in the plane of the molecule.

At the same time, the electrical work done by the field, w, is given by :

$$w = 2Fe_1 a + 2Fe_2 R_Z \theta_1,$$

where R_Z is the length of the X-Z bond.

Now $\partial u/\partial a$ must equal $\partial w/\partial a$, so that

$$2k_1 a = 2Fe_1,$$

and therefore

$$a = \frac{Fe_1}{k_1}.$$

Also, $\partial u/\partial\theta_1 = \partial w/\partial\theta_1$, and therefore

$$2V\quad{}_1 = 2Fe_2R_Z,$$

whence

$$\theta_1 = \frac{Fe_2R_Z}{V}.$$

The induced moment is thus given by:

$$m = 2ae_1 + 2R_Z\theta_1 e_2 = \frac{2Fe_1^{\,2}}{k_1} + \frac{2Fe_2^{\,2}R_Z^{\,2}}{V}.$$

Then, since the polarisability, γ_1, along this axis is given by m/F,

$$\gamma_1 = \frac{2e_1^{\,2}}{k_1} + \frac{2e_2^{\,2}R_Z^{\,2}}{V}.$$

Similarly, if the field is applied in a direction parallel to the X-Z_1 bond,

$$\gamma_2 = \frac{2e_2^{\,2}}{k_2} + \frac{2e_1^{\,2}R_Y^{\,2}}{V},$$

where k_2 is the stretching force constant of the X-Z bond. The force constant for the bending vibrations of the X-Y bond in the plane of the molecule will be essentially the same as that for the X-Z bond, since both modes of vibration involve distortion of the Y-X-Z angle.

If the field is applied in a direction at right angles to the plane of the molecule, there is no appreciable change in the lengths of the bonds, but the X-Y bonds will be bent through an angle θ_2, and the X-Z bonds through an angle θ_3.

Then $u = 2 \times \tfrac{1}{2}V_1'\theta_2^{\,2} + 2 \times \tfrac{1}{2}V_2'\theta_3^{\,2} = V_1'\theta_2^{\,2} + V_2'\theta_3^{\,2}$

and $w = 2Fe_1R_Y\theta_2 + 2Fe_2R_Z\theta_3$,

where V_1' and V_2' are the bending force constants of the X-Y and X-Z bonds respectively, for vibrations at right angles to the plane of the molecule.

Then, since $\partial u/\partial\theta_2 = \partial w/\partial\theta_2$, and also $\partial u/\partial\theta_3 = \partial w/\partial\theta_3$,

$$2V_1'\theta_2 = 2Fe_1R_Y, \quad \text{and} \quad 2V_2'\theta_3 = 2Fe_2R_Z;$$

whence
$$\theta_2 = \frac{Fe_1R_Y}{V_1'}, \quad \text{and} \quad \theta_3 = \frac{Fe_2R_Z}{V_2'}$$

Hence the induced moment is given by:

$$m = 2R_Y\theta_2e_1 + 2R_Z\theta_3e_2$$
$$= \frac{2Fe_1^{\,2}R_Y^{\,2}}{V_1'} + \frac{2Fe_2^{\,2}R_Z^{\,2}}{V_2'}$$

and the polarisability along this axis is then

$$\gamma_3 = \frac{2e_1^{\,2}R_Y^{\,2}}{V_1'} + \frac{2e_2^{\,2}R_Z^{\,2}}{V_2'}$$

The mean polarisability of the molecule is given by the mean of the values along three axes at right angles, i.e.,

$$\gamma = \frac{1}{3}\left(\gamma_1 + \gamma_2 + \gamma_3\right) = \frac{1}{3}\left[\frac{2e_1^{\,2}}{k_1} + \frac{2e_2^{\,2}}{k_2} + \frac{2e_1^{\,2}R_Y^{\,2}}{V} + \frac{2e_2^{\,2}R_Z^{\,2}}{V} + \frac{2e_1^{\,2}R_Y^{\,2}}{V_1'} + \frac{2e_2^{\,2}R_Z^{\,2}}{V_2'}\right].$$

But $e_1R_Y = \mu_Y$, and $e_2R_Z = \mu_Z$, where μ_y and μ_Z are respectively the bond moments of the X-Y and the X-Z bonds.

Now $P_A = \frac{4}{3}\pi N \gamma$,

and therefore

$$P_A = \frac{8\pi N e_1^2}{9k_1} + \frac{8\pi N e_2^2}{9K_2} + \frac{8\pi N \mu_Y^2}{9V} + \frac{8\pi N \mu_Z^2}{9V} + \frac{8\pi N \mu_Y^2}{9V_1'} + \frac{8\pi N \mu_Z^2}{9V_2'}.$$

In this expression for the atomic polarisation, the first two terms represent the contributions from the stretching vibrations of the X-Y and the X-Z bonds respectively, the third and fourth terms the contributions from bending vibrations in the plane of the molecule, and the fifth and sixth terms those from bending vibrations occurring at right angles to the plane. The terms involving the stretching vibrations will be very small compared with the remaining terms. Further, the force constant V for bending in the plane of the molecule will be large as compared with V_1' and V_2' for bending at right angles to this plane. Hence, under these conditions, the only significant terms in the expression are the fifth and sixth terms, and

$$P_A = \frac{8\pi N \mu_Y^2}{9V_1'} + \frac{8\pi N \mu_Z^2}{9V_2'}.$$

If the Y and Z atoms are now assumed to be linked together in pairs, so as to form two similar rings, which are fairly rigid, so that as a first approximation they can be regarded as vibrating as a whole, there are only two independent vibrators instead of four. If, in one of these rings, the atoms Y and Z are subjected to equal mechanical forces, and if they are depressed respectively through angles θ_Y and θ_Z, then $V_1'\theta_Y = V_2'\theta_Z$ . . . (1)

and the bisector of the angle Y-X-Z will be depressed through an angle θ, given by $\theta = (\theta_Y + \theta_Z)/\sqrt{2}$ . . . . (2)

Then the apparent force constant, V', along this "axis" of the ring, will be such that $\frac{1}{2} V'\theta^2 = \frac{1}{2} V_1'\theta_Y^2 + \frac{1}{2} V_2'\theta_Z^2$. . (3)

From (1), we have

$$\theta_Z = \frac{V_1'}{V_2'} . \theta_Y.$$

From (2), $\theta^2 = \frac{1}{2}(\theta_Y + \theta_Z)^2 = \frac{1}{2}\theta_Y^2\left(1 + \frac{V_1'}{V_2'}\right)^2$,

and thence, by substitution in (3),

$$\frac{1}{2} V'\theta_Y^2\left(1 + \frac{V_1'}{V_2'}\right)^2 = V_1'\theta_Y^2 + V_2'\left(\frac{V_1'}{V_2'} . \theta_Y\right)^2$$

$$= V_1'\theta_Y^2\left(1 + \frac{V_1'}{V_2'}\right)$$

Therefore $\frac{1}{2} V'\left(1 + \frac{V_1'}{V_2'}\right) = V_1'$,

or $V' = \frac{2V_1'V_2'}{V_1' + V_2'}$ . . . . (4)

This equation may not be solved completely, but it may be applied in certain special cases.

Case 1. $V_1' = V_2'$.

This applies to the acetylacetonates and the dibenzoylmethane complexes.

In this case, $V' = V_1' + V_2'$.

The expression for the atomic polarisation then reduces to:

$$P_A = \frac{8\pi N}{9V'}\left(\mu_Y^{2} + \mu_Z^{2}\right) = \frac{8\pi N \mu_{res}^{2}}{9V'},$$

where μ_{res} is the resultant moment of the chelate ring.

Case 2. $\mu_Y = \mu_Z$.

This also holds exactly for the complexes of acetylacetone and dibenzoylmethane, and is approximately true for all the complexes considered.

Under these conditions,

$$P_A = \frac{8\pi N \mu_Y^{2}}{9}\left(\frac{1}{V_1'} + \frac{1}{V_2'}\right).$$

But, from equation (4), we have

$$\frac{1}{V_1'} + \frac{1}{V_2'} = \frac{2}{V'},$$

and therefore $$P_A = \frac{8\pi N \mu_{res}^{2}}{9V'}.$$

In this case, the direction of the resultant moment is along the bisector of the angle $Y_1 - X - Z_1$.

Case 3. If the planes of the chelate rings Y_1-X-Z_1 and Y_2-X-Z_2 bend only about the line bisecting the angles Y_1-X-Z_2 and Y_2-X-Z_1. Since all the chelate rings considered are strained to some extent, their rigidity will be such that this assumption is justifiable.

When the applied field is acting in a direction perpendicular to the plane of the molecule,

$$u = 2 \times \tfrac{1}{2} V' \theta^{2} = V' \theta^{2},$$

and $$w = 2F (e_1 R_Y \sqrt{2}\, \theta + e_2 R_Z \sqrt{2}\, \theta).$$

Then, since $\partial u / \partial \theta$ must equal $\partial w / \partial \theta$,

$$\begin{aligned} 2V' &= 2\sqrt{2}\, F (e_1 R_Y + e_2 R_Z) \\ &= 2\sqrt{2}\, F (\mu_Y + \mu_Z) \\ &= 2F \mu_c, \end{aligned}$$

where μ_c is the component of the resultant moment of the chelate ring along the bisector of the angle Y_1-X-Z_1.

Therefore $$\theta = \frac{F \mu_c}{V'} .$$

The induced moment m is given by:

$$\begin{aligned} m &= 2 e_1 R_Y \frac{\theta}{\sqrt{2}} + 2 e_2 R_Z \frac{\theta}{\sqrt{2}} \\ &= \sqrt{2}\, \theta (e_1 R_Y + e_2 R_Z) \\ &= \sqrt{2}\, \theta (\mu_Y + \mu_Z) \\ &= \theta \mu_c \\ &= \frac{F \mu_c^{2}}{V'} . \end{aligned}$$

When the field acts along either of the other two axes, the polarisability of the molecule is zero under these conditions, and the mean polarisability is thus given by:

$$= \frac{1}{3} \frac{\mu_c^{2}}{V'}$$

Hence $$P_A = \frac{8\pi N \mu_c^{2}}{9V'}$$

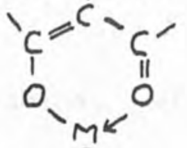
For these special cases, then, this expression for the atomic polarisation is valid, and the only differences which arise are due to the variation of the dipole moment involved between the total resultant moment of the chelate ring and the component of this moment along the bisector of the angle Y_1-X-Z_1. In the complexes which have been studied, however, it is probable that all three conditions discussed are approximately fulfilled, and therefore no large errors are likely to be introduced by taking the direction of μ as the bisector of this angle.

Following Sutton and his co-workers, force constants have been expressed in terms of ergs/radian^2/molecule throughout the discussion that follows, rather than in the more usual units of dynes/cm., since the force constants used in the derivation of the expression for atomic polarisation are for angular, rather than for linear, displacements. If required, they may be converted into the alternative units by multiplying by the square of the effective length of the vibrating system. This length is, however, an uncertain quantity when the vibrations in question are those of a ring system : the units of angular displacement are therefore to be preferred.

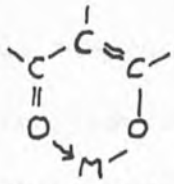
Section 3. Six-membered chelate rings.

(i). Acetylacetonates and related compounds.

In order to provide a logical extension of existing data on the atomic polarisation of the coordination compounds of metals, measurements have been made on a number of compounds which contain the general ring systems in which resonance can occur between the structures I and II.



I.



These compounds included not only the acetylacetonates, but also dibenzoylmethane and salicylaldehyde complexes of metals.

The measurements on aluminium acetylacetonate were carried out as checks on the reproducibility of results obtained with the apparatus, and also in order to compare these results with the work of Finn, Hampson and Sutton (loc. cit.). The molecular polarisation of aluminium acetylacetonate in benzene found in the present work agrees closely with their figure, but the value found for the refractivity is about 3 c.c. lower than theirs. The two sets of measurements made on different specimens of this compound in solution in dioxan agree within the limits of the experimental error.

Finn, Hampson and Sutton's results for ferric acetylacetonate give a somewhat lower value for P_A than that obtained in this work, after correction has been made for their arithmetical error which resulted in an incorrectly low figure for $[R_D]$. The corrected figure is 100.8 c.c., giving P_A as 47.8 c.c.

Measurements were made on the acetylacetonates of aluminium and iron, and on the dibenzoylmethane complexes of iron and beryllium, in solution in both benzene and dioxan, in order to ascertain whether or not measurements made in these two solvents were strictly comparable. It was found in each case that the value of the atomic polarisation found in dioxan solution was slightly higher than that found in benzene solution. The small, but definite increase was never more than 5 c.c. In the case of the dibenzoylmethane complexes, the refractivity, as well as the molecular polarisation, showed an increase, which was quite small (about 3 c.c.) for the beryllium compound, but 16 c.c. for ferric dibenzoylmethane. No great change was, however, apparent in the atomic polarisation value. There is no obvious reason for these increases, for these complexes contain no free hydroxyl or amino-groups, which would tend to form hydrogen bonds with dioxan molecules, leading to high values of the molecular polarisation. While small increases of this kind are not uncommon, especially for polar compounds, the large increase found for the ferric complex is very unusual. There is a possibility that some form of association with the molecules of dioxan may occur, which has an effect upon the electronic polarisation, but not the atomic polarisation; but there is no real evidence for this, and at present the increase remains unexplained.

It was evident, therefore, that any precise comparisons between atomic polarisation figures measured in different solvents must be made with some care; the use of dioxan as a solvent was, however, necessitated on account of the limited solubility of many of the complexes in benzene. Since the corrections to be applied are not much larger than the experimental error, and moreover are difficult to predict, they have been neglected in the following discussion.

Beryllium dibenzoylmethane was found to have an atomic polarisation of 29.1 c.c., very close to the figure of 28.0 c.c. for beryllium acetylacetonate, calculated by the method of Smith and Cleverdon from the data given by Finn, Hampson and Sutton; the substitution of phenyl groups for methyl groups thus makes a negligible difference to the vibrations of the ring in this case. It was found, however, that the atomic polarisation of ferric dibenzoylmethane was nearly 40 c.c. higher than that of the corresponding acetylacetonate. There is a possibility that this increase may be brought about by steric factors, the large size of the phenyl group as compared with the methyl group preventing the molecule of ferric dibenzoylmethane from assuming the same symmetrical structure as the acetylacetonate. The moments of the bonds to the metal atom are so large that distortion through a very small angle would lead to an effect of the magnitude observed. There is no sign of such distortion in the beryllium complex, but as in this case there are only two coordinating molecules of dibenzoylmethane instead of three, forming a tetrahedral structure, an undistorted, symmetrical structure might be possible in this case. The aluminium complex of dibenzoylmethane, which resembles the ferric complex in its structure, and the copper complex, which, being planar in character, might have been expected to undergo distortion of this kind, were unfortunately too insoluble for polarisation measurements to be made.

There is also a possibility that, for some reason which is not clear, the character of the O-Fe bonds in the dibenzoylmethane complex differ somewhat from the corresponding bonds in the acetylacetonates, with the result that both the effective ring moments and the force constants for the bending vibrations are different in the two cases. The unusual changes in the $[R_D]$ value of the dibenzoylmethane complex, when dioxan is substituted for benzene, suggest that there may exist some fundamental difference of this kind.

The complexes of salicylaldehyde closely resemble those of acetylacetone and dibenzoylmethane, the only difference in the chelate ring being that one of the bonds of the ring also forms part of a benzene nucleus. The atomic polarisation of copper salicylaldehyde, however, is 67 c.c., compared with Finn, Hampson and Sutton's figure of 28 c.c. for beryllium acetylacetonate, the only compound with two chelate rings for which they obtained reliable results.

The ring moments of beryllium acetylacetonate and copper salicylaldehyde are not likely to differ greatly, since the organic parts of the rings are so nearly identical. Although the polarity of the bonds in the copper complex, on account of the more electropositive character of beryllium, this increase will probably be largely offset by the difference in the orientation of the chelate rings. The bonds to the beryllium atom are tetrahedrally arranged, each making an angle of about 54° with the axis of symmetry of the ring, whereas the arrangement in the copper complex is square, so that the angle between the Cu-O bonds and the ring moment is only 45°. The component of the Be-O bond moment along the axis of the ring is therefore somewhat smaller than the corresponding component in the copper complex.

From the relationship

$$P_{A_1} = \frac{4\pi N \mu^2}{9 V_o},$$

and considering in each case a molecule with two independent, but equal modes of vibration, we have

$$V_o = \frac{8\pi N \mu^2}{9 P_A}.$$

If, following Finn, Hampson and Sutton, we take the moment of the acetylacetonate ring as 7.5 D., and assume that the moment of the salicylaldehyde ring is of the same magnitude, then this relationship gives a value for the force constant of the bending vibrations of beryllium acetylacetonate of 3.7×10^{-12} erg/radian^2/ molecule, and, for the vibrations of copper salicylaldehyde, 1.4×10^{-12} erg/radian^2/ molecule. Similarly, the ring moments in aluminium and ferric acetylacetonates must be very near to that for the beryllium compound, and, using the same value, the force constants are found to be 3.2×10^{-12} and 2.7×10^{-12} erg/radian^2/molecule respectively.

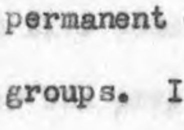
The difference in the arrangement of the chelate rings in these four compounds must play a significant rôle in determining the relative values of the respective force constants. Vibration of the ring would be expected to be least inhibited in the planar copper complex : this is borne out by the much lower force constant for this compound than for the other complexes, which have tetrahedral or octahedral arrangement of the bonds about the metal atom. Unfortunately copper acetylacetonate is too sparingly soluble in non-polar solvents to permit of confirmation of this conclusion through measurement of its polarisation.

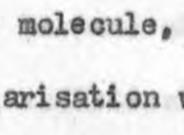
The force constants for the tetrahedral and octahedral complexes would not be expected to differ greatly. The gradation in the values observed may possibly be due to the differing degrees of strain in the chelate rings. It will be shown later that the force constant seems to be particularly large in compounds in which the chelate rings contain five atoms only, so it may be postulated that even in six-membered rings the force constants will be the higher the greater the strain in the ring. Data on the effective radii of atoms in chelate complexes of this type are not available, but, for the purposes of comparison, it may be noted that the radii of Be^{++}, Cu^{++}, Al^{+++} and Fe^{+++} ions are 0.34, 0.80, 0.56 and 0.67 A. respectively. When considered in conjunction with the angles between the valencies of the metal atoms concerned (108° for beryllium, and 90° for aluminium, iron and copper), and the O-O distance in the unstrained molecule of acetylacetone, these suggest that the strain in the ring may reasonably follow the order Be > Al > Fe > Cu .

The high value of the molecular polarisation for the aluminium complex of diethyl malonate is probably due to the existence, at any instant, of a permanent dipole in the molecule, due to the rotation of the six ester groups. Its atomic polarisation would be expected to be approximately the same as that of aluminium acetylacetonate.

(ii). Complexes of salicylaldehyde and its derivatives.

By utilising complex compounds formed by derivatives of salicylaldehyde such as salicylideneaniline, salicylidenemethylimine and salicylaldoxime, it is possible to replace one of the oxygen atoms in the ring system previously discussed by a nitrogen atom, leading to structures which can be represented by resonance between III and IV.


III.


IV

In most cases, the copper complexes of these compounds proved the most suitable for polarisation measurements. Within this class of compound, a rather wide variation in results was obtained, the differences between the P_{2_∞} and $[R_D]$ values lying between the extremes of 21 c.c. in the case of copper salicylaldoxime, and the exceptionally high figure of 132.3 c.c. initially found for copper salicylidene-aniline.

It is evident, on comparison of the results obtained from the complexes of the anils of salicylaldehyde, that the difference found for the complex formed by the unsubstituted anil is exceptionally large, and is presumably not due entirely to atomic polarisation, but is affected by some additional factor not involved in the other compounds. The possibility of the presence of a small proportion of the cis isomer of the complex at once comes to mind, and the measurements were repeated, using a fresh specimen of the substance, which had been purified by precipitation five times before use, instead of the two which are sufficient for the preparation of an analytically pure sample. The value of P_{2_∞} for this second specimen was found to be only 3.5 c.c. less than the figure found for the first preparation, that is, very little more than the experimental error involved in the measurements : the proportion of the impurity, if such exists, is therefore scarcely altered by this method of purification. The proportion must, in any case, be very small, since, owing to its relatively high dipole moment, the molecular polarisation of the pure cis isomer, if it could be prepared, would be extremely high.

No preparation of a pure cis isomer, together with any definite proof of its structure, appears to have been made. Zetzsche, Silbermann and Vieli (9) prepared the complex by dissolving copper powder in an alcoholic solution of the anil, and described it as forming dark brown crystals in star-shaped clusters. Pfeiffer and Glaser (10) prepared it by the action of either aniline or phenylhydroxylamine on the copper complex of salicylaldehyde : they described the appearance as "red-brown needles". Pfeiffer and his co-workers (11) later examined a sample, prepared from cupric acetate and aniline by the addition of salicylaldehyde to the alcoholic solution, with the intention of isolating, if possible, cis and trans isomers. Fractional crystallisation from acetone gave seven fractions, all apparently identical. A second sample, prepared from copper salicylaldehyde and aniline, was examined in the same way, and a very small trace of a green crystalline powder was discovered in the third fraction. Treatment of a larger sample (40 g.) enabled them to isolate and analyse 20 mg. of this compound. The Cu : N ratio was found to be 1.13 : 1, showing that this could not be the cis isomer ; no more detailed investigation was made.

It seems unlikely that this green powder, whatever its nature, could be the cause of the high molecular polarisation figures found for a sample of the complex prepared from copper sulphate and the anil alone. It is, however, of interest to note that the preparation of this complex was first claimed by Schiff (12), using the action of aniline on copper salicylaldehyde, and it was then described as an olive-green, crystalline powder, insoluble in organic solvents. It is possible that this may have been the cis isomer, and that this single preparation was exceptional, and impossible to repeat. An instance of such a nature occurred in the preparation of copper salicylaldehyde-methylimine by Pfeiffer and Glaser (loc. cit.) : on one occasion only, instead of the green needles usually obtained on recrystallisation from chloroform, brown leaflets of the same composition were formed, which, on standing, reverted to the original green form. This preparation proved impossible to repeat.

It is worth noticing that two clearly defined forms of the copper complex of the closely similar 2-hydroxy-1-naphthaldehyde-methylimine were obtained by Pfeiffer and Glaser : a green form, crystallising in long needles, which on heating changed over into shining brown prisms, shown by analysis to have the same composition. The brown form crystallised from pyridine, but if methyl alcohol was added to the hot pyridine solution, the green form of the complex was precipitated. The possibility of dimorphism cannot be ruled out, but it seems likely that these may in fact be the cis and trans isomers of the complex. Pfeiffer and Glaser assumed that the brown form was probably the cis isomer, owing to the similarity of its colour to that of the copper complex of disalicylaldehyde-ethylenediamine: in this compound, the two aldehyde molecules are linked by one molecule of the diamine, so that the arrangement of the bonds about the central copper atom must necessarily be of the cis configuration. The colour of the green form is similar to that of the copper complex of salicylaldehyde-methylimine, which the present work has shown to be a trans compound. Polarisation measurements on these two isomers would be of interest.

In the discussion that follows, it has been assumed therefore that the exceptionally high molecular polarisation observed for copper salicylideneaniline is due to a small trace of the cis isomer. From the analogy of the beryllium complexes of acetylacetone and dibenzoylmethane, it seems likely that the atomic polarisation of trans-copper salicylideneaniline will be very close to that of copper salicylidenemethylimine, i.e., about 61 c.c. This latter value has been confirmed by the work of Charles and Freiser (13), allowing for the fact that the value for the molecular refraction of the complex in this paper was calculated from that of salicylideneaniline, making no allowance for the change in the number of conjugated single and double bonds.

There is a small, but significant difference between the values of the atomic polarisations of copper salicylaldehyde and copper salicylidenemethylimine, which are found to be 67 c.c. and 61 c.c. respectively. It is not likely that the force constants for the bending vibrations in these two molecules will differ appreciably, since the substitution of a nitrogen atom for an oxygen atom in the chelate ring leads to hardly any change in bond angles or bond lengths, and the strain in the ring is therefore almost the same in the two cases; but a difference between the moments of the rings may be expected, on account of the increased electronegative character of oxygen as compared with nitrogen. The moments may be compared using the usual relationship

$$P_A = \frac{8\pi N \mu^2}{9 V_o} \;;$$

assuming the force constants to be equal, we have

$$\frac{\mu_1^2}{\mu_2^2} = \frac{P_{A1}}{P_{A_2}}$$

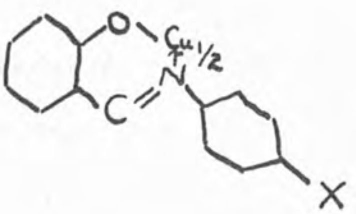
where the suffixes 1 and 2 apply to the salicylidenemethylimine and the salicylaldehyde complexes respectively. If μ_2 is taken, as before, as 7.5 D., then

$$\mu_1 = \mu_2 \sqrt{\frac{P_{A_1}}{P_{A_2}}}$$

$$= \underline{7.2\ D.}$$

The difference of 0.3 D. in the ring moments is of the order to be expected as a result of the change in electronegativity. The ring moment in the seliculaldehyde complex is largely made up of the bond moments of the O-Cu, O→Cu and C= O bonds; of these, the moments of the two last-named are slightly, but appreciably reduced when the nitrogen atom is substituted in the salicylidenemethylimine complex.

The values of the atomic polarisations of the three copper complexes of the p-halogeno-substituted anils lie close together: it is not clear why the value for the bromine-substitute complex should be less than that of the other two, but the difference (7 c.c.) is not very much greater than the experimental error, and may in part be due to errors in calculating the molecular refractions of the complexes, as there may be departures from strict additivity. The atomic polarisation figures are very roughly 10 c.c. less, in each case, than the value for copper salicylideneaniline, if this is supposed to be the same as the atomic polarisation of copper salicylidenemethylimine.



There is a slight degree of strain in the six-membered ring of the complexes of the anils, which will result in the increase of the valency angles in the ring by a few degrees in each case. If we consider the three bond angles at the nitrogen atom, we see that the Cu-N-Ph and the C-N-Ph angles will both be slightly less than the unstrained angle of 120°, in order to compensate for the increase in the Cu-N-C angle. Supposing that these two angles are each decreased by 3°, i.e., are each 117°, then the moment of the ring, which makes an angle of 45° with the Cu-N bond, acts at an angle of 72° to the Ph-N bond. The moment of the Ph-X group, where X is an atom of one of the halogens, acts in the direction of the Ph-N bond, and the component of this moment, $\mu_{(Ph-X)}$, in the direction of the ring moment is therefore equal to $\mu_{(Ph-X)}\cos 72°$, or $0.31\,\mu_{(Ph-X)}$.

The moment $\mu_{(Ph-X)}$ is entirely due to the moment of the C-X bond. The values for the C-X bond moments, whether X is an atom of chlorine, bromine or iodine, do not differ greatly : the actual values are as follows :

C-Cl	1.58 D.
C-Br	1.56 D.
C-I	1.40 D.

The components of these moments in the direction of the ring moment are respectively about 0.49, 0.48 and 0.43 D., acting in the reverse sense to the moment of the ring of the unsubstituted complex.

The latter has already been estimated as 7.2 D., and the resultant ring moments for the substituted complexes are therefore 6.7_1, 6.7_2 and 6.7_7D respectively. Substituting these values in the usual relationship, the corresponding force constants are then respectively 1.40, 1.58 and 1.46 erg /radian^2/molecule.

The closely similar nature of these three complexes and of copper salicylidenemethylimine makes it probable that all four force constants are the same, since only substituents are altered, and the vibrating ring of six atoms remains unchanged. Considering of the necessarily approximate nature of the assumptions made, these results are not in conflict with this view. This is revealed by reversing the calculation. Assuming that the force constants all have the value 1.40×10^{-12} erg / radian^2/ molecule, which was previously calculated for the salicylidenemethylimine complex, the expected values of the atomic polarisations of the halogen-substituted compounds would be 53, 53 and 55 c.c. respectively. The only anomalous figure, therefore, is the low value of 47 c.c., instead of 53 c.c., which was observed for the bromo-compound.

The values of the atomic polarisations of the salicylaldoxime complexes of copper and nickel are much lower than those of any of the other complexes formed by compounds of the salicylaldehyde series. The atomic polarisation of the copper complex, for example, is only 21 c.c., compared with the value of 61 c.c. found for copper salicylidenemethylimine. The ring moments of the two complexes are not likely to be very different, since the chelate rings are identical; yet, if the ring moment of 7.2 D., calculated above for the salicylidenemethylimine complex, is used to calculate the bending force constant for the vibrations of the ring in copper salicylaldoxime, a value of 4.1×10^{-12} erg /radian^2/molecule is obtained. This result indicates a higher degree of rigidity in the structure of the molecule, and a possible explanation of this would be the existance of a hydrogen bond, linking the hydroxyl group of one salicylaldoxime residue with the phenolic oxygen atom of the other. Such an arrangement would hold the molecule in a more rigid, planar shape, and some evidence for this is provided by the absence of any moment due to the rotation of free hydroxyl groups. There is strong evidence for the existence of a similar type of bond in nickel dimethylglyoxime, which gives none of the reactions characteristic of the hydroxyl group : no reaction is given with acetic anhydride (14) or with methylmagnesium iodide (15). Moreover, infra-red spectra show no evidence of the presence either of free, or of normally hydrogen-bonded hydroxyl groups in this compound, and it has been shown, by X-ray analysis ofthe crystal (16) that the O...H...O distance is unusually short, indicating that there may be present an exceptionally strong bond.

In the measurements made on the salicylaldoxime complexes, the use of exceedingly dilute solutions was necessary, on account of the sparingly soluble character of these compounds, especially the nickel complex. The difference between the atomic polarisations of the two complexes, 7.7 c.c., is therefore not much larger than the experimental error involved in the measurements, and accurate calculation of the ring moment in the nickel complex is therefore not possible. On the grounds of the more electropositive character of nickel as compared with copper, a ring moment rather higher than that in the copper complex may be expected, and the experimental results are in the sense expected from this. By analogy with the change in ring moment on substituting an oxygen atom for a nitrogen atom in the chelating ring, a reasonable estimate would probably be 7.5 D. It is unlikely that the force constant would differ greatly from that which applies in the copper complex.

The chelate ring of nickel benzeneazo-p-cresol bears a close resemblance to that of copper salicylideneaniline : the only difference lies in the substitution of a nitrogen atom for a C-H group. Nevertheless, the atomic polarisation of the azo-compound is lower than that of the salicylideneaniline derivative by about 35 c.c., although the substitution of a nickel atom for a copper atom might be expected to increase the moments of the bonds from oxygen and nitrogen to the central atom, and therefore to increase the resultant moment of the chelate ring.

The ring moment of the salicylaldehydemethylimine complex is due mainly to the moments of three bonds : the large moments of the N-Me and O-Me bonds, which are both highly polar, and the moment of the C = N double bond, which Everard and Sutton (17) estimate to be about 1.3 D. In nickel benzeneazo-p-cresol, the magnitudes of the first two of these bond moments are almost unchanged, but the moment of the C = N bond has disappeared. Assuming, as before, that the C-N-Me angle is distorted to 126°, and that the ring moment acts at an angle of 45° to the N-Me bond, the component of the C = N bond moment in the direction of the ring moment of the salicylidenemethylimine complex is 1.3 cos 9°, or approximately 1.3 D. If the ring moment of the nickel salicylidenemethylimine complex is taken as 7.5 D. , the moment of the chelating ring in nickel benzeneazo-p-cresol is therefore reduced to 6.2 D.

A further reduction in the ring moment is brought about by the introduction of a dipole due to thetwo unshared electrons on the nitrogen atom of the azo group which is not co-ordinated to the nickel atom. The atomic dipole so formed is directed out of the chelate ring, and so has a component along the axis of the ring moment which acts in the reverse sense to the latter. The magnitude of the atomic dipole may be taken, from the dipole moment of ammonia, as about 1.5 D. , since almost the whole dipole moment of the ammonia molecule is due to an effect of this kind. Assuming the same bond angles as before, it may easily be shown that the atomic dipole makes an angle of 54° with the ring moment, and its component in this direction is therefore 1.5cos 54°, that is, about 0.9 D. The resultant moment of the ring is thus $6.2 - 0.9 = 5.3$ D.

Using this value for the ring moment, and the experimental value of the atomic polarisation, the force constant, calculated in the usual manner, is found to be 1.8×10^{-12} erg/radian^2/molecule.

It is possible that this increase of the force constant in comparison with the values for complexes of the anil type may be due to a slightly increased strain in the chelate ring, brought about by the substitution of a nitrogen atom for a methine group. The Ph-N=N angle in both cis-and trans-azobenzene has been shown to be 121° (18, 19), but the unstrained angle Ph-C=N is 125°. Although this difference is small, implying only a slight increase of strain in the ring, the difference observed may be a reflection of the sensitivity of the force constant to changes in the strain of the ring, as suggested by the force constants found for the acetylacetonates (v. supra).

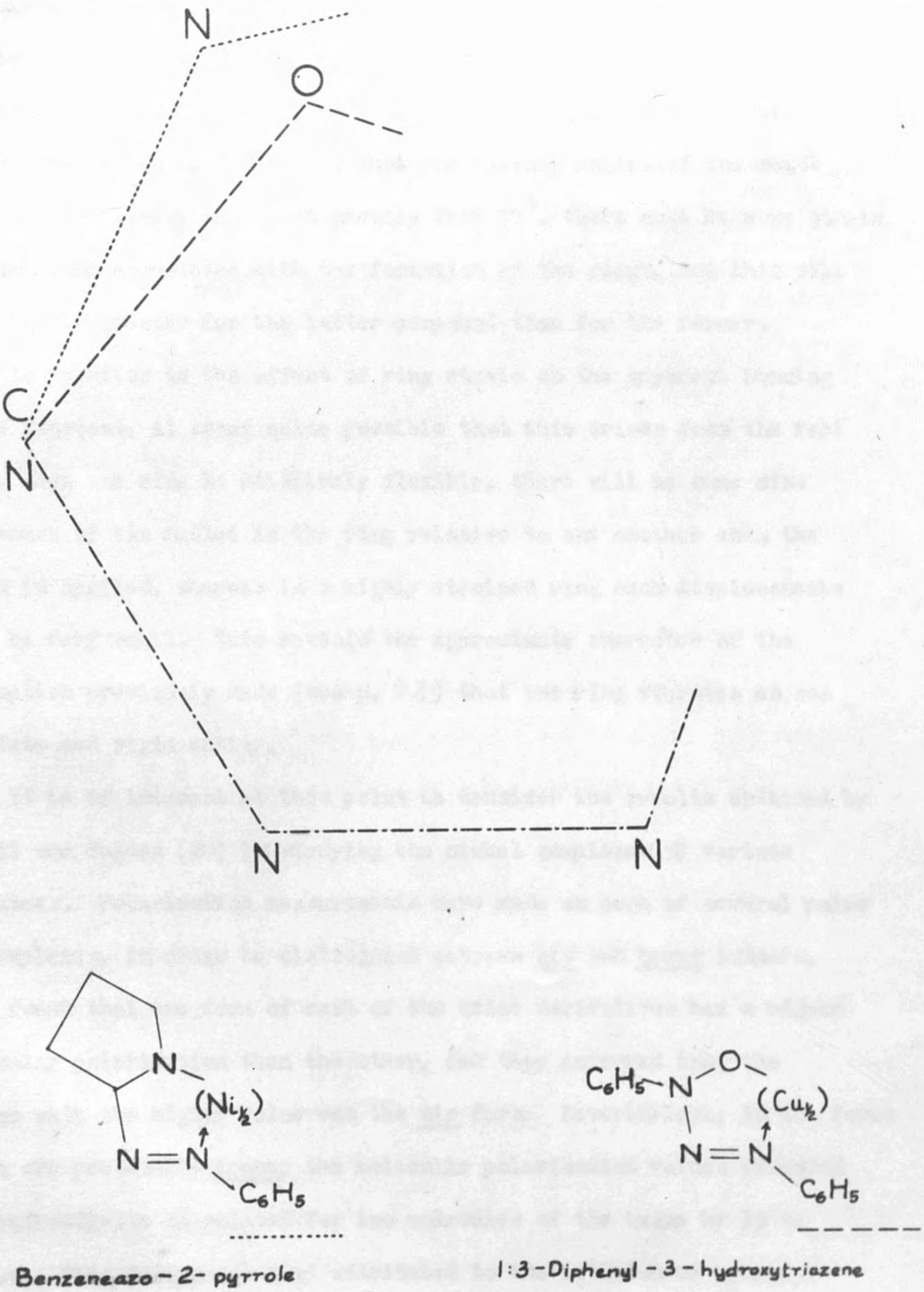
Section 4. Five-membered chelate rings.

Only two compounds of this type were found to be sufficiently soluble for measurements to be made, and in each case the atomic polarisation was found to be unexpectedly low, having the values of 14 c.c. and 21 c.c. for copper 1:3-diphenyl-3-hydroxytriazene and nickel benzeneazo-2-pyrrole respectively. This is not very different from the usually accepted "normal" values of atomic polarisations of 5 to 15 % of the electronic polarisation (9 and 18 % respectively).

The chelate ring of copper 1:3-diphenyl-3-hydroxytriazene bears a close resemblance to that of nickel benzeneazo-p-cresol, and it is probably approximately correct to assume that the ring moments are of the same magnitude, provided that a correction is made to allow for the less electropositive character of the copper atom. The ring moment of nickel benzeneazo-p-cresol has been estimated as 5.3 D.: if the ring moment of the copper complex is taken as 5.0 D., a value for the force constant of 3.0×10^{-12} erg/radian^2/molecule is obtained. This large increase over the value of 1.8×10^{-12} found for the force constant of the benzeneazo-p-cresol complex reflects the considerable increase in strain, and consequently in rigidity, in the formation of a five-membered ring, as compared with a ring of six atoms, in which the strain, though present, is slight.

The moment of the ring of nickel benzeneazo-2-pyrrole is probably somewhat larger than that of the triazene complex, as the pyrrole ring has itself a moment of 1.8 D. The component of this moment in the direction of the ring moment is 1.8 cos 45°, that is, 1.3 D., acting in the same direction as the ring moment. The resultant ring moment is therefore 5.3 + 1.3 = 6.6 D. This gives a value for the force constant of 3.6×10^{-12} erg/radian^2/molecule : this value, which is appreciably higher than that found for the triazene complex, suggests an increased strain in the chelating ring of the azo compound. That such a strain exists is demonstrated by the adjoining diagram, which represents the two undistorted rings superimposed, omitting in each case the central metal atom, since the lengths of the bonds to it are not known. The following dimensions are used :

Bond lengths :	C —N	1.48 A.
	C—N in pyrrole ring	1.42
	N=N	1.20
	N—N	1.47
	N —C	1.41
Bond angles :	—C—	110°
	—N—	110°
	—N=	121°
	—N= in pyrrole ring	105°
	—C= in pyrrole ring	110°


N
O
C
N
N
N
N
(Ni½)
N=N
C6H5
C6H5
N
O
(Cu½)
N=N
N
C6H5
Benzeneazo-2-pyrrole
1:3-Diphenyl-3-hydroxytriazene

This analysis of the problem indicates that in the molecules of 1:3-diphenyl-3-hydroxytriazene and benzeneazo-2-pyrrole the nearest distance of approach of the nuclei of the two atoms which become linked, in the complex, to the metal atom are 2.6 and 2.9 A., respectively. Hence, bearing in mind the fact that the valency angles of the metal atom are not likely to depart greatly from 90°, there must be some strain in each case associated with the formation of the rings, and this will be slightly greater for the latter compound than for the former.

In relation to the effect of ring strain on the apparent bending force constant, it seems quite possible that this arises from the fact that, when the ring is relatively flexible, there will be some displacement of the nuclei in the ring relative to one another when the field is applied, whereas in a highly strained ring such displacements will be very small. This reveals the approximate character of the assumption previously made (see p. 92) that the ring vibrates as one complete and rigid entity.

It is of interest at this point to consider the results obtained by Cavell and Sugden (20) in stydying the nickel complexes of various glyoximes. Polarisation measurements were made on each of several pairs of complexes, in order to distinguish between <u>cis</u> and <u>trans</u> isomers. They found that one form of each of the oxime derivatives had a higher molecular polarisation than the other, and they inferred that the isomer with the higher value was the <u>cis</u> form. Nevertheless, in the forms which are presumably <u>trans</u>, the molecular polarisation values exceeded the refractivity calculated for two molecules of the oxime by 35 to 40 c.c. This difference they attributed to the rotation of hydroxyl groups in the molecule, but it has since been shown conclusively (see "Copper and nickel salicylaldoxime") that these groups are held firmly by hydrogen bonds, and are not free to rotate. The difference must in fact be due to the atomic polarisations of these compounds. The values obtained for some of them are shown below; in the second column, they have been corrected by allowing for a contribution of 12 c.c. to the molecular refractivity made by the four bonds to the nickel atom.

Glyoxime.	P_A.	P_A corr.
α-methyl-<u>n</u>-propyl	40 c.c.	28 c.c.
α-methyl-<u>n</u>-butyl	35 c.c.	23 c.c.
α-methylbenzyl	35 c.c.	23 c.c.

It is probable that in reality the values of the atomic polarisations of these three compounds are the same : the experimental accuracy of the measurements was not high, only one or two solutions being used in each case, and a value of 25 c.c. may therefore be assumed.

The ring moment in the glyoxime complexes must be high, on account of the two bond moments of the C=N groups, each of magnitude 1.3 D., both of which enhance the resultant moment of the ring. The bond angles of the ring, which is under considerable strain, are uncertain, but if it is assumed that they are those of a regular pentagon, i.e. 108°, the two C=N bond moments each make an angle of 18° with the axis of symmetry of the ring. The components of these moments in the direction of the ring moment will therefore increase it by an amount $2 \times 1.3\cos 18^{\circ} = 2.5$ D.

If the ring moment of a five-membered ring nickel complex of the triazene type is 5.3 D., the ring moment of a nickel glyoxime complex is then 7.8 D., a value which is close to the ring moment of 7.5 D. assumed for nickel salicylaldoxime. This value, together with Cavell and Sugden's atomic polarisation results, gives a force constant for the bending vibrations of the rings of these complexes of 4.1×10^{-12} erg/radian^{2}/molecule, a figure which is of interest, since it is exactly the same as that calculated previously for the complexes of salicylaldoxime, which have been postulated to have a rigid structure similar to that of the glyoxime complexes.

As a result of these considerations, it is suggested that the atomic polarisation values are best interpreted in terms of the effective ring moments and bending force constants given in Table III. The grouping of the compounds into the classes shown is indicated in part by the actual P_A values obtained, but is more clearly revealed in the force constants derived after reasonable assumptions have been maderegarding the moments of the ring systems concerned.

Table III.

Complex.	P_A.	Ring moment	Bending force constant (erg/radian^2/molecule)
Tetrahedral and octahedral complexes.			
Beryllium acetylacetonate.	28.0	7.5	3.7×10^{-12}
Aluminium acetylacetonate.	45.2	7.5	3.2
Ferric acetylacetonate.	52.6	7.5	2.7
Planar complexes with six-membered rings.			
Copper salicylaldehyde.	67.3	7.5	1.4
Copper salicylidenemethylimine.	61.4	7.2	1.4
Copper salicylidene-*p*-chloraniline.	53.4	6.7	1.4
Copper salicylidene-*p*-bromaniline.	46.6	6.7	1.6
Copper salicylidene-*p*-iodoaniline.	53.0	6.8	1.5
Nickel benzeneazo-*p*-cresol.	26.0	5.3	1.8
Planar complexes joined by hydrogen bonds.			
Copper salicylaldoxime.	21.0	7.2	4.1
Nickel salicylaldoxime.	28.7	7.5	4.1
Nickel complexes of glyoximes.	25	7.8	4.1
Planar complexes with five-membered rings.			
Copper 1:3-diphenyl-3-hydroxytriazene.	14.0	5.0	3.0
Nickel benzeneazo-2-pyrrole.	20.7	6.6	3.6

REFERENCES.

Introduction.

1. Cartwright and Errera, Acta Physicochim. U.R.S.S., 1935, 3, 649. (Chem. Abstr. , 1936, 30, 4091.)
2. Cartwright and Errera, Proc. Roy. Soc., 1936, 154, A, 138.
3. Groves and Sugden, J., 1937, 1779.
4. Watson and Ramaswamy, Proc. Roy. Soc., 1936, 156, A, 144.
5. Højendahl, Nature, 1926, 117, 892.
6. Jenkins, J., 1936, 862.
7. Hassel and Naeshagen, Z. physikal. Chem., 1929, 6, B, 445.
8. Le Fèvre and Le Fèvre, J., 1935, 1696.
9. Hammick; Hampson and Jenkins, J., 1938, 1263.
10. Coop and Sutton, J., 1938, 1269.
11. Smith and Angus, Proc. Roy. Soc., 1932, 137, A, 372.
12. Jensen, Z. anorg. Chem., 1936, 226, 225.
13. Mann and Purdie, J., 1935, 1549.
14. Cavell and Sugden, J., 1935, 621.
15. Hampson, Trans. Farad. Soc., 1934, 30, 877.
16. Curran and Wenzke, J. Amer. Chem. Soc., 1935, 57, 2162
17. Finn, Hampson and Sutton, J., 1938, 1254.
18. Frank and Sutton, Trans. Farad. Soc., 1937, 33, 1307
19. Sutton, New and Bentley, J., 1933, 652.
20. Crawford and Cross, J., Chem. Phys., 6, 525.
21. Davidson and Sutton, J., 1939, 347.
22. Cox, Pinkard, Wardlaw and Webster, J., 1935, 459.
23. Cox and Webster, J., 1935, 731.

Chapter I.

1. Debye, Handbuch der Radiologie, Marx, 1925, 6, 625.

2. Few, Smith and Witten, Trans. Farad. Soc., 1952, 48, 211.

3. Few, Thesis, London, 1949.

4. Groves, J., 1939, 1144.

5. Sayce and Briscoe, J., 1925, 315.

6. Sugden, J., 1933, 768.

7. Ball, J., 1930, 570.

8. Hartshorn and Oliver, Proc. Roy. Soc., 1929, 152, A, 664

9. Debye, Physikal. Z., 1912, 13, 97.

10. Sugden, Trans. Farad. Soc., 1934, 30, 720.

11. Smith and Cleverdon, Trans. Farad. Soc., 1949, 45, 109.

12. Halverstadt and Kumler, J. Amer. Chem. Soc., 1942, 64, 2988.

13. Maxwell, Electricity and Magnetism, Oxford, 1873, 2, 388.

Chapter II.

1. Few and Smith, J., 1949, 753.

2. Broughton, Trans. Farad. Soc., 1934, 30, 367.

3. Smith and Witten, Trans. Farad. Soc., 1951, 47, 1307.

4. Young, "Inorganic Syntheses", 2, 25.

5. Finn, Hampson and Sutton, J., 1938, 1254.

6. Booth and Pierce, J. Phys. Chem., 1933, 37, 59.

7. Elkins and Hunter, J., 1935, 1598.

8. Hodgson and Foster, J., 1942, 30.

9. Charrier and Beretta, Gazz. chim. ital., 1926, 56, 865.

10. Pfeiffer, Hesser, Pfitzner, Scholl and Thielert, J. prakt. Chem., 1937, 149, 217.

11. O. Fischer, Ber., 1886, 19, 2252.

12. Pfeiffer and Glaser, J. prakt. Chem., 1939, 153, 265.

13. Bamberger and Rising, Ann., 1901, 316, 257.

14. Elkins and Hunter, J., 1938, 1346.

15. Auwers and V. Meyer, Ber., 1888, 21, 784.

16. Galatis, J. prakt. Chem., 1938, 151, 331.

17. Ley and Werner, Ber., 1907, 40, 705.

18. Vogel, "Textbook of Practical Organic Chemistry", Longmans, 1948, p. 833.

19. Auwers and V. Meyer, Ber., 1889, 22, 705.

20. Vogel, "Textbook of Practical Organic Chemistry", Longmans, 1948, p. 683.

21. Atack, J., 1913, 1317.

22. Feigl and Bondi, Ber., 1931, 64, 2819.

23. Titschenko, J. Russ. Phys. Chem. Soc., 1899, 31, 784.

24. Erdmann and van der Smissen, Ann., 1908, 361, 32.

Chapter III.

1. Curran, J.Amer. Chem. Soc., 1945, 67, 1835.
2. Vogel, Cresswell, Jeffery and Leicester, J., 1952, 531.
3. De Gaouck and Le Fèvre, J., 1938, 741.
4. Finn, Hampson and Sutton, J., 1938, 1254.
5. Bergmann and Weizmann, Trans. Farad. Soc., 1936, 32, 1318.
6. Cowley and Partington, J., 1933, 1259.
7. Van Vleck, Theory of Electric and Magnetic Susceptibility.
8. Barriol and Régnier, J. chim. phys., 1952, 49, 213.
9. Zetzsche, Silbermann and Vieli, Helv. chim. Acta., 1925, 8, 596.
10. Pfeiffer and Glaser, J. prakt. Chem., 1939, 153, 265.
11. Pfeiffer and Krebs, J. prakt. Chem., 1940, 155, 77.
12. Schiff, Ann., 1869, 150, 197.
13. Charles and Freiser, J. Amer. Chem. Soc., 1951, 73, 5223.
14. Barker, Chem. News, 130, 99.
15. Brady and Muers, J., 1930, 1599.
16. Godycki, Rundle, Voter and Banks, J. Chem. Phys., 1951, 19, 1205.
17. Everard and Sutton, J., 1949, 2318.
18. Hampson and Robertson, J., 1941, 409.
19. De Lange, Robertson and Woodward, Proc. Roy. Sdc., 1939, 171,A, 398.
20. Cavell and Sugden, J., 1935, 621.