MOLECULAR POLARISATION STUDIES.

A Thesis submitted to the
University of London
for the Degree of
Doctor of Philosophy.

By:

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October, 1952.

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 sincerely to express his appreciation of the help and encouragement that he has received from Dr. Smith during the course of this work. Grateful thanks are also due to Professor E.E. Turner, F.R.S. for his interest in the work, to Dr. D.M. Hall for her advice on some of the organic preparations, and 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.

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INTRODUCTION

This investigation is concerned chiefly with the study of substituted diphenyls; the remaining substances dealt with are those necessary to make the position more clear where a lack of agreement in existing data renders their interpretation difficult.

The first molecular polarisation measurements on diphenyl and its derivatives were published in 1928. There had been considerable controversy concerning the structure of the diphenyl molecule and it was thought that a study of the molecular polarisations of 4,4'-disubstituted diphenyls would help to clarify the situation. This was one of the earliest attempts at aiding the elucidation of molecular structure by dipole moment studies and, the method being in its early stages of development, the results were not as conclusive as was hoped.

Bretscher (1) made measurements, in benzene solutions, of diphenyl, 4,4'-difluoro-, 4,4'-dichloro- and 4,4'-dibromodiphenyl and found that they each had zero dipole moment. These results he was readily able to explain on the basis of a diphenyl molecule having coplanar rings. However, he also measured the moments of 4,4'-diamino- and 4,4'-dimethoxydiphenyl and found values of 1.43D and 1.52D respectively; for these results he offered no explanation.

In the same year Williams (2) published polarisation data for a large number of compounds including several diphenyl derivatives and he arrived at the conclusion that it was not possible to express the structure of diphenyl and its derivatives by a simple spacial arrangement. Shortly after this Williams and Weissberger (3), in a paper devoted more specifically to the structure of diphenyl, confirmed Bretscher's results and explained satisfactorily the previous anomalous results for 4,4'-dialkoxydiphenyls on the basis of angular oxygen bonds. They had, however, to resort to a folded structure in the case of 4,4'-diaminodiphenyl since their measurements on p-phenylene diamine showed it to have a moment indistinguishable from zero. Later work has failed to confirm this and the accepted value of the dipole moment of p-phenylene diamine is about 1.5D (4), (5), thus removing the barrier to the explanation of the moment of 4,4'-diaminodiphenyl on the basis of a molecule having coplanar rings.

In the following year Weissberger and Williams (6) reviewing the position showed that for 4,4'-disubstituted diphenyls having substituents of the type -Cl or $-NO_2$, formulae in which the rings were coaxial but in planes inclined to one another were valid equally with formulae in which the rings were coplanar. Also, for 4,4'-disubstituted diphenyls in which the substituent groups contained oxygen linkages with mutually inclined valencies they discussed the possibility of rotation within the molecule giving rise to cis and trans type isomers. They did not however reach any positive conclusions, preferring to wait for further experimental results; this was also their attitude to the then still anomalous case concerning p-phenylene diamine and 4,4'-diaminodiphenyl.

In the same paper these authors considered the case of 2,2'-dicarboxymethyldiphenyl by the same technique of comparison with the corresponding benzene derivative i.e. dimethyl phthalate. Here the dipole moment of the latter is higher than that of any of the isomeric dicarboxymethyl diphenyls but some light was thrown on the subject by the consideration of the possibilities of cis-trans isomerism in the coaxial rings. Free rotation about the central bond of the diphenyl nucleus was shown to give a plausible explanation of the experimental results.

The results of an investigation similar to that just described were published in the same year by Bretscher (7) who expressed the view that, as regards polarisation measurements, there remained no evidence in favour of the Kaufler formula for diphenyl. He also deduced from his results for 2,2'-dinitrodiphenyl and 2,2'-dichlorodiphenyl the rotation of the rings relative to one another.

Weissberger and Sangewald (8) measured the moments of an assortment of compounds which included the isomeric monochlorodiphenyls together with 2,2'-dichloro- and 3,3'-dichlorodiphenyl. To the disubstituted diphenyls they applied the formula, based on the assumption of free rotation about the central bond,

$$\mu \text{ resultant } = \sqrt{2}.\mu$$

where μ was the value for chlorobenzene. From their results they deduced that the restriction to free rotation was small compared with that exhibited by dichlorethane. They further concluded that it was not possible to give a quantitative treatment of the rotatability of the rings in diphenyl on the basis of dipole moment measurements since the polarisation of the hydrocarbon nuclei was not accessible to quantitative study. Later results by Naeshagen (9) confirmed this point of view.

The first mathematical treatment of the moments induced in the unsubstituted ring of a monosubstituted diphenyl was that used by Hampson and Weissberger (10) in the interpretation of their redetermined results for the monochlorodiphenyls. This was an extension of the theory applied by them to the substituted naphthalenes (11) and was based on earlier work by Smallwood and Herzfeld (12) and Frank (13). For the symmetrical dichlorodiphenyls Hampson and Weissberger considered that the electrostatic attractive and repulsive forces largely compensate, and that it is primarily the London dispersive forces between the chlorine atoms that determine the configurations of the molecules. Their calculations on this basis showed that in the 2,2'-dichlorodiphenyl there would be considerable resistance to free rotation while in the 3,3'-dichlorodiphenyl there would be no significant inhibition of rotation.

Le Fèvre and Le Fèvre (14) measured a large number of mono- and disubstituted diphenyls together with their corresponding benzene derivatives in an investigation designed to give some information on the tautomeric effects in diphenyl derivatives. They proposed that since the mesomeric and tautomeric effects operate by the same mechanism, then the presence of mesomerism may be taken as evidence for the possibility of the existance of tautomeric effects. They also made calculations similar to those of Hampson and Weissberger (10) on the induced moments in the unsubstituted ring of monosubstituted diphenyl derivatives. The conclusions drawn from their experimental work were that mesomerism certainly existed and that the independent conjugation of the nuclei was generally not so complete as might have been expected from earlier discussions on the subject.

Le Fèvre and Vine (15) made measurements on a series of 2,2'-disubstituted diphenyls in which the substituent groups were large. They compared the values of the moments obtained with those of the related substances in which an additional pair of substituents had been added in the

4,4-positions, in an attempt to determine whether the substitution of large groups in the 2,2'-positions affected the collinearity of the 4,1,1',4'carbon atoms. The results were not in disagreement with the generally accepted view that the spacial arrangement of all derivatives of diphenyl is rectilinear. Small changes in moment were found with every pair of compounds studied but the authors did not consider it possible to decide whether these arose from departures from linearity or from other causes. The results indicated that several of the compounds were non-coplanar, the benzenoid rings being approximately at right angles to one another.

After a gap of several years Lumbroso (16) reinvestigated the subject of the angles between the planes of the rings. He showed that 4,4'-substituents have little effect on this angle, which is primarily determined by the 2,2'-substituents, and discussed numerous other factors affecting the rotation including those dealt with previously by Hampson and Weissberger (10).

The latest work, published since many of the measurements reported here were made, has been that of Everard, Kumar and Sutton (17) and Everard and Sutton (18) which deals with the electronic displacements in conjugated systems. The chief point arising from this work would appear to be the inadequacy of the Hampson and Weissberger treatment and the necessity for a non-classical inductive effect within the conjugated system acting through the medium of the π-electrons similarly to the mesomeric effect.

The work reported in this thesis was designed to add to the knowledge of the effects upon the polarity of the molecule of the introduction of substituents in various positions, which is of importance in relation to the spacial arrangement within the molecules and to the character of the central bond. A systematic investigation of the apparent dipole moments of numerous diphenyl derivatives in benzene solutions has been carried out, the compounds chosen being those with essentially simple substituent groups accessible to straightforward vectorial analysis.

CHAPTER I.

METHODS OF RESEARCH

Section I.

Apparatus

The application of the Clausius-Mosotti-Debye equation to the determination of the molecular polarisation of a polar compound in the gaseous state was extended by Debye to the case of dilute solutions of a polar compound dissolved in a non-polar solvent. For the calculation of the molecular polarisation and the dipole moment of a compound by this method it is necessary to determine the dielectric constants, refractive indices, and densities of a series of solutions of graded, moderately low, concentrations. The apparatus required for the determination of these quantities will be described in this section.

Determination of Dielectric Constants.

It was desired to measure dielectric constants ranging between 2 and 3 with an accuracy of about ± 0.0001 and for this purpose an apparatus based on the heterodyne **beat** principle appeared most satisfactory. The apparatus used was that designed by Few, Smith and Witten (1) and built by A.V. Few (2) to whom the present author is indebted for valuable advice on its use and maintenance. In it one side of the tuned circuit in each of the two oscillators was earthed, thus enabling the adjustment of the tuning condensers without changes in the frequency due to hand capacitance. Variations of frequency were reduced by supplying the screen-grid and anode potentials from a single unit, the beat frequency being insensitive to deliberately imposed variations of these potentials. The two oscillators were connected to the same low tension source. All anode leads and screen-grid leads were decoupled to prevent interaction, the use of electron coupling to mix the two high frequency oscillations (vide Groves (3)) completely eliminated all tendency for 'locking-in' to occur. High quality short wave tuning condensers were used, and the inductances were made of 24 S.W.G. enamelled copper wire closely wound onto Paxolin formers.

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., 2in. 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}	1μF - 350 volts
C_8	1μF - 800 volts
C_{10}	0.25μF - 450 volts
C_{14}, C_{15}	2μμF 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

The apparatus (Figures 1 and 2) consisted of a crystal controlled oscillator operating at a frequency of 10^6 cycles per second, and a variable frequency oscillator containing in the circuit the precision condenser and the dielectric cell. Since the precision condenser used had a capacity range of $300\mu\mu F$ it could be matched against the dielectric cell with the maximum accuracy over the whole of the required range if the capacity of the latter, with air as dielectric material, was approximately $100\mu\mu F$. To ensure full use of the scale of the precision condenser the inductance was chosen to give resonance at a frequency of about 10^6 c.p.s. with a total capacity of about $450\text{-}500\mu\mu F$ in the circuit. This figure allows about $100 - 150\mu\mu F$ for the minimum values of the adjustment condensers, lead capacities, etc. By introduction of these quantities into the equation,

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

the required value of the inductance was found to be about 50 microhenries.

The fixed frequency obtained from the quartz controlled oscillator was mixed with that from the variable oscillator in a special valve, the output from which was fed to an anode bend detector. An earphone was necessary in the detector anode circuit for rapid approximate setting of the main condensers when matching a new solution involving a large change of dielectric constant. The final setting to very low beat rates, about 1 - 2 per second, was made by using the microammeter in series with the earphone, the deflection of this meter increasing

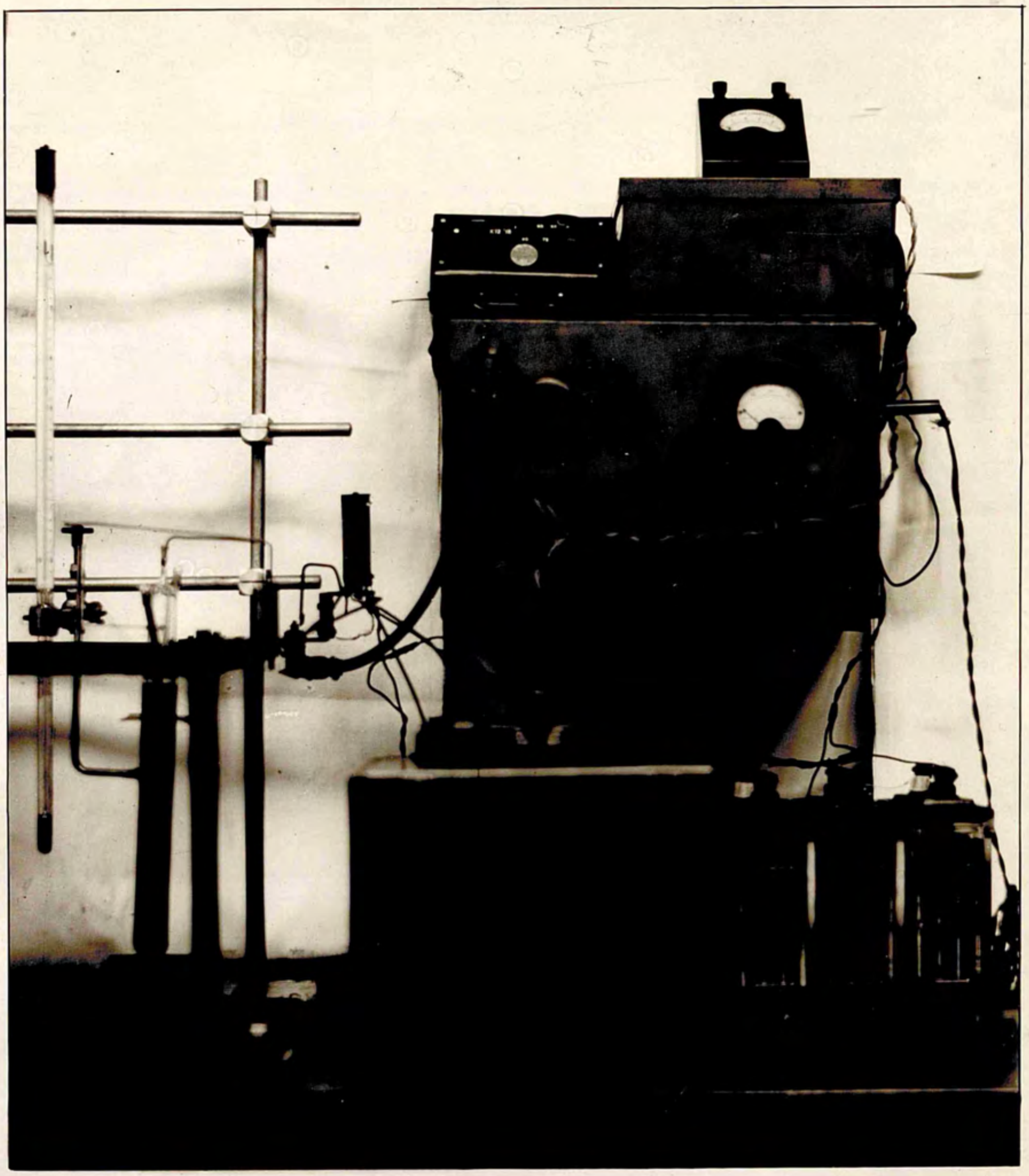


FIG. I. HETERODYNE BEAT APPARATUS.

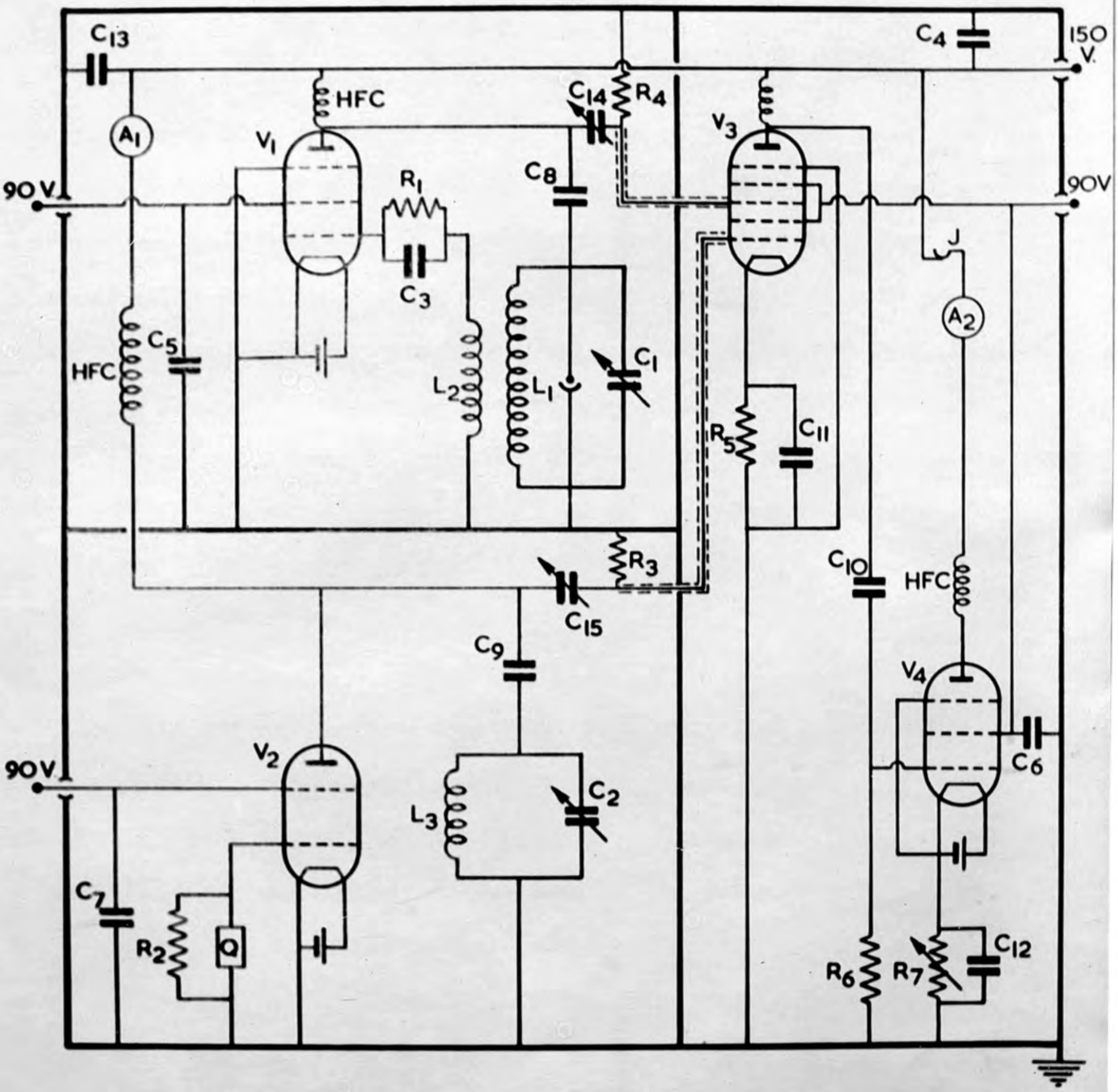


FIG. 2. CIRCUIT DIAGRAM OF HETERODYNE BEAT APPARATUS

decreasing with each beat. Maximum change of deflection during each beat was attained by adjusting each oscillator separately to give the same increase in detector anode current above that obtained when both oscillators were switched off.

The use of the substitution technique made it possible to introduce either the dielectric cell or the precision condenser into the tuned circuit, the other meanwhile being earthed on both sides. This allowed very rapid matching of the capacity of the precision condenser to the capacity of the dielectric cell, thereby minimising the errors due to the possible frequency drift of one of the oscillators. The oscillators were housed in metal containers; interconnections and connections to the dielectric cell and precision condenser were made by screened cable.

High Tension Supply.

In this investigation the high tension supply was drawn from the A.C. mains using a Clarke's 'Atlas' eliminator from which a number of set values of the potential could be picked off. A potential of 150 volts on the anodes and of 90 volts on the screen grids of the valves was found to be the most satisfactory combination of the available values. 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. (Figure 3.)

Since it can be operated by a bell-push situated at a

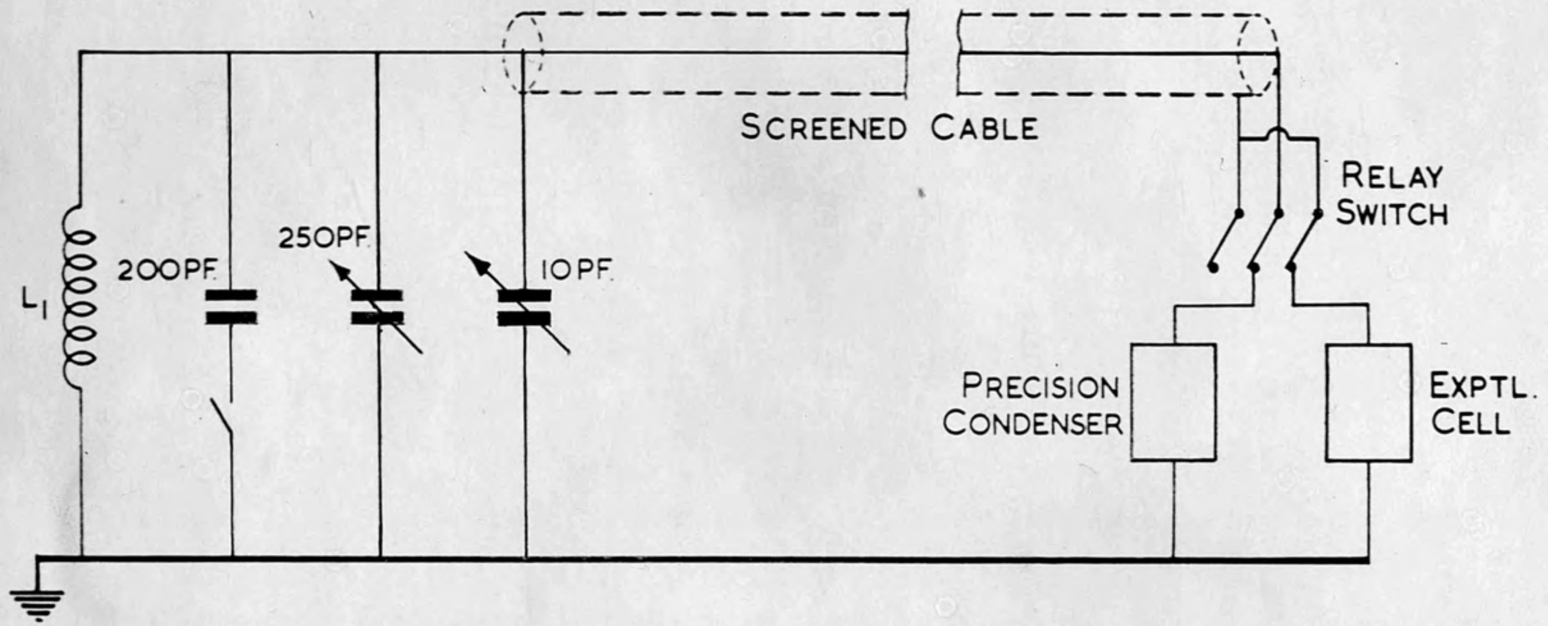


FIG. 3. VARIABLE FREQUENCY OSCILLATOR TUNED CIRCUIT

convenient point this switch is preferable to the mercury cup type. Stray capacities were reduced by positioning the relay near to the dielectric cell platform and the precision condenser, thus permitting the use of short leads. The connection from the oscillator compartment to the relay was made by low capacity screened cable, and rigid 12 S.W.G. brass rods were used for the leads to the dielectric cell platform and to the precision condenser these being arranged so that the earthed lead provided adequate screening of the radio frequency lead. The relay connections were arranged so that when the dielectric cell was in the oscillator circuit both sides of the precision condenser were earthed. Repeated tests indicated that the capacity associated with the relay unit remained constant during use, but to ensure correct operation the relay contacts were cleaned with a fine emery paper and finally polished with silk before each set of measurements.

Precision Condenser.

A Sullivan N.P.L. certificated, direct drive, precision variable air condenser was used, having a minimum capacity of 65μμF and a maximum capacity of 365μμF. The condenser had a finely divided degree scale consisting of 720 directly engraved divisions, and was fitted with a simple microscope and a vernier reading directly to one-twentieth of a scale division. This could be increased to one-fortieth of a scale division by estimation, such a division corresponding approximately to 0.01μμF.

Using a dielectric cell with a capacity of 100μμF when air was the dielectric the scale accuracy enabled the dielectric constants of the solutions to be determined to an accuracy of ± 0.0001. The taper bearing of the condenser allowed very small increments of capacitance to be made and by applying a small torque to the capstan head the beat frequency could be changed by a few cycles per second. This showed complete freedom from backlash in the condenser and it was possible to adjust it to a far higher degree of precision than that with which the scale could be read.

The condenser was calibrated by the 'step' method, using the heterodyne beat apparatus. The precision condenser was adjusted to read zero, and by operating the relay a small fixed condenser was introduced into the circuit. The fixed condenser used was due to the capacity associated with the leads from the relay to the dielectric cell platform. The oscillators were then matched to zero beats by adjustment of the trimming condensers in the variable frequency oscillator, the fixed condenser was then removed from the circuit by the operation of the relay and the oscillators were again matched by adjustment of the precision condenser. The new reading was recorded. The precision condenser was readjusted to zero and the above operations repeated. The mean of several readings was taken as the correct capacity increment.

The precision condenser was then adjusted to this mean reading and the process repeated for the second 'step'. In this fashion the whole of the scale of the condenser was calibrated. Checking repeats were made at several points of the scale and the calibration was found to be satisfactory within the limits of the scale reading accuracy. The results obtained are shown in Figure 4.

While it was endeavoured to adjust the capacity of the precision condenser so that when it was in the circuit the beat frequency was the same as when the dielectric cell was in the circuit, it was also desirable to determine the corresponding change in the beat frequency when the precision condenser was adjusted by the minimum capacitance change detectable on the scale.

From

$$f = \frac{1}{2\pi\sqrt{LC}} \qquad (1)$$

differentiation with respect to C (L remaining constant) gives

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

dividing (1) by (2)

$$\frac{df}{f} = -\frac{dC}{2C} \qquad (3)$$

As $f = 10^6$ c.p.s. and $C = 500 \times 10^{-12}$ F (approx.), for a change of capacity $dC = 0.01 \times 10^{-12}$ F, from (3),

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

$$\text{i.e. } df = 10 \text{ c.p.s.}$$

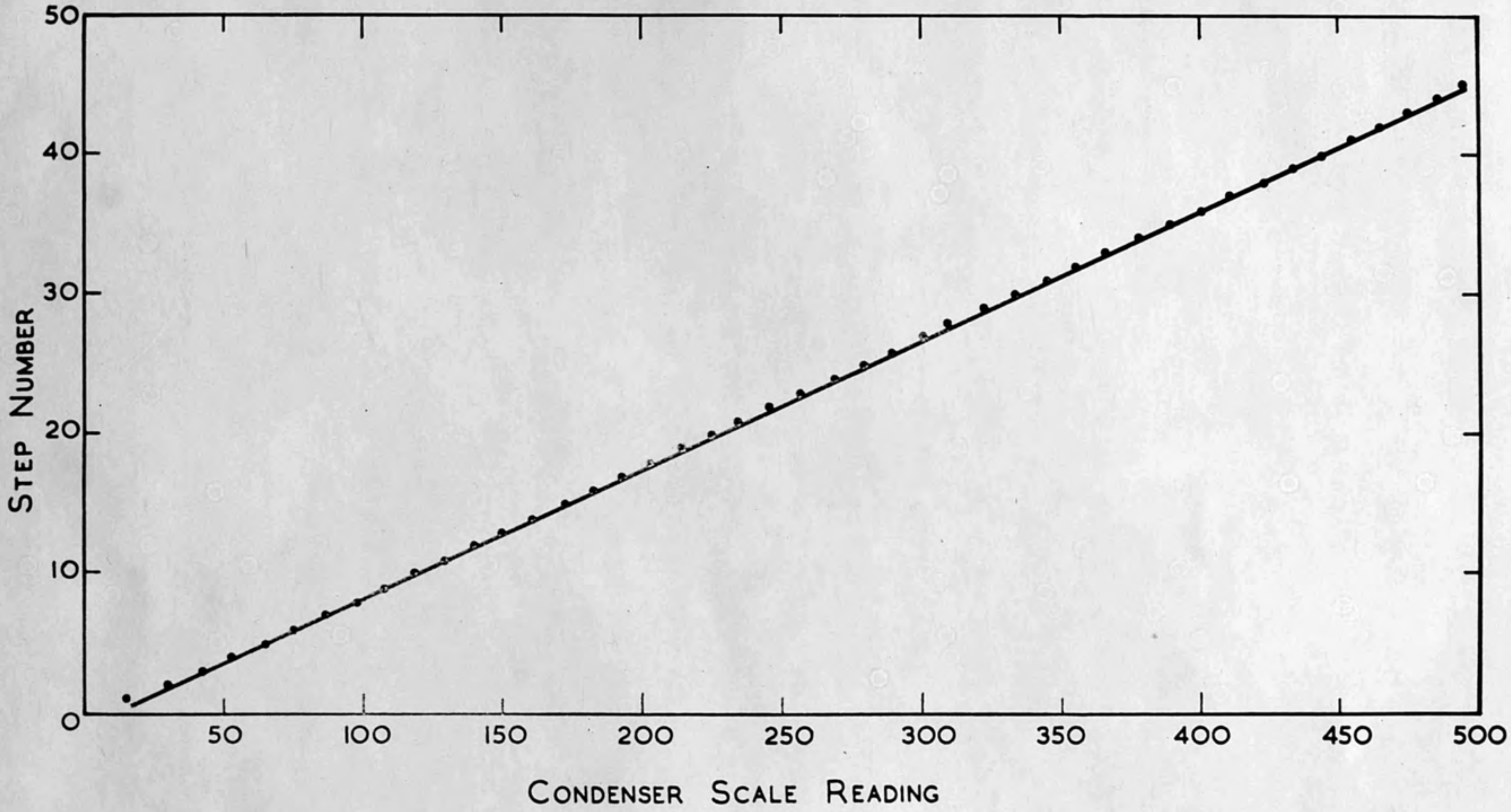


FIG.4. CALIBRATION OF PRECISION CONDENSER SCALE

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

Dielectric Cell. (Figure 5)

The dielectric cell was basically of the type first introduced by Sayce and Briscoe (4) . Access to the annular space was provided by two 3mm. bore capillary tubes which, together with the outer platinum electrode connection tube were supported by glass tie-arms connecting them to the main body of the cell. These arms greatly increased the cell's resistance to mechanical strain, and therefore improved the stability of its electrical capacity. The platinum wire serving as a connection to the inner surface of the cell was extended along the axis and fused into a glass cup at the top of the cell.

The cell was silvered to within 5cm. of the internal seal by the method introduced by Sugden (5), four applications of the silvering solution being found to give a satisfactory coating. The presence of a gold-leaf guard-ring fitted to the outer surface rendered it impossible to see the level of the silvering solution and it was necessary to add a constant volume of the solution for each coating in an attempt to get uniform upper edges to the resulting plates. When not in use the cell was kept filled with pure benzene to preserve the silvered surfaces.

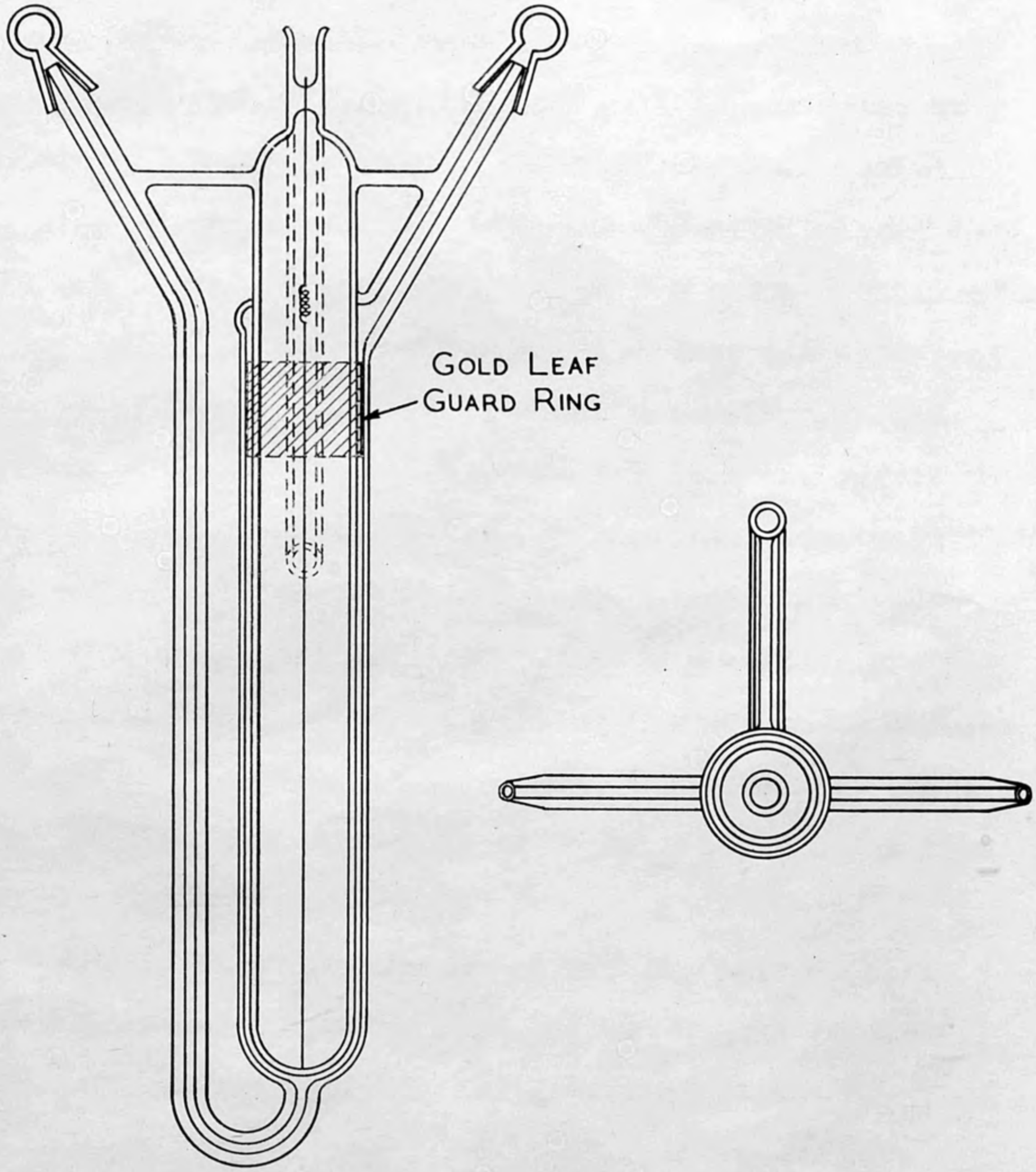


FIG. 5. DIELECTRIC CELL

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. Also earthing the outer plate provides an almost complete electrostatic screen and the cell approximates very closely to a perfect condenser. However, there does exist a small edge effect, due chiefly to the capacity between the edges of the inner silvered surface and the earthed thermostat and it was with the idea of reducing this that the gold-leaf guard-ring was introduced; the dielectric involved in the edge effect is partly the solution in the cell and partly the outer glass wall of the cell. In addition there exists a very small effect due to the capacity between the inner platinum connecting wire and the earthed thermostat, the dielectric again being mixed, involving the air space between the wire and the inner glass cell wall, the solution, and the two glass walls. This effect is of a much lower order than the former and can be neglected.

The edge effect of the Sayce and Briscoe type of cell has been studied in detail by Ball (6) and Sugden (loc.cit.) in their study of the absolute dielectric constants of liquids up to a value of about 30. On ignoring the edge effect the experimentally determined values were found to be slightly lower than the absolute values, the discrepancy increasing with increase of the dielectric constant of the substance under examination. The edge capacity correction, C, involving a mixed dielectric, was shown by Sugden (loc.cit.)

to be related to the dielectric constant of the liquid, ϵ_1, and to that of the outer wall, ϵ_2, by the following equation

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

where d_1 and d_2 are the thicknesses of the dielectric layers of liquid and glass wall respectively. The edge effect is therefore neither proportional to, nor independent of, the dielectric constant of the liquid.

The present work has involved the measurement of dielectric constants of solutions varying only slightly from that of the pure solvent which had itself a dielectric constant of 2.27 so that the edge correction is small. It was determined by the technique of Sugden in which the capacity of the cell was measured both near to, and remote from, earthed conductors, the change of capacity being a measure of the cell correction. A copper collar was constructed which fitted closely the outer glass wall of the cell. It was about 3cm. long and was earthed. By allowing the collar to slide below the level of the edge of the silvered surfaces, and also to move up above these surfaces, this earthed screen simulated the absence and presence of the earthed thermostat water.

The dielectric cell was supported in an air thermostat at 23°, remote from earthed conductors. The collar was adjusted to a position below the level of the edge of the silvered surfaces and the capacity, with nitrogen as dielectric, was then determined. The collar was moved up so that its upper edge was at the level generally occupied by the surface of the thermostat water, and the capacity again determined. This value was slightly greater than in the former case, the difference corresponding to the capacity between the inner silvered surface and earthed material outside the cell. The procedure was then repeated with liquids covering the dielectric range 1.9 to 2.7. A graph was plotted (Figure 6.) giving the variation of the edge correction with dielectric constant of the liquid contained in the cell (line I) together with the figures obtained by Few (loc.cit. p.18) for a cell not having a guard-ring (line II). The correction in the latter case is seen to be about ten times that found in the present investigation. Few, following previous workers, showed that the edge correction was cancelled by the correction to be applied on account of the use of $\epsilon = 1$ for the dielectric constant of nitrogen in the calculation of results, in such a manner that the calculated dielectric constants were correct within the limits of experimental error. In the present work this is found to hold only up to the value $\epsilon = 2.6$ (vide Method of Calculation of Dielectric Constants). This includes all measurements except that upon the most concentrated solution of 4- nitrodiphenyl and in this case the necessary corrections were made.

The dielectric cell was supported in the thermostat by a brass stand which was constructed so that the cell could

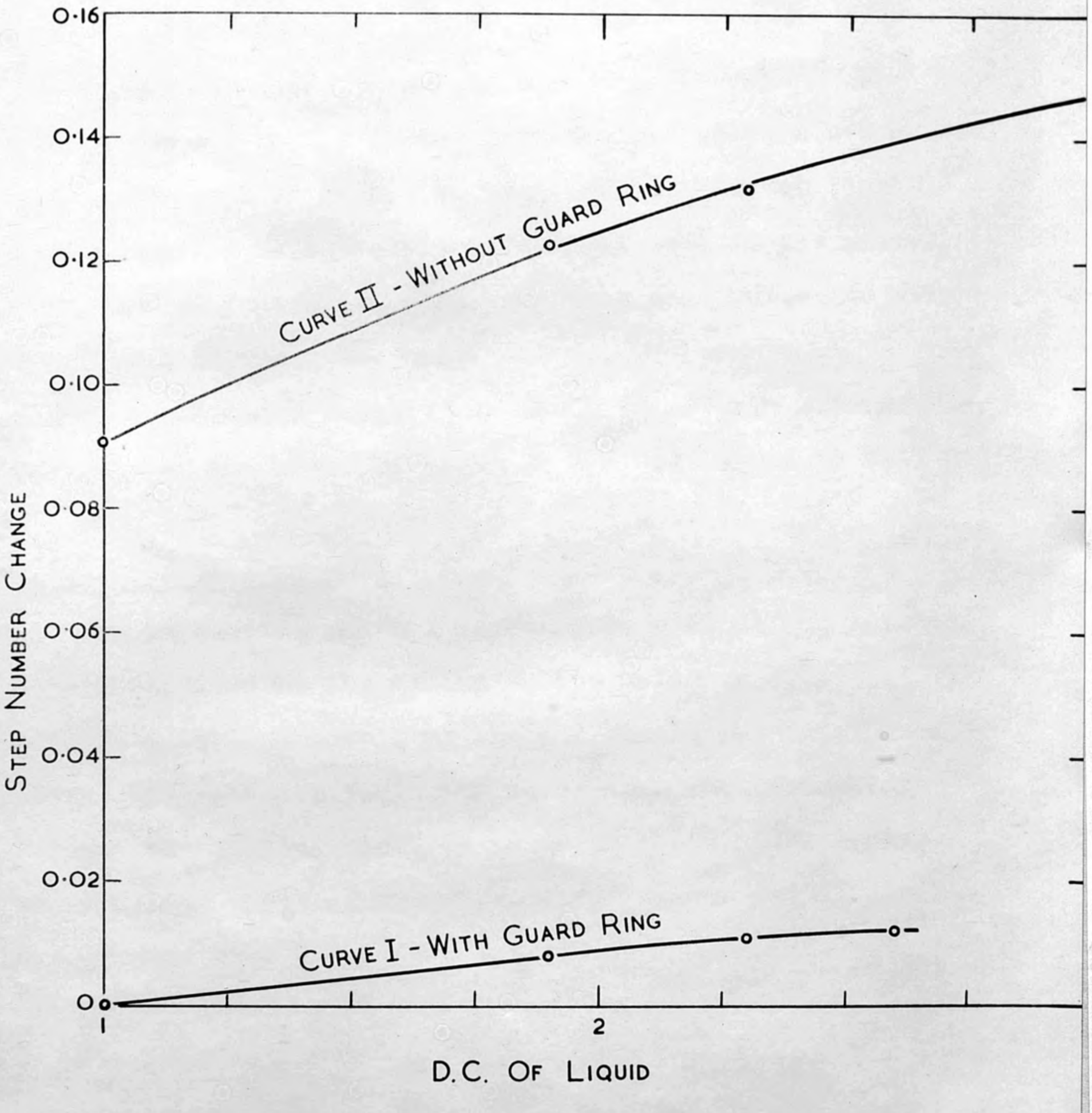


Fig. 6. Dielectric Cell Edge Correction

be easily inserted and removed. It was important to ensure that the stand did not strain the cell, since otherwise changes in its capacity resulted.

A Distrene platform was bolted onto the side of the thermostat and it was fitted with two stainless steel mercury cups. Two rods of 12 S.W.G. brass, bent twice at right angles, served as connections from the cell to the mercury cups, and further brass rods were used as connections from these cups to the relay unit.

The cell had a capacity of about $90 \mu\mu F$ with nitrogen as dielectric, and required about 20 c.c. of liquid to fill it.

Refractive Indices

The refractive indices of the pure solvent and solutions were determined at the sodium D-line using an Abbé refractometer. The cell of the instrument was maintained at 25° by rapidly circulating water from the thermostat through the heating block by means of a centrifugal pump. The absolute error of the refractive indices was in general not greater than $\pm$ 0.0001.

Densities

The densities were determined relative to the density of water at 4° as unity. For this a modified Sprengel type pyknometer (Figure 7.) was used with a capacity of a little over fourteen cubic centimetres. It had two fine

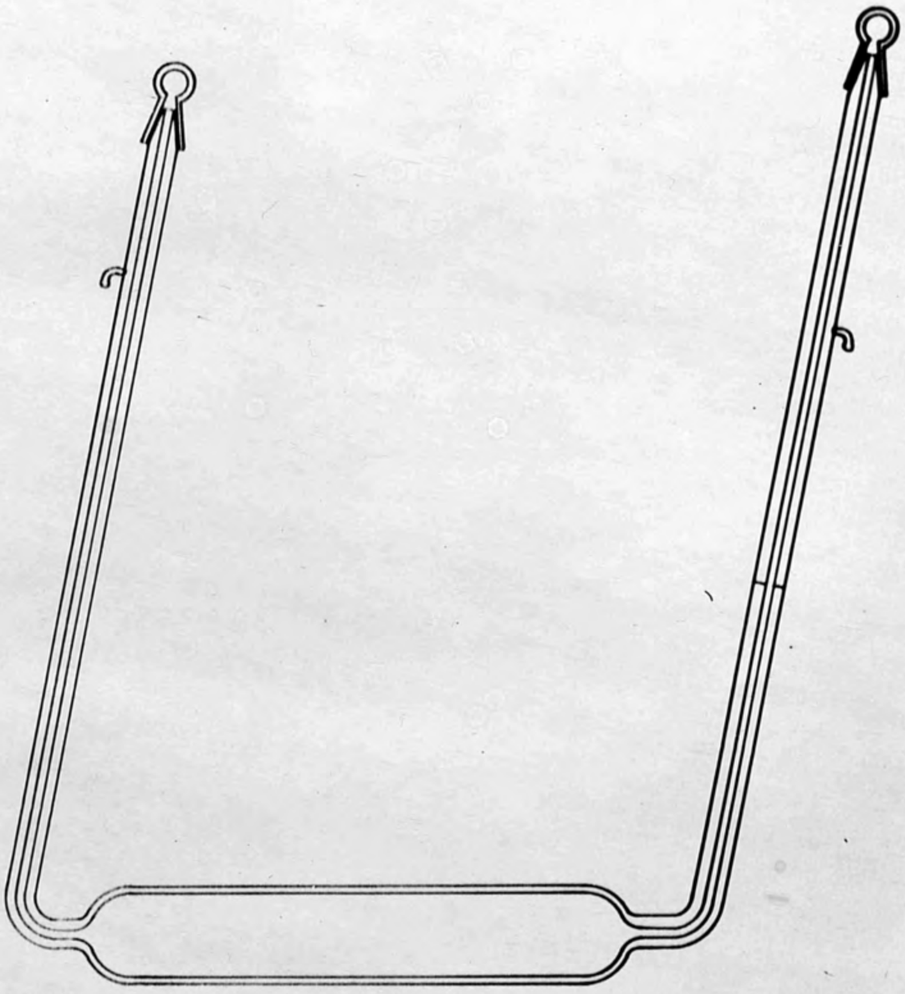


FIG 7. PYKNOMETER

bore capillary side arms which were fitted with ground glass caps to prevent losses by evaporation, and it was provided with a removable stainless steel stirrup for easy attachment to the balance. When in the thermostat it was supported by a brass frame.

Repeated tests with boiled out, distilled water indicated that the accuracy of the densities depended, for the most part, on the sensitivity of the balance used and not on the adjustment of the pyknometer to constant volume, the absolute error being about ± 0.00002.

Weighings

A Stanton Model C.B.3. balance was used in the preparation of the solutions and for the determination of the densities. It had a sensitivity of 2.3 divisions per milligram throughout the range used, enabling the weighings to be made accurate to 0.1 milligram. Stainless steel weights were calibrated against a N.P.L. certificated five milligram rider, and all glass apparatus to be weighed was carefully cleaned and handled with silk throughout. All apparatus 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 by more than two degrees during the course of the day, but in order to prevent large frequency drifts the apparatus was shielded from direct sunlight.

The thermostat was filled to a constant level with water which was earthed, the level being marked on the glass wall of the tank. It was kept efficiently agitated by the use of an electrically driven stirrer. A toluene-mercury spiral regulator operated the carbon filament heating lamp through a Sunvic Type E.A.2. electronic relay and was adjusted to maintain the thermostat at 25^{o} ± 0.002^{o}. The temperature registered by the Beckmann thermometer showed no detectable variation when it was moved to numerous points in the thermostat; the thermometer had previously been calibrated by comparison with a N.P.L. certificated thermometer.

Section II.

Method of Calculation of the Dielectric Constants

No attempt has been made in this investigation to determine absolute dielectric constants, attention having been paid primarily to the accurate determination of the relative dielectric constants of solutions differing only slightly from the value for the pure solvent.

Two reference substances were used in the determination of dielectric constants, namely

pure dry benzene $\epsilon_{25} = 2.2725$ (Hartshorn and Oliver(7))

dry nitrogen $\epsilon_{25} = 1.0005$ (I.C.T.)

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

If C_o = capacity of the cell in vaccuo,

then, $C_o\epsilon_N$ = capacity of cell with nitrogen as dielectric,

$C_o\epsilon_B$ = " " benzene " ,

$C_o\epsilon_S$ = " " solution " .

If R_N, R_B and R_S are the corresponding step numbers and C_L is the capacity of the cell leads to the relay unit etc. (assumed constant throughout the course of a run),

then,

$$C_o\epsilon_N + C_L = R_N \qquad (1)$$

$$C_o\epsilon_B + C_L = R_B \qquad (2)$$

$$C_o\epsilon_S + C_L = R_S \qquad (3)$$

From (1) and (2)

$$C_o \left(\epsilon_B - \epsilon_N \right) = R_B - R_N \qquad (4)$$

From (1) and (3)

$$C_o \left(\epsilon_S - \epsilon_N\right) = R_S - R_N \qquad (5)$$

Then

$$\frac{\epsilon_S - \epsilon_N}{\epsilon_B - \epsilon_N} = \frac{R_S - R_N}{R_B - R_N} \qquad (6)$$

$$\text{and } \epsilon_S = \frac{R_S - R_N}{R_B - R_N} \left(\epsilon_B - \epsilon_N \right) + N \qquad (7)$$

Hence a knowledge of the readings R_S, R_B and R_N and of the values ϵ_B and ϵ_N, the dielectric constants can be calculated from equation (7).

If

$$\frac{R_S - R_N}{R_B - R_N} = K,$$

then the values of ϵ_S when $K = 1$, 1.25 and 1.50 are

2.2725, 2.5905_0, 2.7085_0 .

Whereas, if the dielectric constant of nitrogen is assumed to be unity, then the corresponding values of ϵ , again calculated by equation (7), are

2.2725, 2.5906_3, 2.7087_5,

and the error introduced is

zero $+ 0.0001_3$, $+0.0002_5$.

The values for the solutions being slightly higher in this case than those calculated using 1.0005 as the dielectric constant of nitrogen.

In previous investigations it had been found that the error introduced by assuming that the dielectric constant of nitrogen is unity instead of 1.0005 was nullified by the cell edge correction.

Evaluation of the Edge Correction

Using the graph of the edge correction (Figure 6, line I) the following corrected values of the dielectric constants, for K = 1.25 and 1.50, may be obtained;

$$\epsilon_1 = 2.5906_6 \quad \text{and} \quad \epsilon_2 = 2.7088_0$$

for which the corresponding uncorrected values are

$$\epsilon_1 = 2.5906_3 \quad \text{and} \quad \epsilon_2 = 2.7087_5 \quad .$$

The effect of the edge correction being zero at the dielectric constant of the calibrating liquid, benzene.

The total errors, nitrogen error and edge correction are tabulated below.

d.c. of solution	Nitrogen error	Edge error	Total error
2.2725	-	-	-
2.59	$+0.0001_3$	-0.0003_3	$+0.0001_0$
2.71	$+0.0002_5$	-0.0000_5	$+0.0002_0$

Thus it may be seen that if the dielectric constant of nitrogen is assumed to be unity and if the cell edge correction is ignored, the resulting dielectric constants, up to a value of $\epsilon = 2.6$, are free from both errors within the accuracy allowed by the scale of the precision condenser i.e. within ± 0.0001. This, as it has been stated above, is sufficient to cover all the measurements made in this investigation excepting that on the most concentrated solution of 4-nitrodiphenyl, and in this case the necessary adjustments have been made. The values of α obtained from the corrected and uncorrected figures in this instance were found to be identical.

Section III.

Calculation of the Molecular Polarisations and Dipole Moments

The molecular polarisation of a polar compound consists of two parts, the distortion polarisation, P_D, resulting from the displacement of the electrons and the atomic nuclei by the applied electric field, and the orientation polarisation, P_μ , due to the presence of the permanent dipole. It was first shown by Debye (8) that in the case of a polar compound the Clausius-Mosotti equation requires a further term due to the presence of the permanent dipole and the equation deduced by Debye was

$$P_2 = P_D + P_\mu = \frac{4\pi N\alpha}{3} + \frac{4\pi N\mu^2}{9kT} \qquad (1)$$

The derivation of this equation involved the assumption that the molecules are sufficiently far apart to prevent any interaction between them, and this restricts the use of the equation to gases at low pressures. Debye, however, pointed out the analogy of the kinetic behaviour of a solute in dilute solution and the equation derived for the molecular polarisation of a substance in the ideal gas state should be applicable to the case of a substance at low concentration in a non-polar solvent, provided that there is no specific mutual interaction. The polarisation of the solution, P_{12}, is then equal to the polarisation contributions of the solvent and solute,

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

The subscripts 1, 2 and 12 refer to the solvent, solute and solution respectively. From this equation the molecular polarisation of the solute can be calculated, assuming that the polarisation of the solvent remains constant over the range studied. The value of P_2 derived from this equation varies with the concentration of the solution in a manner which, so far, cannot be calculated on any theoretical basis.

Two methods are available for the determination of the molecular polarisation at infinite dilution, $P_{2\infty}$, the first of which involves a graphical extrapolation of the curve produced by plotting the calculated polarisation at each concentration against the weight fraction of the solute present. Sugden (9) has shown that the calculation of P_2 from equation (2) can be simplified by the use of the specific polarisations. The molecular polarisation, P_2, being equal to the product of the specific polarisation, p_2, and the molecular weight, M_2, it follows from equation (2)

$$P_{12} = P_1f_1 + P_2f_2$$

that

$$p_{12} = p_1w_1 + p_2w_2 \qquad (3)$$

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

Also,

$$p_{12} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot v_{12} \qquad (4)$$

where v_{12} is the specific volume of the solution.

Since $$w_1 = 1 - w_2 \qquad (5)$$

then, from (3) and (5)

$$p_2 = p_1 + \frac{p_{12} - p_1}{w_2} \qquad (6)$$

and therefore

$$P_2 = M_2 p_2 = M_2 \left\{ p_1 + \frac{p_{12} - p_1}{w_2} \right\} \qquad (7)$$

The values of P_2, calculated by equation (7), are then plotted against the weight fraction of the solute present and the curve extrapolated to $w_2 = 0$.

This method of calculation of P_2 is subject to two disadvantages. Firstly, the calculation of $P_{2\infty}$ at a particular concentration involves the difference between two terms, p_{12} and p_1, which are nearly equal, and the percentage error in P_2 increases as w_2 decreases. Secondly, there is no knowledge of the manner in which P_2 varies with the concentration of the solute present. Consequently the extrapolation is, in many cases, uncertain.

The second method available, and that which was used in this investigation, is due to Smith and Cleverdon (10). In it the dielectric constant of the solution is assumed to vary with the weight fraction of the solute present according to the relation

$$\epsilon_{12} = \epsilon_1 + \alpha w_2 + \alpha' w_2 \qquad (8)$$

where α and α' are constants.

The value of the parameter α was determined by plotting the values of $\frac{\epsilon_{12} - \epsilon_1}{w_2}$ against w_2 and extrapolating linearly to $w_2 = 0$, the intercept at $w_2 = 0$ giving $\bar{\alpha}$. In this extrapolation proportionately greater weight was placed upon the values of $\frac{\epsilon_{12} - \epsilon_1}{w_2}$ corresponding to the higher concentrations, as these were liable to a smaller error than the values at the lower concentrations.

The specific volumes of the solutions were assumed to vary linearly with the weight fraction of the solute, according to the relation

$$v_{12} = v_1 + \beta w_2 \qquad (9)$$

where β is a constant.

The value of $\bar{\beta}$ was determined by the relation

$$\beta = \frac{\Sigma(v_{12} - v_1)}{\Sigma w_2}$$

this having the advantage that less weight is placed on the values of $(v_{12} - v_1)$ at low concentrations where the possible experimental error in $\frac{(v_{12} - v_1)}{w_2}$ is large. In most cases the value of β calculated at each concentration was constant, within the limits of experimental error, but any case in which it is found to vary with concentration may be dealt with graphically and the limiting value of β at $w_2 = 0$ obtained as in the case of the parameter α.

From the limiting values of the parameters α and β, the molecular polarisation at infinite dilution was calculated using the equation derived by Halverstat and Kumler (11)

$$P_2 = M_2 p_2 = M_2 \left\{ \frac{3\bar{\alpha} v_1}{(\epsilon_1 + 2)^2} + (v_1 + \bar{\beta}) \cdot \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \right\} \quad (10)$$

This equation may readily be derived by the combination of equation (4) with equations (6), (8) and (9) and differentiating the resultant expression. This method of calculation has the advantage over the former in that linear extrapolations are used which are based on reasonable assumptions; also any errors in the experimentally determined values of ϵ_{12} and v_{12} are evident before combination into polarisation terms, where individual errors become masked.

In practice the value of $P_{2\infty}$ by graphical extrapolation of the $P_2 - w_2$ curve to $w_2 = 0$, and also the value of P_2 obtained by the linear extrapolation of P_2 against the volume polarisation $\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2}$, to the value of P_2 at $\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$ i.e. the volume polarisation of the solvent, gives values which are in good agreement with those obtained from the parameters, but with a greater degree of uncertainty, and provide a check on these calculations.

Calculation of Dipole Moments.

From equation (1) it is evident that in order to determine the orientation polarisation and hence the dipole moment of a compound, it is necessary to evaluate the distortion polarisation. The dipole moment follows from the values of the distortion and molecular polarisations by substitution in equation (11)

$$P_{\mu} = P_{2\infty} - P_D = \frac{4\pi N\mu^2}{9kT} \qquad (11)$$

The distortion polarisation is itself composed of two terms, the electronic and the atomic polarisations. It was shown by Maxwell (12) that for a non-polar substance $\epsilon = n_{\infty}^2$, and substitution of the n_{∞}^2 value into the Lorentz-Lorenz molecular refraction equation leads to a value of the molecular refraction which is identical with the molecular polarisation calculated from the Clausius-Mosotti equation. Thus

$$[R_{\infty}] = P_D = P_A + P_E \qquad (12)$$

In the case of a polar compound, the molecular refraction calculated for light of long wavelength (infra red) is equal to the electronic and atomic polarisations, the oscillations being so rapid that only electrons and nuclei undergo displacement, the presence of a permanent dipole having no influence on the refractive index. Therefore, by observation of the refractive index in the infra red region of the spectrum, the total distortion polarisation can be calculated. This procedure is experimentally troublesome owing to the difficulty of observing the refractive indices in the infra red region. By measurements of the refractive index for light in the visible region, at which frequencies only the electrons undergo displacement, the electronic polarisation can be calculated. Sugden (13) has indicated that this value of the electronic polarisation is generally 1 - 2 c.c. greater than the value obtained by extrapolation of the refractive indices to infinite wavelength using a one-term Sellmeier equation. In general the atomic polarisation is small, usually not more than 5 c.c., and Jenkins (14) has pointed out that, although conflicting results exist, the more accurate the work, the lower is the value assigned for the atomic polarisation of a particular compound. There seems to be no clear relationship between dipole moment and atomic polarisation, and P_A values cannot be allotted to groups. The procedure now most usually adopted is to make a small allowance for P_A, and the total distortion polarisation is assumed to be equal to 1.05 $[R_D]$ where $[R_D]$ is the molecular refraction calculated for light at the wavelength of the sodium D-line. In the present work values of the dipole moment have been calculated assuming $P_D = [R_D]$ in order to facilitate comparison with existing data, but the values used in the discussion section of this thesis are exclusively those derived by the latter procedure, following Le Fèvre and Le Fèvre (15) who found that the total polarisation of diphenyl and of 4,4'-dichlorodiphenyl differed only slightly from the corresponding $[R_D]$ figures.

The molecular refractions may be calculated using an expression analagous to equation (7)

i.e.

$$[R_D] = M_2 r_2 = M_2 \left\{ r_1 + \frac{r_{12} - r_1}{w_2} \right\} \qquad (13)$$

where

$$r_{12} = \frac{n^2_{12} - 1}{n^2_{12} + 2} \cdot v_{12} \qquad (14)$$

and

$$r_1 = \frac{n^2_1 - 1}{n^2_1 + 2} \cdot v_1 \qquad (15)$$

Combination of equations (9), (13), (14) and (15) with the expression

$$n^2_{12} = n^2_1 + \nu w_2 \qquad (16)$$

i.e. the assumption of a linear variation of n^2_{12} with w_2, in a manner similar to that of Halverstat and Kumler for obtaining the molecular polarisation at $w_2 = 0$ leads to the following equation

$$[R_D] = M_2 \left\{ \frac{3\bar{\nu} v_1}{(n^2_1 + 2)^2} + (v_1 + \bar{\beta}) \cdot \frac{n_1^2 - 1}{n_1^2 + 2} \right\} \qquad (17)$$

where the parameter $\bar{\nu}$ is obtained from the expression

$$\bar{\nu} = \frac{\sum (n^2_{12} - n^2_1)}{\sum w_2} \qquad (18)$$

This method has the advantage that less reliance is placed on the values of $(n^2_{12} - n^2_1)$ at low concentrations where possible experimental errors are high.

The dipole moments were then determined using equation (11)

i.e.

$$P_\mu = P_{2\infty} - P_D = \frac{4\pi N \mu^2}{9kT}$$

hence

$$\mu = \sqrt{\frac{9kT}{4\pi N} \cdot P_\mu} \qquad (19)$$

$$= 0.22148\sqrt{P_\mu} \quad \text{at } 25^\circ \qquad (20)$$

where μ is expressed in Debye units i.e. 10^{-18} e.s.u.

It is evident that the uncertainty in the value assumed for the atomic polarisation causes a corresponding uncertainty in the calculated dipole moment, apart from any error in the value of the molecular polarisation or electronic polarisation. For molecules of low molecular weight (ca. 50-100) and possessing dipole moments greater than 1.5D the error introduced is small. For of higher molecular weight (ca. 200-300) and possessing dipole moments between 1.0 and 1.5D the error is of a larger order, as is readily seen from the results tabulated in Chapter II, Section II, e.g. in the case of 4-iododiphenyl

$$\mu\,(P_D = [R_D]\,) = 1.45D$$

and $$\mu\,(P_D = 1.05\,[R_D]\,) = 1.39D$$

The molecular polarisation is, therefore, the more satisfactory property on which to base comparisons between different polar molecules, especially in cases where the dipole moments differ only slightly.

Observational Errors

The accuracy with which P_2 can be measured depends not only upon the accuracy of the dielectric constant and specific volume determinations, but also upon the concentration of the solution, for as the concentration diminishes so does the quantity $(p_{12} - p_1)$ and errors in p_2, and hence P_2, may become considerable. The error in p_2 due to the above variables can be determined as follows:

from (6),

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

since p_1 is constant

$$\Delta p_2 = \frac{\Delta p_{12}}{w_2} \qquad (21)$$

and from (4),

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

partial differentiation with respect to ϵ_{12} gives

$$\frac{\partial p_{12}}{\partial \epsilon_{12}} = \frac{3v_{12}}{(\epsilon_{12} + 2)^2} \qquad (22)$$

and partial differentiation with respect to v_{12} gives

$$\frac{\partial p_{12}}{\partial v_{12}} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \qquad (23)$$

From equation (21) using equations (22) and (23)

$$\Delta p = \frac{1}{w_2} \left\{ \frac{3v_{12}\Delta \epsilon_{12}}{(\epsilon_{12} + 2)^2} + \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \Delta v_{12} \right\} \qquad (24)$$

If the error in the dielectric constants is ± 0.0001 and in the specific volumes is ± 0.00002, then at the average values of $\epsilon = 2.3$ and $v = 1.1$, the corresponding errors in p_2 are as follows,

at $w_2 = 0.05$ $\Delta p_2 = \pm 0.05\%$

at $w_2 = 0.01$ $\Delta p_2 = \pm 0.2\%$

The error in the value of the molecular polarisation at infinite dilution is more difficult to ascertain but by assuming a linear variation of P_2 with w_2, as is found to be permissable in most cases, the error is probably not greater than ± 0.02%, and in some cases is probably less than this.

The accuracy with which (R_D) can be measured also depends, not only on the accuracy of the refractive indices and specific volumes, but also on the concentration of the solution. By a procedure analagous to that used for the determination of the errors in p_2, the error in (R_D) can be calculated from equation (13)

i.e.

$$\Delta r_2 = \frac{1}{w_2}\left(\frac{6n_{12}v_{12}\Delta n_{12}}{(n_{12}^2 + 2)^2} + \frac{n_{12}^2 - 1}{n_{12}^2 + 2} . \Delta v_{12} \right) \qquad (25)$$

If the error in the refractive indices is ± 0.0001 and the error in the specific volumes is, as before, ± 0.00002, then at the average values of $n = 1.50$ and $v = 1.1$ the corresponding errors in r_2 are as follows

at $w_2 = 0.05$ $\quad r_2 = \pm 0.1\%$
at $w_2 = 0.01$ $\quad r_2 = \pm 0.6\%$

The errors determined above are due to the limitations imposed by the measuring instruments used, and do not take into account systematic errors, and errors due to the evaporation of solvent and/or solute, or to the entrance of moisture during the course of a "run". These possible errors, however, have been minimised by adopting the procedure described in the following section.

Section IV.

Experimental Procedure

In the early work undertaken to determine the overall accuracy of the apparatus, using compounds such as p-chloroaniline (16) that had been the subject of accurate measurements by previous workers, it was found that in order to arrive at an accurate value of the molecular polarisation and hence of the dipole moment of a polar substance, it was desirable to use about six solutions of graded concentrations, preferably in the range 1 - 10% w/w. Any attempt to work with more dilute solutions generally resulted in a large error in the calculated molecular polarisation. It is also evident that many values have been published which are subject to errors due to the above factor, and to the use by some investigators of too few solutions. For example, the value of the molecular polarisations of 2-chlorodiphenyl and 3-chlorodiphenyl at infinite dilution in benzene were reported by Weissberger and Sangewald (17) as 90.5 c.c. and 123 c.c. respectively, later Hampson and Weissberger (18) using the same samples reported values of 100.2 c.c. and 113.5 c.c. respectively, a change in each case of the order of 10%.

Preparation of the Solutions

The solutions were prepared in 150 c.c. 'Quickfit', ground glass stoppered flasks, which were graduated at 90 c.c., 100 c.c., and 110 c.c. so that an approximately known volume of solvent could be rapidly introduced. They were cleaned before each 'run' with alcohol-nitric acid cleaning mixture and washed well with distilled water. They were then dried overnight in an electrically heated oven controlled at 120° and after cooling in a dessicator dry nitrogen was passed into them from a cylinder in order to displace the air. The outsides of the flasks were carefully cleaned with silk and the flasks placed in the balance case and weighed accurately to 0.1 mg. The solute was then introduced rapidly into the flasks which were again weighed accurately to 0.1 mg. The solvent was added directly from its container by use of the transference apparatus (Figure 8), the volume added being controlled by the operation of the screw-clip. A sample of the solvent was transferred to a further 150 c.c. flask by the same technique at the same time, so that any possible slight contamination of the solutions by water vapour during the period between preparatio and use, also occurred with the solvent. The solution flasks were then weighed accurately to 0.1 mg.

This procedure was adopted throughout the work, the method of adding the solute depending on its physical state. Thus liquid solutes were introduced to the flasks from a burette closed at its upper end by a tube of drying agent, and solid solutes, in a finely powdered condition, were introduced into the flasks with the aid of a short-necked funnel.

Determination of the Dielectric Constants

Owing to the high dielectric constant of water, the dielectric constants of the solutions were very sensitive to traces of moisture. In order to minimise the errors possibly introduced the dielectric constants were measured before the determination of the refractive indices and densities.

The thermostat was filled with water at approximately 25° and equilibrium conditions allowed to become established; at the same time the heterodyne beat apparatus was switched on and allowed to warm up during one hour before any measurements were taken. The dielectric cell was dried by passing nitrogen through it during the same period. The ground glass caps were then fitted in position and the dielectric cell was lowered into the brass stand in the thermostat bath, fifteen minutes being allowed for the cell to reach the temperature of the thermostat. The tuning condensers were then adjusted for resonance with the cell in the circuit, and the capacity of the precision condenser was roughly matched to that of the cell. The thermostat motor was then switched off, as slight variations in the level of the water contained in the bath were found to affect the stray capacities to a small extent, the precision condenser was finally accurately matched to the capacity of the cell by visual observation of the beat frequency, care being taken always to match on the high capacity side of the zero beat position. The cell was then lifted slightly from its holder and replaced, the reading again being noted; this procedure was repeated at least once more, and was necessary in order to confirm that the cell and its lead were correctly in position. In general the readings were identical but occasionally there was a slight shift, and then they were repeated until a constant value was obtained.

The cell was removed from the thermostat and the outside dried, and was filled with pure solvent by use of the transference apparatus (Figure 8), the delivery tube having been ground to fit inside the cell's side arm, this prevented the entrance of air and moisture into the cell. It was then replaced in the thermostat and the readings noted as before. The solvent was poured out of the cell, and the cell was rinsed out three times with the first of the solutions before being filled with it. The cell was then replaced and the readings taken. This procedure was repeated with the remaining solutions and, finally, the nitrogen and pure solvent readings were rechecked. If there had been any slight shift in the capacity of the cell or of the stray capacities associated with it, these nitrogen and solvent repeat readings were different from the values recorded initially, and the mean values were used in computing the dielectric constants of the solutions.

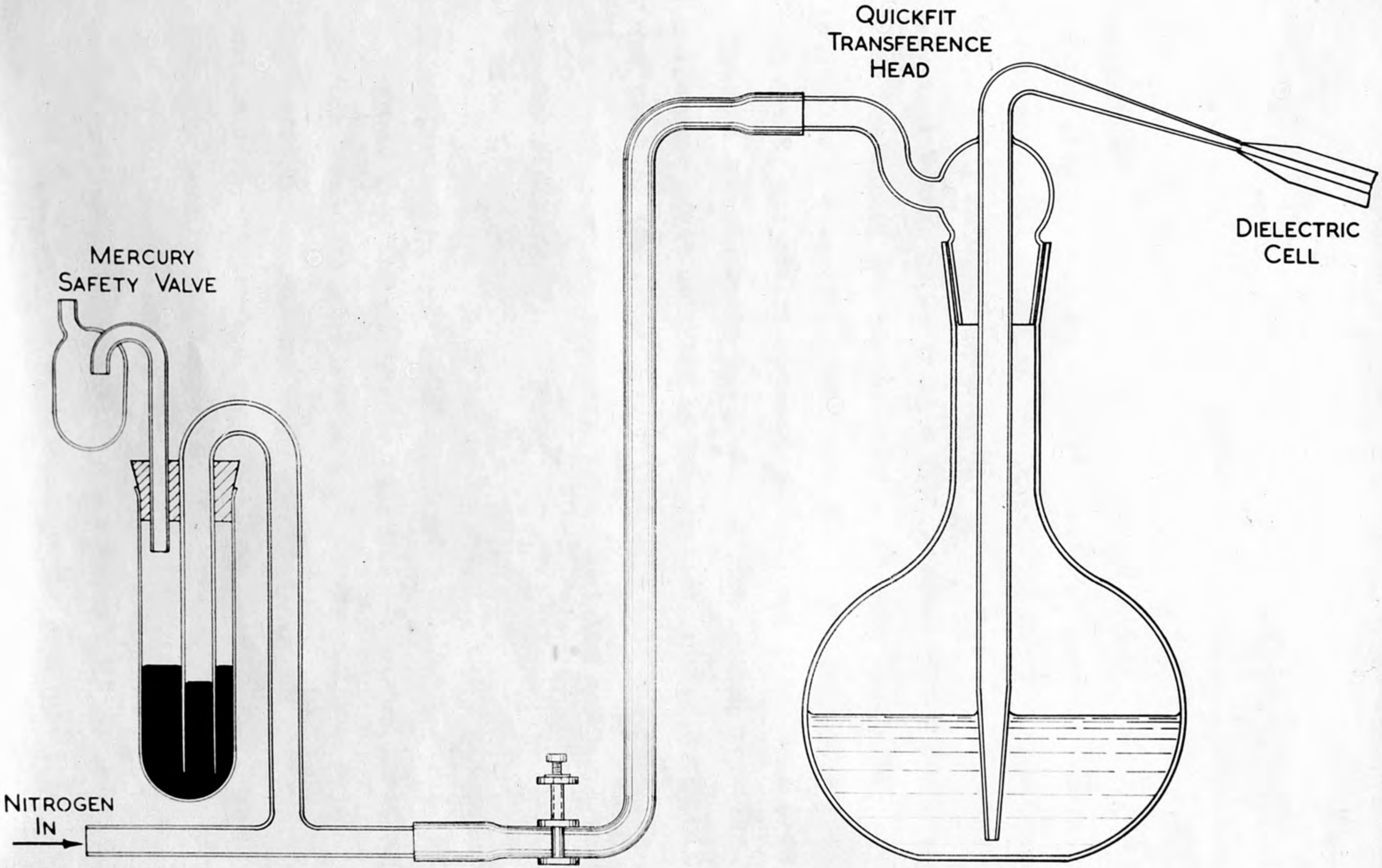


FIG 8. APPARATUS FOR TRANSFERENCE OF LIQUIDS

Determination of Densities

The pyknometer was dried by passing nitrogen through it for thirty minutes from a cylinder, the outside was cleaned with silk and it was weighed accurately to 0.1 mg.; this procedure was then repeated to constant weight. It was then filled with the solvent by application of suction from a water pump, and placed in the thermostat for twenty minutes. While still in the thermostat the pyknometer was adjusted to constant volume by applying a filter paper to the arm other than the marked one and removing the excess liquid by capillary attraction. The pyknometer was carefully cleaned and dried, the stainless steel stirrup and glass caps were attached and the whole was placed in the balance case for weighing. After weighing it was emptied, rinsed twice with the first of the solutions, filled with this solution and then the above procedure repeated. The remaining solutions were treated similarly.

Determination of Refractive Indices

Water from the thermostat bath was circulated rapidly through the block of the Hilger Abbé refractometer by a centrifugal pump and the block was left for ten minutes to attain constant temperature. The pure solvent was poured into the cell of the instrument and allowed to warm up to 25°. The refractometer was then adjusted and the reading noted, at least two repeat readings being made to ascertain that the liquid was at equilibrium. The cell was then cleaned with lens tissue and pure acetone, wiped dry and the above operations repeated for each of the solutions in turn.

CHAPTER II.

Section I.

Preparation and Purification of Materials

In the purification of the materials considerable attention was given to the exclusion of moisture from the final products. Each solid product was freed from traces of moisture by evacuating the desiccator in which it was stored. It was then kept under nitrogen in a tightly stoppered bottle in a desiccator. Batches of solvent and all liquid products were stored under nitrogen in tightly stoppered vessels. In the case of vacuum distilled products nitrogen was let into the apparatus at the end of the distillation. Liquid solutes were used not more than three days after their final distillation and during this time the vessels were stored in a desiccator.

The physical constants of the materials, together with the values obtained by other investigators, are recorded at the end of each purification method. When more than one sample was purified the average values are quoted, together with a maximum variation. Unless otherwise stated boiling points have been corrected to one atmosphere pressure.

BENZENE

Benzene was purified similarly to the method of Few and Smith (1). Commercial "crystallisable" grade was shaken with concentrated sulphuric acid, washed twice each with water and with 5% aqueous potassium hydroxide, and then a further four times with water. After drying over phosphoric oxide it was fractionally crystallised over this drying agent until it formed a glassy crystalline mass on freezing. It was then distilled from phosphoric oxide. The middle fraction was collected and was in each case of constant boiling point, to within 0.02°.

Boiling point 79.8°

$d_4^{25} = 0.87368 \pm 0.00003$

$n_D^{25} = 1.4980 \pm 0.0001$

Few and Smith (1) give Boiling point 79.7°

$d_4^{25} = 0.87368 \pm 0.00003$

$d_D^{25} = 1.4981 \pm 0.0001$

Nat. Bureau of Standards Specification $d_4^{25} = 0.87368$

Jenkins and Sutton (2) give $d_4^{25} = 0.8736$.

2-NITRODIPHENYL and 4-NITRODIPHENYL

2-Nitrodiphenyl and 4-Nitrodiphenyl were prepared by the method of Bell, Kenyon and Robinson (3). 120g of diphenyl were dissolved in twice their weight of glacial acetic acid and the solution was heated to 70°. To this there was then added, in small quantities, three molecular amounts of fuming nitric acid (d=1.51). The solution immediately darkened and, when about one-third of the nitric acid had been added, a visible and steady reaction began. The remainder of the acid was then added more slowly, the whole addition taking about ninety minutes. After cooling the 4-nitrodiphenyl which crystallised out was filtered off, using a sintered glass filter, and the mother liquor diluted with water.

The oil obtained on diluting the mother liquor was separated, washed with warm water, dried and then slowly distilled under reduced pressure through a short fractionating column. The middle fraction, boiling range 116-118°/ca.0.5mm.Hg., was collected and allowed to solidify. Following Gull and Turner (4) it was then dissolved in absolute alcohol to give a saturated solution at 20° which was cooled to 0° and the 2-nitrodiphenyl that crystallised was filtered off and dried. The process was then repeated until constant melting point was attained.

The 4-nitrodiphenyl obtained above was recrystallised to constant melting point from absolute alcohol.

	2-Nitrodiphenyl	4-Nitrodiphenyl
Yield	(middle fraction) 35g. (23%)	(after first recrystallisation) 75g. (48%)
Melting point	38.0°	114.0°
Bell, Kenyon and Robinson (3) give	35 -37°	and 114°
Gull and Turner (4) give	37 -38°	
Gomberg and Bachmann (5) give	36.7°	and 114°
Elks, Haworth and Hey (6) give	37°	and 113°

3-NITRODIPHENYL

3-Nitrodiphenyl was prepared by the method of Elks, Haworth and Hey (6). 138g. of m-nitroaniline were added to 320 ml. of concentrated hydrochloric acid, the whole heated until the base had dissolved and then cooled, with stirring, to below 5°. To this cold suspension was then added gradually, with continuous stirring, a solution of 68g. of sodium nitrite in 100 ml. of water, the whole being maintained below 5°. The diazonium salt solution was then filtered through glass wool and run into two litres of benzene, at 5-10°, with vigorous mechanical stirring.

A solution of 320g. of sodium acetate trihydrate in 800 ml. of water was gradually added to the stirred mixture, the temperature being maintained below 10° and the stirring was continued at this temperature for three hours. At the end of this period the reaction mixture was allowed to come to room temperature and the stirring maintained for a further forty-five hours.

On completion of the stirring the reaction mixture was filtered at the pump and the residue washed with benzene. The benzene layer of the filtrate was separated, washed several times with water and dried over calcium chloride. The benzene was distilled off and the residue distilled at reduced pressure; the middle fraction, boiling range 190-210° / 20-30 mm. Hg., was collected. On solidifying it was recrystallised from petroleum ether (40-60° fraction) the solution being boiled with blood charcoal and filtered during the process. It was then recrystallised to constant melting point from absolute alcohol.

Yield (after first recrystallisation)	90g. (45%)
Melting point	60.5°
Gomberg and Bachmann (5) give	61°
Elks, Haworth and Hey (6) give	61°

2,2'-DINITRODIPHENYL

2,2'-Dinitrodiphenyl was prepared according to the method of Shaw and Turner (7). The copper powder needed for the reaction was prepared similarly to Davey and Latter (8).

Crystalline 'A.R.' copper sulphate was dissolved in water at room temperature and the solution made just acid by the addition of a few millilitres of sulphuric acid. To this solution was added gradually, with stirring, a slight deficiency of 'A.R.' zinc dust made into a paste with water. The precipitated copper powder was collected on a Buchner funnel, washed with distilled water, alcohol and ether, sucked dry at the pump and finally dried in a vacuum desiccator.

100g. of o-chloronitrobenzene was heated in a wide glass tube in a Wood's metal bath until the molten o-chloronitrobenzene was boiling briskly. The upper parts of the tube were then wiped with filter paper to remove traces of moisture and copper powder was added, a few grams at a time, over twenty minutes, the melt being stirred continuously with a 'milk scale' thermometer. Care was taken not to let the melt get more than ten degrees above the boiling point of the starting material.

When 60-70g. of copper powder had been added the melt became very viscous. After heating for a further ten minutes it was allowed to cool slightly and to it was added an equal volume of o-dichlorobenzene with vigorous stirring. The mass was filtered hot and on cooling the 2,2'-dinitrodiphenyl was precipitated from the filtrate by the addition of light petroleum (40-60° fraction). The product was purified by extraction with light petroleum (60-80° fraction) in a Soxhlet apparatus. The extracted solid was filtered at the pump, washed with solvent and finally recrystallised from light petroleum (100-120° fraction).

Numerous batches were prepared.

Average yield (after Soxhlet extraction) 43g. (55%)

Melting point 125.5°

Williamson and Rodebush (9) give 124.5°

Fuson and Cleveland (10) give 123.5 - 124.5°.

2-AMINODIPHENYL (o-XENYLAMINE)

2-Aminodiphenyl was prepared by the reduction of 2-nitrodiphenyl with iron filings, water and glacial acetic acid. 75g. of iron filings were just covered with water in a four litre beaker, to this was added ten millilitres of glacial acetic acid and the whole was then heated in a briskly boiling water bath. When the mixture began to effervesce 50g. of finely ground 2-nitrodiphenyl were added with vigorous stirring, a wooden stick being used for the purpose. Since it was essential that the reaction mixture should not be cooled down, boiling water was added at intervals to prevent it drying up and the stirring was continued for a further fifteen minutes after the vigorous frothing had ceased.

On cooling the mass was made alkaline with ammonia and extracted with a large bulk of cold acetone and filtered at the pump through a pad of filter papers, the top papers being scraped off whenever they tended to become blocked. The acetone was then distilled off leaving the crude amine and water that had not been used in the reduction process. Since the amines were only to be used as intermediates in the preparations of the corresponding halogenodiphenyls they were not required in a state of great purity and, therefore, the only purification process used in the case of the mono-aminodiphenyls was to dissolve the residue from the distillation in hot dilute hydrochloric acid, filter the solution and make alkaline with ammonia. The precipitated amine was then washed several times with water by decantation. The light brown mass of amine solidified on cooling and stirring, was filtered and dried.

Several batches were prepared.

Average yield	32g. (75%)
Melting point	45-46°

Some of the amine was purified by recrystallisation of its hydrochloride and then precipitation by addition of ammonia. It was filtered, washed thoroughly with water and dried.

Melting point 49-50°

Fichter and Sulzberger (11) give 44-45°
Scarborough and West (12) give 49-50°
Morgan and Walls (13) give 47-48°
Pearl (14) gives 44-45°

3-AMINODIPHENYL (m-XENYLAMINE)

3-Aminodiphenyl was prepared from 3-nitrodiphenyl by a process identical to that given above. Several batches were prepared on the above scale.

Average yield 34g. (80%)
Melting point 27-29°

Fichter and Sulzberger (11) give 30°
Campaigne and Reid (15) give 31-31.5°

4-AMINODIPHENYL (p-XENYLAMINE)

4-Aminodiphenyl was prepared from 4-nitrodiphenyl similarly to the preparation of 2-aminodiphenyl given above. Several batches were prepared on the above scale.

Average yield 32g. (75%)
Melting point 47-48°

Morgan and Walls (13) give 50-52°

2,2'-DIAMINODIPHENYL

2,2'-Diaminodiphenyl was prepared by the reduction of 2,2'-dinitrodiphenyl using the method of Shaw and Turner (7) on which the preparations described above for mono-aminodiphenyls are a slight variation. The 2,2'-dinitrodiphenyl was reduced in 50g. batches, 110g. of iron filings being used in each case. After precipitation from dilute hydrochloric acid solution by addition of ammonia and washing with water the amine was filtered off and purified by extraction with light petroleum (40-60° fraction) in a Soxhlet apparatus. Finally the light fawn product was filtered off, washed with a little solvent and dried.

Average yield	26.5g.	(70%)
Melting point	81°	
Sako (16) gives	78-80°	
Labriola and Felite (17) give	80-81°	
Williamson and Rodebush (9) give	78.5°	

2-FLUORODIPHENYL

2-Fluorodiphenyl was prepared according to the method of Schiemann and Roselius (18). 50g. of 2-aminodiphenyl were dissolved in hot dilute (1:1) hydrochloric acid and the solution cooled in ice with vigorous stirring. The resulting suspension was then diazotised, the whole being maintained below 10° throughout. A slight excess of sodium nitrite solution was added dropwise and the unreacted nitrous acid was decomposed by the addition of urea until the evolution of nitrogen ceased. The diazonium salt solution was filtered through glass wool and to the filtrate there were then added 110 ml. of concentrated fluoboric acid (42% w/w). The resulting yellow precipitate of diphenyl-2-diazonium borofluoride was filtered off, washed with water, sucked dry and finally dried in a vacuum desiccator. Its decomposition temperature was determined using a small amount in a melting point apparatus.

Yield of diazonium borofluoride 67.5g. (85%)

Decomposition temperature 95°

The bulk of the diazonium borofluoride was decomposed in an apparatus closed to the atmosphere. This consisted of a two-necked flask maintained at about ten degrees above the decomposition temperature, in a Wood's-metal bath, to which was attached a long air condenser terminating in a water trap to absorb the boron trifluoride evolved. To the other neck of the flask was fitted a wide tube with a piston, from which the diazonium borofluoride was added in small quantities.

After the decomposition was completed caustic soda solution was added and the mixture steam distilled. The 2-fluorodiphenyl solidified in the condenser and this had to be drained periodically to prevent it from becoming blocked. The solid product was filtered from the distillate and recrystallised to constant melting point from absolute alcohol.

Yield (after first recrystallisation, on basis of amine used) 33g. (65%)

Melting point 74.5°

Schiemann and Roselius (18) give Decomposition temperature 81°

Melting point 72°

3-FLUORODIPHENYL

3-Fluorodiphenyl was prepared from 3-aminodiphenyl by a procedure identical to that described above for 2-fluorodiphenyl. The diazonium borofluoride, from 50g. of amine, was obtained as a yellow powder (Schiemann and Roselius got a grey diazonium borofluoride).

Yield	71.5g. (90%)
Decomposition temperature	89°

In view of the low decomposition temperature the vessel in which this process was carried out was conveniently heated in a boiling water bath. The product, after steam distillation, was a colourless liquid that crystallised by scratching. This was recrystallised by obtaining a saturated solution in absolute alcohol at 30° and then cooling to 0° in a refrigerator. This process was repeated to give constant melting point.

Yield (calculated as for 2-fluorodiphenyl)	28g. (55%)
Melting point	29.5°

Schiemann and Roselius (18) give	Decomposition temperature	91°
	Melting point	26-27°

4-FLUORODIPHENYL

4-Fluorodiphenyl was prepared from 4-aminodiphenyl by the method of Schiemann and Roselius (18) which is identical to that given above for 2-fluorodiphenyl. 50g. of amine were used and the produce was recrystallised to constant melting point from absolute alcohol.

Yield of diazonium borofluoride	68.5g.	(86%)
Decomposition temperature	126°	
Yield (calculated as above)	29g.	(57%)
Melting point	75.0°	

Schiemann and Roselius (18) give	Decomposition temperature	116°
	Melting point	$74-75^{\circ}$
Adam and Russell (19) give	" "	74.5°

2,2'-DIFLUORODIPHENYL

2,2'-Difluorodiphenyl was prepared by the method of Schiemann and Roselius (20). 35g. of 2,2'-diaminodiphenyl was suspended in concentrated hydrochloric acid and maintained below 5° throughout its diazotisation. On addition of 130 ml. of fluorboric acid (42%w/w) to the filtered diazonium salt solution diphenyl-2,2'-bis-diazonium borofluoride was obtained as a yellow precipitate. It was filtered off, washed, dried and finally decomposed to 2,2'-difluorodiphenyl. After steam distillation the product was recrystallised to constant melting point from absolute alcohol.

Yield of diazonium borofluoride	59g.	(80%)
Decomposition temperature	156°	
Yield (calculated as above)	23.5g.	(65%)
Melting point	118.5°	

Schiemann and Roselius (20) give	Decomposition temperature	134°
	Melting point	117°
Faber (21) gives	" "	117.5°

2-CHLORODIPHENYL

2-Chlorodiphenyl was prepared by the method of Zaheer and Faseeh (22), based on the Sandmeyer reaction. Cuprous chloride was obtained by bubbling sulphur dioxide through a warm solution of 30g. of crystalline copper sulphate and 10g. of sodium chloride until the supernatant liquid was almost colourless. After cooling, the precipitated cuprous chloride was filtered off, washed with sulphurous acid and sucked dry. While this reduction was proceeding 50g. of 2-aminodiphenyl was diazotised and the excess nitrous acid decomposed, as described in the preparation of 2-fluorodiphenyl, and the diazonium salt solution was filtered through glass wool.

The filtrate was run dropwise into a beaker containing a solution of the freshly prepared cuprous chloride in concentrated hydrochloric acid and the whole was then left at room temperature with occasional stirring until the evolution of nitrogen had ceased. The bulk was then made alkaline with sodium hydroxide and steam distilled, some of the 2-chlorodiphenyl crystallising in the condenser as an off white solid. It was extracted from the distillate with ether and the combined extracts dried over anhydrous sodium sulphate, after which the solution was filtered, the solvent distilled off and the product fractionally distilled at reduced pressure.

The column used for the fractionation was twelve inches long and packed with Fenske helices. The outside was wound with resistance wire, between layers of asbestos paper, for external heating, and this was lagged with asbestos rope. The complete apparatus, which was used for the purification of all liquid products in this investigation, is shown diagrammatically in Figure 9. The first and last runnings were collected separately from the bulk which distilled steadily as a colourless liquid at 111-113°/3 mm. Hg. The distillate solidified on cooling and was recrystallised by the method used in the purification of 2-fluorodiphenyl.

Yield (middle fraction of distillate)	33.5g. (60%)
Melting point	32.5°

Zaheer and Faseeh (22) give 31°

Elks, Haworth and Hey (6) give 34°

3-CHLORODIPHENYL

An attempt was first made to prepare 3-chlorodiphenyl by the method of Elks, Haworth and Hey (6) which was similar to the preparation described above for 3-nitrodiphenyl, the starting material being m-chloroaniline and the sodium acetate used in that preparation was replaced here (following the authors) by sodium hydroxide. On distilling the product under reduced pressure there was obtained as distillate a bright yellow compound that readily solidified in the air condenser and was obviously not 3-chlorodiphenyl. The preparation was repeated three times with similar results.

3-Chlorodiphenyl was eventually prepared by the Sandmeyer method. 50g. of 3-aminodiphenyl were diazotised by the method described above. The resulting diazonium salt

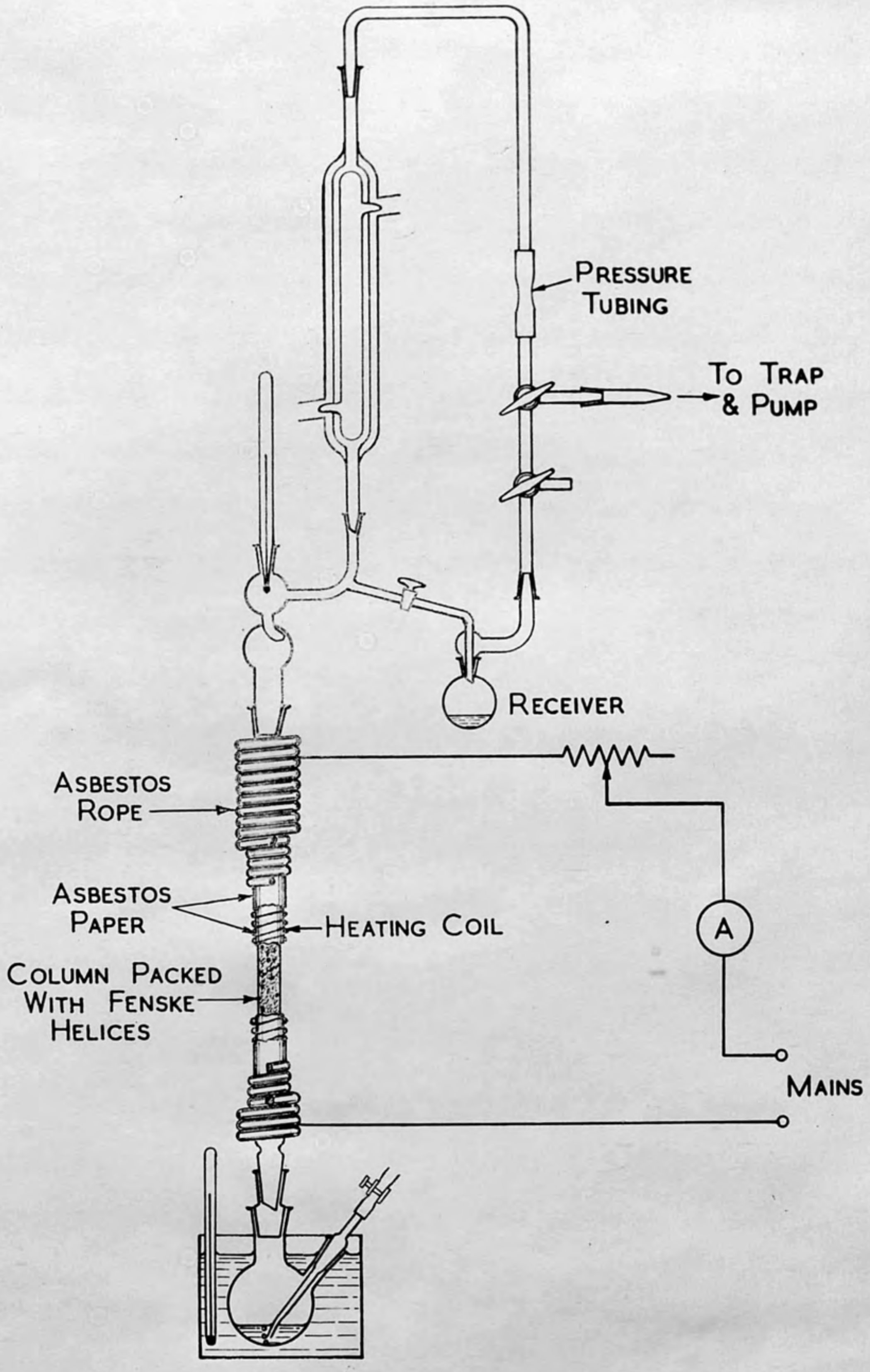


FIG. 9.
VACUUM FRACTIONATION APPARATUS

solution was treated with urea, filtered through glass wool and then added dropwise to a cooled solution of freshly prepared cuprous chloride in concentrated hydrochloric acid. The reaction mixture was then allowed to stand at room temperature until the evolution of nitrogen had ceased, made alkaline with sodium hydroxide and steam distilled. The distillate was extracted with ether and the combined extracts dried over anhydrous sodium sulphate. It was then filtered, the ether distilled off and the residue fractionated under reduced pressure in the apparatus previously described. The middle fraction, a colourless liquid of constant boiling point, was collected for use.

Yield (middle fraction of distillate)	14g.	(25%)
Boiling point	104° / 1mm. Hg.	
Gomberg and Bachmann (5) give	284-285°	
Elks, Haworth and Hey (6) give	150-160°/ 6mm. Hg.	

4-CHLORODIPHENYL

4-Chlorodiphenyl was prepared by the Sandmeyer method similarly to its isomers, 50g. of 4-aminodiphenyl being used. After addition of the filtered diazonium salt solution to the solution of cuprous chloride in concentrated hydrochloric acid the reaction mixture was warmed, with stirring, in a water bath maintained at 40-45°, until the evolution of nitrogen ceased. It was then made alkaline and steam distilled, the water being emptied from the condenser occasionally to prevent blocking since the 4-chlorodiphenyl readily solidified.

The solid product was filtered from the distillate and recrystallised to constant melting point from absolute alcohol.

Yield (after first recrystallisation)	31g. (55%)
Melting point	77.0°
Gomberg and Bachmann (5) give	77.7°
Elks, Haworth and Hey (6) give	77°
Adam and Russell (19) give	75.5°

2,2'-DICHLORODIPHENYL

2,2'-Dichlorodiphenyl was prepared by the method of Mascarelli and Gatti (23). 2g. of 2,2'-dinitrodiphenyl were mixed with 4 ml. of thionyl chloride in a Carius tube and the tube carefully sealed. It was then placed in a Carius furnace and heated at 210° for eight hours. After being left overnight to cool the end of the tube was heated in a Bunsen flame and when hot the excess pressure blew out. The tube was then opened more fully and the product washed into a flask with carbon tetrachloride. This was treated with water, made alkaline with sodium hydroxide and steam distilled. The product was separated from the distillate in carbon tetrachloride solution and after removal of the solvent it solidified on cooling.

The above procedure was repeated many times in order to obtain a sufficient quantity of product. It was found to be essential to use pure starting material since crude 2,2'-dinitrodiphenyl (i.e. not extracted in a Soxhlet) gave very poor yields.

The combined products were dissolved in light petroleum (40-60° fraction) and refluxed with 5g. of charcoal. After filtering and cooling a white crystalline mass was obtained. Further treatment with charcoal and several recrystallisations from methyl alcohol however were necessary to give a product of constant melting point.

Average yield (after first recrystallisation)	80%
Melting point	61.5°
Mascarelli and Gatti (23) give	59°
Williamson and Rodebush (9) give	59-60.5°
Schwechten (24) gives	60.5°
Hampson and Weissberger (25) give	60.2-62°
Dobbie, Fox and Gauge (26) give	59°

2-BROMODIPHENYL

2-Bromodiphenyl was prepared by the Sandmeyer reaction. 50g. of purified 2-aminodiphenyl were dissolved in warm dilute hydrobromic acid and then cooled in ice to below 5°. Meanwhile an aqueous solution of 30g. of copper sulphate and 18g. of sodium bromide was treated slowly with an excess of finely powdered sodium sulphite. The precipitated cuprous bromide was filtered off, washed with sulphurous acid and sucked dry.

The cold suspension of 2-aminodiphenyl hydrobromide was diazotised in the usual manner and unreacted nitrous acid decomposed with urea. The resulting solution was filtered through glass wool and added dropwise to a solution of the cuprous bromide in concentrated hydrobromic acid. The reaction mixture was then warmed, with stirring, in a water bath maintained at 40-45° until the evolution of nitrogen had ceased. The product was isolated in the manner described for 2-chlorodiphenyl and from the final distillation was collected as middle fraction a colourless liquid of constant boiling point.

Yield (middle fraction)	34.5g. (50%)
Boiling point	128°/ca. 6 mm.Hg.
Zaheer and Faseeh (22) give	160°/ 11 mm. Hg.

3-BROMODIPHENYL

3-Bromodiphenyl was prepared by the method of Huber, Rossow, Renoll and Mowry (27). 50g. of 2-aminodiphenyl were dissolved in 110 ml. of pyridine and treated with 31.5 ml. of acetyl chloride, the whole being continuously stirred and cooled to maintain it at 10-15°. After standing for an hour the mixture was poured into 150 ml. of concentrated hydrochloric acid containing crushed ice, filtered, washed and dried to give crude 2-acetoaminodiphenyl.

Yield	59g.	(97%)
Melting point (after recrystallisation from aqueous acetic acid)		118°

59g. of 2-acetoaminodiphenyl were dissolved in 500 ml. of glacial acetic acid and treated rapidly with a solution of 15 ml. of bromine in 380 ml. of glacial acetic acid.

After standing overnight the whole was poured into a large quantity of water and the 2-acetoamino-5-bromodiphenyl that separated was filtered off and dried.

Yield	76g. (93%)	
Melting point (after recrystallisation from methylated spirit)		127°

This material was then dissolved in 120 mls. of hot alcohol containing 90 ml. of concentrated hydrochloric acid and refluxed for four hours. The resulting liquid was poured into a litre of water and sufficient sodium hydroxide solution added to liberate the free base. On cooling the 2-amino-5-bromodiphenyl solidified. It was filtered off, redigested with hot water, filtered and dried.

Yield	62g. (96%)
Melting point	53-55°

The yield of 2-amino-5-bromodiphenyl was dissolved in 200 ml. of ethyl alcohol and 28 ml. of concentrated sulphuric acid were added slowly, the temperature being kept below 50°. After cooling to 5° it was diazotised with 25 g. of sodium nitrite, and 3g. of ether-washed copper bronze were then added. On warming gently a vigorous evolution of gases occurred at 40-45° and a cooling bath was applied. When this evolution had subsided the solution was refluxed for two hours and then steam distilled at 150-180°. The distillate was extracted with benzene and the extract treated successively with dilute sodium hydroxide solution, water and concentrated sulphuric acid. It was then dried over potassium carbonate, the benzene distilled off and the 3-bromodiphenyl fractionated under reduced pressure using the apparatus described under 2-chlorodiphenyl. The middle fraction, a colourless liquid of constant boiling point, was collected.

Yield	26.5g. (45% on last stage; 35% on basis of 2-aminodiphenyl used)
Boiling point	113° /1mm. Hg.
Gomberg and Bachmann (5) give	299-301°
Marvell, Gimsberg and Meueller (28) give	163-173°/17mm.Hg.
Huber, Renoll, Rossow and Mowry (27) give	158-167°/11mm.Hg.

4-BROMODIPHENYL

The author is indebted to Professor E.E. Turner for the loan of a sample of 4-bromodiphenyl. Its solution in absolute alcohol was boiled with charcoal, filtered and the material recrystallised to constant melting point.

Melting point	90.5°
Gomberg and Bachmann (5) give	91.2°
Adam and Russell (19) give	89°
Elks, Haworth and Hey (6) give	90°
Gomberg and Bachmann (29) give	89.5-90°

2,2'-DIBROMODIPHENYL

2,2'-Dibromodiphenyl was prepared by the method described by Schwechten (24). 18.4g. of 2,2'-diaminodiphenyl were diazotised in dilute sulphuric acid solution in the usual manner and filtered. To the filtered solution was then added an aqueous solution of 24 g. of potassium bromide and 15g. of mercuric nitrate and 83 ml. concentrated hydrobromic acid.

The yellow precipitate which formed, of probable composition $(C_{12}H_8N_4)\ (HgBr_3)_2$, was filtered off, washed with water and acetone, and sucked dry. In daylight this compound turned bright green but the coloured matter was readily removed on washing with acetone, giving an intense green solution.

Yield 104g. (95%)

Two batches of the complex were prepared on this scale. In the first the complex salt was mixed with twice its weight of finely powdered potassium bromide and a sample was heated cautiously in a test-tube to determine whether or not the decomposition was too vigorous. It was then put in a Pyrex tube, 100 cm. long and 3 cm. internal diameter, one end of which was closed and the other was fitted with an air condenser. The mixture was spread along the tube and heated, starting from the condenser end, sufficiently strongly to decompose the complex. On cooling, the inorganic matter was extracted with water and the organic material with ether and the solvent then removed.

Yield (crude) 12.5g. (40%)

The decomposition temperature of the second batch of complex was found by the same method as was used for the diazoniumborofluorides.

Decomposition temperature 175°

The bulk was then mixed with an equal weight of potassium bromide and decomposed gradually in a vessel maintained at 185° in a Wood's Metal bath, the apparatus being identical to that used in the preparation of 2-fluorodiphenyl. Steam distillation of the resultant mass gave a clean solid product.

Yield from steam distillation 18.5g. (59%)

The crude material obtained by the first method was also steam distilled and the combined yields were recrystallised to constant melting point from methyl alcohol, being treated with charcoal during the process.

Melting point	81.5°
Schwechten (24) gives	80-81°
Dobbie, Fox and Gauge (26) give	81°

2-IODODIPHENYL

2-Iododiphenyl was prepared by the general method for aromatic iodo-compounds. 25g. of 2-aminodiphenyl were dissolved in dilute (1:1) hydrochloric acid, cooled in ice and diazotised. After addition of urea to decompose any unreacted nitrous acid the diazonium salt solution was treated dropwise with an excess of a cold solution of potassium iodide with shaking. The shaking was continued until the evolution of nitrogen ceased and the reaction mixture was treated with sodium metabisulphite to remove traces of iodine. It was then extracted with ether, the combined extracts washed twice with 10% sodium hydroxide solution and twice with water. After drying over anhydrous sodium sulphate the ether was distilled off and the residue was fractionated under reduced pressure in the apparatus described under 2-chlorodiphenyl. The middle fraction, a colourless liquid of constant boiling point, was collected.

Yield (middle fraction)	24.5g. (60%)
Boiling point	108°/ca. 0.5mm. Hg.
Zaheer and Faseeh (22) give	181°/21mm. Hg.
Cook (30) gives	140°/3-4mm. Hg.
Bowden (31) gives	189-192°/ 36mm.Hg.
Goodman and Wise (32) give	176.5°/ 21mm.Hg.

3-IODODIPHENYL

3-Iododiphenyl was prepared using the method of Campaigne and Reid (15). 25g. of 3-aminodiphenyl were dissolved in dilute sulphuric acid and diazotised in the usual manner. The resulting solid, yellow diazonium salt was mixed with 500 ml. of toluene and vigorously shaken. To the suspension there was then added dropwise a solution of potassium iodide, the whole being maintained below 5° throughout. The resulting red complex decomposed slowly at room temperature and was left to stand overnight. The black toluene layer that separated was washed successively with sodium metabisulphite solution, sodium hydroxide solution and water. It was then dried over anhydrous sodium sulphate, filtered and the toluene distilled off. The residue was fractionated under reduced pressure as described above and the middle fraction, a colourless liquid of constant boiling point, was collected.

Yield (middle fraction)	24g. (58%)
Boiling point	138° /ca.1mm.Hg.
Bowden (31) gives	188-189°/16mm.Hg.
Campaigne and Reid (15) give	149-152°/ 1mm.Hg.

4-IODODIPHENYL

4-Iododiphenyl was prepared from 4-aminodiphenyl by the general method. 25g. of the amine were dissolved in 1:1 hydrochloric acid and diazotised, concentrated potassium iodide solution being then added to the filtered diazonium salt solution. The resultant mixture was allowed to stand overnight and was then heated on a water bath for thirty minutes. The product was filtered at the pump and washed successively with sodium metabisulphite solution, sodium hydroxide solution and water.

After being sucked dry the product was recrystallised from aqueous acetic acid, the initial solution being boiled with three successive 5g. quantities of charcoal. Some difficulty was, however, encountered due to impurities coming out in the first crop of crystals. To overcome this a slight deficiency of solvent was used so that when boiling much of the impurity remained undissolved as a bright red oil. The final product was an off-white solid of constant melting point.

Yield (after first recrystallisation)	27g. (65%)
Melting point	114.0°
Schlenk (33) gives	112°
Rupe and Iselin (34) give	113-114°
Brand and Stephen (35) give	113°

IODOBENZENE

Iodobenzene was prepared by the method of Lucas and Kennedy (36). 50g. of aniline were dissolved in dilute hydrochloric acid and to this was added a large quantity of crushed ice. The aniline was diazotised and the resulting mixture was filtered through glass wool. An aqueous solution containing 89g. of potassium iodide was added to it with stirring and the whole was allowed to stand overnight. It was then heated under reflux on a steam bath until no more nitrogen was evolved when it was left to settle.

After standing the bulk of the aqueous layer was siphoned off and the residue made alkaline and steam distilled directly. The last third of the steam distillate was collected separately and added to the aqueous layers from the earlier distillate. This was then acidified with 10ml. of concentrated sulphuric acid and once more steam distilled. The yields were combined and dried over calcium chloride. After filtering the product was fractionated under reduced pressure using the apparatus previously described. The middle fraction, a colourless liquid of constant boiling point, was collected.

Yield (middle fraction)	77g. (70%)
Boiling point	38°/2mm.Hg.
Davis and Brewster (37) give	$184-186^{\circ}$
Varma and Sreenivasmurthyachar (38) give	$186-189^{\circ}$
Lucas and Kennedy (36) give	$77-78^{\circ}$/20mm.Hg.
and	$63-64^{\circ}$/8mm.Hg.

Section II.

TABLES OF EXPERIMENTAL RESULTS

All polarisation and refraction values are expressed in c.c.

The 2-Fluorodiphenyl (Series II) measurements were carried out towards the end of this investigation as a check on the author's early technique.

μ is the dipole moment calculated on the assumption that $P_D = (R_D)$ whilst μ' is that obtained on the assumption that $P_D = 1.05\ (R_D)$.

1. 2-Fluorodiphenyl in Benzene. (Series I)
2. 2-Fluorodiphenyl in Benzene. (Series II)
3. 3-Fluorodiphenyl in Benzene.
4. 4-Fluorodiphenyl in Benzene.
5. 2-Chlorodiphenyl in Benzene.
6. 3-Chlorodiphenyl in Benzene.
7. 4-Chlorodiphenyl in Benzene.
8. 2-Bromodiphenyl in Benzene.
9. 3-Bromodiphenyl in Benzene.
10. 4-Bromodiphenyl in Benzene.
11. 2-Iododiphenyl in Benzene.
12. 3-Iododiphenyl in Benzene.
13. 4-Iododiphenyl in Benzene.
14. 2-Nitrodiphenyl in Benzene.

cont.

15. 3-Nitrodiphenyl in Benzene.

16. 4-Nitrodiphenyl in Benzene.

17. 2,2'-Difluorodiphenyl in Benzene.

18. 2,2'-Dichlorodiphenyl in Benzene.

19. 2,2'-Dibromodiphenyl in Benzene.

20. 2,2'-Dinitrodiphenyl in Benzene.

21. Iodobenzene in Benzene.

1. 2-Fluorodiphenyl in Benzene (Series I).

$100\ w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14459	1.4980
0.5725	2.2779	1.14312	1.4983
1.0632	2.2868	1.14195	1.4987
1.8078	2.2968	1.14006	1.4991
2.3773	2.3046	1.13857	1.4994
2.8719	2.3111	1.13742	1.4999
3.7650	2.3233	1.13514	1.5006
4.6780	2.3354	1.13281	1.5012

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2449	0.936	-0.2568	0.1572
2.2461	1.342	-0.2483	0.1975
2.2473	1.345	-0.2506	0.1825
2.2482	1.352	-0.2532	0.1766
2.2497	1.343	-0.2497	0.1985
2.2518	1.349	-0.2510	0.2072
2.2536	1.344	-0.2518	0.2052

M.W. = 172.192 $\bar{\alpha} = 1.339$ $\bar{\beta} = -0.2513$ $\bar{\nu} = 0.1961$

$P_{2\infty} = 89.18$ $[R_D] = 51.53$ $P\mu = 37.65$ $P\mu' = 35.07$

$\mu = 1.36$ $\mu' = 1.31$

2. 2-Fluorodiphenyl in Benzene (Series II)

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4980
1.0240	2.2860	1.14205	1.4987
1.5003	2.2927	1.14082	1.4989
1.8791	2.2975	1.13987	1.4992
3.0648	2.3137	1.13691	1.5000

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2461	1.315	-0.2510	0.2051
2.2467	1.346	-0.2533	0.1800
2.2476	1.329	-0.2528	0.1916
2.2500	1.346	-0.2516	0.1958

M.W. = 172.192 $\bar{\alpha} = 1.335$ $\bar{\beta} = -0.2521$ $\bar{\gamma} = 0.1928$

$P_{2\infty} = 89.02$ $[R_D] = 51.38$ $P\mu = 37.64$ $P\mu' = 35.07$

$\mu = 1.36$ $\mu' = 1.31$

3. 3-Fluorodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4980
1.1203	2.2917	1.14184	1.4988
1.6617	2.3014	1.14046	1.4991
2.2278	2.3111	1.13904	1.4994
2.4646	2.3156	1.13846	1.4996
3.2667	2.3291	1.13654	1.5001
3.3654	2.3314	1.13621	1.5002
4.4766	2.3503	1.13352	1.5009

n^2_D	ϵ_{12}/w_2	v_{12}/w_2	n^2_D/w_2
2.2440	-	-	-
2.2464	1.716	-0.2481	0.2142
2.2477	1.739	-0.2503	0.1986
2.2482	1.733	-0.2505	0.1885
2.2488	1.749	-0.2499	0.1948
2.2503	1.733	-0.2473	0.1929
2.2506	1.751	-0.2499	0.1961
2.2527	1.738	-0.2480	0.1943

M.W. = 172.192 $\bar{\alpha}$ = 1.730 $\bar{\beta}$ = -0.2490 $\bar{\gamma}$ = 0.1953

$P_{2\infty}$ = 101.97 $[R_D]$ = 51.62 $P\mu$ = 50.35 $P\mu'$ = 47.77

μ = 1.57 μ' = 1.53

4. 4-Fluorodiphenyl in Benzene

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14454	1.4981
0.5190	2.2806	1.14330	1.4984
1.1198	2.2903	1.14175	1.4989
1.6251	2.2984	1.14050	1.4992
2.2328	2.3079	1.13901	1.4996
2.6494	2.3142	1.13796	1.5000
2.9683	2.3192	1.13713	1.5002
3.4652	2.3269	1.13590	1.5006

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2443	-	-	-
2.2452	1.553	-0.2389	0.1734
2.2467	1.592	-0.2492	0.2143
2.2476	1.596	-0.2486	0.2031
2.2488	1.583	-0.2477	0.2015
2.2500	1.575	-0.2484	0.2151
2.2506	1.572	-0.2496	0.2122
2.2518	1.571	-0.2493	0.2164

M.W. = 172.192 $\bar{\alpha} = 1.604$ $\bar{\beta} = -0.2485$ $\bar{\nu} = 0.2099$

$P_{2\infty} = 97.90$ $[R_D] = 52.12$ $P_\mu = 45.78$ $P_{\mu'} = 43.17$

$\mu = 1.50$ $\mu' = 1.46$

5. 2-Chlorodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14459	1.4980
1.0334	2.2874	1.14167	1.4988
1.5409	2.2940	1.14028	1.4991
2.1712	2.3034	1.13845	1.4996
2.4536	2.3075	1.13774	1.4999
3.1671	2.3167	1.13573	1.5004
3.5204	2.3216	1.13471	1.5009
4.3726	2.3342	1.13227	1.5017

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2464	1.441	-0.2826	0.2322
2.2473	1.395	-0.2797	0.2142
2.2488	1.421	-0.2828	0.2211
2.2497	1.428	-0.2792	0.2323
2.2512	1.395	-0.2798	0.2273
2.2527	1.394	-0.2806	0.2471
2.2551	1.411	-0.2818	0.2539

On plotting n_D against w_2/ one gets $\bar{\nu} = 0.256$ which would indicate that n_D for benzene given above is in error by 0.0001.

M.W. = 188.649 $\bar{\alpha} = 1.411$ $\bar{\beta} = -0.2808$ $\bar{\nu} = 0.256$

$P_{2\infty} = 98.60$ $[R_D] = 57.16$ $P\mu = 41.44$ $P\mu' = 38.58$

$\mu = 1.43$ $\mu' = 1.38$

6. 3-Chlorodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4980
0.8622	2.2885	1.14216	1.4988
1.3345	2.2968	1.14082	1.4993
1.4790	2.2994	1.14040	1.4994
2.2495	2.3136	1.13821	1.5001
2.9636	2.3267	1.13618	1.5008
3.9578	2.3450	1.13337	1.5019

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2464	1.855	-0.2853	0.2784
2.2479	1.824	-0.2855	0.2922
2.2482	1.820	-0.2853	0.2840
2.2503	1.829	-0.2850	0.2801
2.2524	1.830	-0.2848	0.2834
2.2551	1.831	-0.2842	0.2805

M.W. = 188.649 $\bar{\alpha}$ = 1.820 $\bar{\beta}$ = -0.2847 $\bar{\nu}$ = 0.2826

$P_{2\infty}$ = 112.90 $[R_D]$ = 57.72 $P\mu$ = 55.18 $P\mu'$ = 52.30

μ = 1.65 μ' = 1.60

7. 4-Chlorodiphenyl in Benzene

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14461	1.4980
0.9463	2.2903	1.14198	1.4989
1.6477	2.3028	1.13997	1.4996
2.1235	2.3117	1.13857	1.5001
2.6418	2.3211	1.13710	1.5006
3.0548	2.3292	1.13590	1.5010
3.5108	2.3378	1.13459	1.5013
4.9308	2.3634	1.13056	1.5025

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2467	1.884	-0.2800	0.2853
2.2488	1.840	-0.2816	0.2913
2.2503	1.848	-0.2844	0.2967
2.2518	1.840	-0.2843	0.2953
2.2530	1.855	-0.2851	0.2946
2.2539	1.860	-0.2854	0.2820
2.2575	1.844	-0.2849	0.2738

M.W. = 188.649 $\bar{\alpha} = 1.850$ $\bar{\beta} = -0.2843$ $\bar{\nu} = 0.2863$

$P_{2\infty} = 113.99$ $[R_D] = 57.87$ $P\mu = 56.12$ $P\mu' = 53.23$

$\mu = 1.66$ $\mu' = 1.62$

8. 2-Bromodiphenyl in Benzene

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4979
1.1689	2.2877	1.13977	1.4989
1.8598	2.2964	1.13680	1.4995
2.8137	2.3084	1.13297	1.5002
3.6557	2.3190	1.12948	1.5009
4.0989	2.3252	1.12742	1.5013
4.6656	2.3294	1.12532	1.5017

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2437	-	-	-
2.2467	1.299	-0.4149	0.2567
2.2485	1.287	-0.4205	0.2420
2.2506	1.276	-0.4140	0.2452
2.2527	1.273	-0.4141	0.2462
2.2539	1.286	-0.4196	0.2488
2.2551	1.277	-0.4137	0.2443

M.W. = 233.108 $\bar{\alpha} = 1.279$ $\bar{\beta} = -0.4159$ $\bar{\nu} = 0.2480$

$P_{2\infty} = 106.68$ $[R_D] = 60.80$ $P\mu = 45.88$ $P\mu' = 42.84$

$\mu = 1.50$ $\mu' = 1.45$

9. 3-Bromodiphenyl in Benzene

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14452	1.4980
1.3745	2.2932	1.13858	1.4992
2.1059	2.3045	1.13524	1.4998
2.9722	2.3174	1.13171	1.5006
3.2150	2.3220	1.13060	1.5008
4.1031	2.3348	1.12670	1.5015
4.7750	2.3453	1.12368	1.5023
5.2729	2.3540	1.12164	1.5027

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2476	1.390	-0.4322	0.2619
2.2494	1.440	-0.4407	0.2564
2.2518	1.456	-0.4310	0.2624
2.2524	1.489	-0.4330	0.2613
2.2545	1.478	-0.4343	0.2559
2.2569	1.489	-0.4364	0.2702
2.2581	1.513	-0.4339	0.2674

M.W. = 233.108 $\bar{\alpha} = 1.506$ $\bar{\beta} = -0.4345$ $\bar{\nu} = 0.2632$

$P_{2\infty} = 115.34$ $[R_D] = 60.209$ $P\mu = 55.13$ $P\mu' = 52.12$

$\mu = 1.64$ $\mu' = 1.60$

10. 4-Bromodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14459	1.4980
0.5154	2.2806	1.14239	1.4984
1.2248	2.2914	1.13926	1.4991
1.7120	2.2989	1.13715	1.4995
1.9057	2.3018	1.13629	1.4997
2.4967	2.3107	1.13371	1.5002
3.0626	2.3196	1.13135	1.5008

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2452	1.576	-0.4269	0.2328
2.2473	1.546	-0.4352	0.2690
2.2485	1.543	-0.4357	0.2634
2.2491	1.537	-0.4355	0.2676
2.2506	1.530	-0.4358	0.2643
2.2524	1.537	-0.4323	0.2742

M.W. = 233.108 $\bar{\alpha}$ = 1.553 $\bar{\beta}$ = -0.4343 $\bar{\gamma}$ = 0.2666

$P_{2\infty}$ = 117.41 $[R_D]$ = 60.38 $P\mu$ = 57.03 $P\mu$ = 54.01

μ = 1.67 μ' = 1.63

11. 2-Iododiphenyl in Benzene

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4980
0.8993	2.2808	1.14001	1.4988
1.4505	2.2858	1.13717	1.4994
2.0141	2.2919	1.13426	1.4999
2.6443	2.2978	1.13108	1.5004
3.0305	2.3024	1.12912	1.5009
3.2094	2.3039	1.12824	1.5011
3.9546	2.3119	1.12440	1.5018

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2464	0.922	-0.5126	0.2669
2.2482	0.917	-0.5136	0.2896
2.2497	0.963	-0.5144	0.2816
2.2512	0.955	-0.5120	0.2723
2.2527	0.985	-0.5115	0.2871
2.2533	0.979	-0.5104	0.2898
2.2554	0.995	-0.5113	0.2883

M.W. = 280.11 $\bar{\alpha} = 0.897$ $\bar{\beta} = -0.5119$ $\bar{\gamma} = 0.2843$

$P_{2\infty} = 100.05$ $[R_D] = 67.13$ $P\mu = 32.92$ $P\mu' = 29.56$

$\mu = 1.27$ $\mu' = 1.20.$

12. 3-Iododiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4980
1.0788	2.2849	1.13897	1.4990
1.4705	2.2893	1.13694	1.4995
2.0026	2.2952	1.13403	1.5000
2.8073	2.3043	1.12984	1.5008
3.4686	2.3119	1.12646	1.5014
3.7644	2.3146	1.12489	1.5017
4.9218	2.3273	1.11885	1.5028

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2470	1.148	-0.5228	0.2781
2.2485	1.144	-0.5223	0.3060
2.2500	1.136	-0.5288	0.2996
2.2524	1.131	-0.5265	0.2992
2.2542	1.135	-0.5236	0.2941
2.2551	1.119	-0.5241	0.2949
2.2584	1.113	-0.5236	0.2926

M.W. = 280.11 $\bar{\alpha}$ = 1.157 $\bar{\beta}$ = -0.5245 $\bar{\nu}$ = 0.2952

$P_{2\infty}$ = 112.70 $[R_D]$ = 66.68 $P\mu$ = 46.02 $P\mu'$ = 42.69

μ = 1.50 μ' = 1.45

13. 4-Iododiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4980
1.0507	2.2843	1.13902	1.4991
1.3481	2.2873	1.13745	1.4994
2.0467	2.2956	1.13378	1.5001
2.4159	2.2996	1.13176	1.5005
3.0618	2.3075	1.12833	1.5012
3.6434	2.3142	1.12527	1.5018

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2473	1.119	-0.5330	0.3140
2.2482	1.094	-0.5252	0.3115
2.2503	1.128	-0.5296	0.3078
2.2515	1.123	-0.5323	0.3105
2.2536	1.143	-0.5320	0.3135
2.2554	1.144	-0.5311	0.3129

M.W. = 280.11 $\bar{\alpha} = 1.110$ $\bar{\beta} = -0.5313$ $\bar{\nu} = 0.3120$

$P_{2\infty} = 109.65$ $[R_D] = 67.02$ $P\mu = 42.63$ $P\mu' = 39.28$

$\mu = 1.45$ $\mu' = 1.39$

14. <u>2-Nitrodiphenyl in Benzene</u>.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14459	1.4980
0.9915	2.3477	1.14139	1.4990
1.2801	2.3716	1.14048	1.4992
2.1704	2.4409	1.13761	1.5001
2.5328	2.4684	1.13636	1.5004
3.0716	2.5111	1.13459	1.5009
3.4107	2.5378	1.13355	1.5012

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2470	7.584	-0.3227	0.3026
2.2476	7.739	-0.3211	0.2812
2.2503	7.758	-0.3216	0.2903
2.2512	7.733	-0.3249	0.2843
2.2527	7.767	-0.3256	0.2832
2.2536	7.777	-0.3237	0.2815

M.W. = 199.200 $\bar{\alpha} = 7.720$ $\widehat{\beta} = -0.3237$ $\widehat{\gamma} = 0.2854$

$P_{2\infty} = 337.98$ $[R_D] = 58.77$ $P\mu = 279.21$ $P\mu' = 276.27$

$\mu = 3.70$ $\mu' = 3.68$

15. 3-Nitrodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14459	1.4980
1.0458	2.3726	1.14108	1.4990
1.5716	2.4233	1.13935	1.4996
1.9760	2.4626	1.13800	1.5000
2.4938	2.5130	1.13633	1.5005
2.9697	2.5597	1.13474	1.5010
3.2971	2.5917	1.13364	1.5013
4.1664	2.6775	1.13068	1.5022

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2470	9.573	-0.3356	0.2869
2.2488	9.594	-0.3334	0.3054
2.2500	9.619	-0.3335	0.3036
2.2515	9.643	-0.3312	0.3007
2.2530	9.671	-0.3327	0.3031
2.2539	9.681	-0.3321	0.3003
2.2566	9.721	-0.3339	0.3024

M.W. = 199.200 $\bar{\alpha} = 9.523$ $\bar{\beta} = -0.3330$ $\bar{\nu} = 0.3014$

$P_{2\infty} = 404.99$ $[R_D] = 58.83$ $P\mu = 346.16$ $P\mu' = 343.21$

$\mu = 4.12$ $\mu' = 4.10$

16. 4-Nitrodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14459	1.4980
1.1622	2.3968	1.14069	1.4993
1.5389	2.4381	1.13933	1.4997
2.1324	2.5031	1.13743	1.5003
2.4178	2.5341	1.13646	1.5007
3.0743	2.6059	1.13423	1.5013
3.5503	2.6582	1.13266	1.5020
4.3400	2.7469	1.13000	1.5029

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2479	10.697	-0.3356	0.3356
2.2491	10.764	-0.3418	0.3314
2.2509	10.816	-0.3358	0.3234
2.2521	10.822	-0.3363	0.3350
2.2539	10.845	-0.3370	0.3220
2.2560	10.864	-0.3360	0.3380
2.2587	10.933	-0.3362	0.3387

M.W. = 199.200 $\bar{\alpha} = 10.668$ $\bar{\beta} = -0.3367$ $\bar{\nu} = 0.3327$

$P_{2\infty} = 447.67$ $[R_D] = 59.81$ $P\mu = 387.86$ $P\mu' = 384.87$

$\mu = 4.36$ $\mu' = 4.35$

17. 2,2'-Difluorodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14454	1.4981
0.8103	2.2898	1.14192	1.4984
1.4294	2.3030	1.13994	1.4987
2.3099	2.3217	1.13726	1.4990
2.7155	2.3344	1.13548	1.4993
4.1031	2.3610	1.13162	1.4999

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2443	-	-	-
2.2452	2.131	-0.3233	0.1111
2.2461	2.134	-0.3218	0.1259
2.2470	2.130	-0.3158	0.1169
2.2479	2.280	-0.3336	0.1326
2.2497	2.157	-0.3149	0.1316

M.W. = 190.184 $\bar{\alpha} = 2.120$ $\bar{\beta} = -0.3209$ $\bar{\nu} = 0.1267$

$P_{2\infty} = 122.49$ $[R_D] = 50.52$ $P\mu = 71.97$ $P\mu' = 69.45$

$\mu = 1.88$ $\mu' = 1.85$

18. 2,2'-Dichlorodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4980
0.8710	2.2913	1.14150	1.4986
1.3960	2.3020	1.13955	1.4991
2.1093	2.3172	1.13708	1.4996
2.3441	2.3221	1.13622	1.4998
2.6680	2.3290	1.13507	1.5001
3.2365	2.3412	1.13302	1.5005

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2458	2.162	-0.3582	0.2067
2.2473	2.111	-0.3631	0.2364
2.2488	2.120	-0.3575	0.2276
2.2494	2.116	-0.3583	0.2304
2.2503	2.118	-0.3579	0.2361
2.2515	2.131	-0.3584	0.2317

M.W. = 223.098 $\bar{\alpha}$ = 2.095 $\bar{\beta}$ = -0.3587 $\bar{\nu}$ = 0.2305

$P_{2\infty}$ = 140.14 $[R_D]$ = 61.20 $P\mu$ = 78.94 $P\mu'$ = 75.88

μ = 1.97 μ' = 1.93

19. 2,2'-Dibromodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4980
1.0275	2.2868	1.13884	1.4988
1.6191	2.2956	1.13554	1.4992
2.3093	2.3059	1.13164	1.4997
2.9714	2.3154	1.12794	1.5002
3.9712	2.3305	1.12235	1.5009
4.6202	2.3403	1.11867	1.5014

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2468	1.395	-0.5625	0.2335
2.2476	1.425	-0.5608	0.2224
2.2491	1.447	-0.5621	0.2208
2.2506	1.444	-0.5614	0.2221
2.2527	1.461	-0.5608	0.2191
2.2542	1.467	-0.5617	0.2208

M.W.= 312.016 $\bar{\alpha} = 1.400$ $\bar{\beta} = -0.5614$ $\bar{\nu} = 0.2216$

$P_{2\infty} = 136.37$ $[R_D] = 66.52$ $P\mu = 69.85$ $P\mu' = 66.52$

$\mu = 1.87$ $\mu' = 1.81$

20. 2,2'-Dinitrodiphenyl in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14459	1.4981
0.2506	2.3022	1.14349	1.4983
0.3720	2.3169	1.14294	1.4984
0.6009	2.3448	1.14201	1.4986
0.7729	2.3655	1.14129	1.4987
0.9357	2.3861	1.14054	1.4989
1.3687	2.4399	1.13876	1.4992

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2443	-	-	-
2.2449	11.848	-0.4389	0.2394
2.2452	11.946	-0.4435	0.2419
2.2458	12.028	-0.4294	0.2496
2.2461	12.032	-0.4270	0.2329
2.2467	12.145	-0.4328	0.2565
2.2476	12.233	-0.4214	0.2411

M.W. = 244.200 $\bar{\alpha}$ = 11.785 $\bar{\beta}$ = -0.4309 $\bar{\nu}$ = 0.2441

$P_{2\infty}$ = 593.26 $[R_D]$ = 62.46 $P\mu$ = 530.80 $P\mu'$ = 527.68

μ = 5.10 μ' = 5.09

21. Iodobenzene in Benzene.

$100w_2$	ϵ_{12}	v_{12}	n_D
0.0000	2.2725	1.14462	1.4980
1.1250	2.2860	1.13792	1.4987
1.8641	2.2949	1.13357	1.4991
2.4291	2.3015	1.13015	1.4994
3.1596	2.3103	1.12587	1.4999
4.6528	2.3285	1.11691	1.5007
5.5135	2.3484	1.11181	1.5012
6.7262	2.3541	1.10459	1.5019

n_D^2	ϵ_{12}/w_2	v_{12}/w_2	n_D^2/w_2
2.2440	-	-	-
2.2461	1.198	-0.5956	0.1867
2.2473	1.201	-0.5928	0.1770
2.2482	1.194	-0.5957	0.1729
2.2497	1.195	-0.5934	0.1804
2.2521	1.205	-0.5956	0.1741
2.2536	1.196	-0.5951	0.1741
2.2557	1.213	-0.5951	0.1739

M.W. = 204.02 $\bar{\alpha} = 1.198$ $\bar{\beta} = -0.5949$ $\bar{\nu} = 0.1755$

$P_{2\infty} = 79.38$ $[R_D] = 39.70$ $P\mu = 39.68$ $P\mu' = 37.69$

$\mu = 1.40$ $\mu' = 1.36$

CHAPTER III.

DISCUSSION OF RESULTS

Section 1.

Survey of Relevant Published Data.

Published data relevant to the present investigation may be divided into two sections, firstly data dealing with the substituted diphenyls and secondly those relating to the monosubstituted benzenes. A collection has been made of all the existing figures and they will be discussed shortly. However, before any attempt can be made at comparing these figures among themselves or with those obtained in the present work it has been found necessary to recalculate them by the method used for the results reported in Chapter II, namely that of Halverstadt and Kumler (1), and this has been carried out in all cases where the published figures have been sufficiently detailed. In order to do this all methods of expressing the concentrations of the solutions had to be converted into percentage compositions by weight ('weight percent') and the following derivations of the necessary conversion equations were made.

Convertion of Mole Fractions to Weights Percent:

Let f_2 be the mole fraction of the solute,

w_2 be the weight fraction of the solute and let $W_2 = 100w_2$,

i.e. W_2 is the concentration of the solute in weight percent.

Then, since

$$f_2 = \frac{n_2}{n_1 + n_2}$$

where n_1 and n_2 are the numbers of gram moles of solvent and solute respectively,

for 100g. of solution

$$f_2 = \frac{\frac{W_2}{M_2}}{\frac{100-W_2}{M_1} + \frac{W_2}{M_2}}$$

where M_1 and M_2 are the molecular weights of the solvent and solute respectively.

Thus

$$\frac{f_2\ (100-W_2)}{M_1} + \frac{f_2W_2}{M_2} = \frac{W_2}{M_2}$$

and hence

$$W_2 = \frac{\frac{100f_2}{M_1}}{\frac{1-f_2}{M_2} + \frac{f_2}{M_1}}$$

i.e.

$$W_2 = \frac{100f_2M_2}{M_1 + f_2(M_2 - M_1)} \qquad (1)$$

Conversion of Molarity to Weight Percent:

Let x_2 be the molarity of the solute,

M_2 be the molecular weight of the solute,

v_{12} ($= 1/d_{12}$) be the specific volume of the solution,

and let $v_{12} = v_1 + \beta w_2$

where v_1 is the specific volume of the pure solvent, w_2 is the weight fraction of the solute and β is a constant.

Now x_2 g.mols./litre

$$\equiv x_2M_2 \text{ g./litre}$$

$$\equiv \frac{x_2M_2}{1000} \text{ g./c.c.}$$

$$\equiv \frac{x_2M_2}{1000d_{12}} \text{ g./g.} = w_2$$

$$\equiv \frac{x_2M_2}{10d_{12}} \text{ g./100g.} = \frac{x_2M_2v_{12}}{10} = W_2$$

But $v_{12} = v_1 + \beta w_2$,

hence

$$W_2 = \frac{x_2M_2\ (v_1 + \beta w_2)}{10}$$

$$= \frac{x_2M_2(100v_1 + \beta W_2)}{1000}$$

i.e. $$W_2 = \frac{100x_2M_2v_1}{1000 - x_2M_2\beta} \qquad (2)$$

The application of equation (1) is straightforward and presents little difficulty. However, equation (2) requires a knowledge of the values of β and v_1, and it has been found that in most cases in which the concentrations are recorded as molarities the values of the densities of the solvent and solutions are not given. This necessitates the assumption of a value for v_1, the accuracy of which cannot be determined, and also the use of the value of β found in the present work. Thus results calculated by this second method are subject to errors, the magnitudes of which are not determinable, and its application cannot be regarded as wholly satisfactory.

Table 1. contains a summary of the published values for the molecular refractions, the molecular polarisations at infinite dilution and the dipole moments of the substituted diphenyls relevant to the present investigation together with the figures obtained by recalculation on the basis of Halverstadt and Kumler's method.

Table 1.

	Published figures			Recalculated figures			
	$[R_D]$ (c.c.)	$P_{2\infty}$ (c.c.)	μ (D)	$[R_D]$ (c.c)	$P_{2\infty}$ (c.c)	μ (D)	
2-nitrodiphenyl	$(P^0_A + {}_0 = 305)$		3.79	Insuffient data			(2)
	56.0	351	3.80	55.0	358	3.86	(3)
	56.7	366.4	3.82	56.7	376.3	3.96	(4)
3-nitrodiphenyl	$(P^0_A + 0 = 323)$		3.90	Insuffient data			(2)
4-nitrodiphenyl	$(P^0_A + {}_0 = 390)$		4.28	Insuffient data			(2)
	56.0	425	4.17	55.0	431.2	4.29	(3)
	58.8	457.3	4.41	Same method as here			(5)
4-fluorodiphenyl	55.6	98	1.50	50.1	97.7	1.53	(3)
2-chlorodiphenyl	55.6	90.5	1.30	55.0	91.0	1.33	(6)
	$(P^0_A + {}_0 = 44)$		1.44	Insufficient data			(2)
	56.8	100.2	1.45	56.9	98.7	1.43	(7)
3-chlorodiphenyl	56.7	123	1.79	57.6	123.4	1.80	(6)
	57.9	113.5	1.64	58.0	113.8	1.65	(7)
4-chlorodiphenyl	55.6	103	1.53	57.1	105.2	1.54	(6)
	$(P^0_A + {}_0 = 56)$		1.63	Insufficient data			(2)
	57.6	112.6	1.63	57.7	111.2	1.62	(7)
	55.	108	1.58	55.2	107.5	1.60	(3)

4-bromodiphenyl	58	117	1.64	58.1	119.0	1.73	(3)
	60.5	115.9	1.65	Same method as here			(5)
2,2'-dinitrodiphenyl	65	596	5.12	Insufficient data			(8)
	66	623	5.19	58.4	595.0	5.13	(9)
2,2'-dichlorodiphenyl	62.0	124.1	1.72	Insufficient data			(8)
	65.9	131	1.77	58.6	131.2	1.89	(6)
	60.5	136	1.91	60.4	137.1	1.94	(7)

The above results are summarised here for convenience and will be dealt with in relation to the figures now obtained in the following sections of this chapter. There are, however, three cases in Table 1. which are not at first sight self-consistent and require some further explanation. The anomalies occur in the figures for 4-fluorodiphenyl and 4-chlorodiphenyl due to Le Fèvre and Le Fèvre (3) and in those for 3-chlorodiphenyl due to Weissberger and Sangewald (6). In each of these instances the authors' value for the orientation polarisation is greater than that obtained upon recalculation and yet the value of the dipole moment is found to be greater in the case of the recalculated figures. This, it is almost certain, is due to the use of different values for the universal constants and would have been apparent in more cases had the original and the recalculated figures fallen sufficiently closely with their differences in the same sense as those mentioned above. As an illustration of this effect one may take the two sets of figures for 4-nitrodiphenyl in Table 1. derived from the measurements of Le Fèvre and Le Fèvre (3) from which it may be seen that the increase in the moment on recalculation is much greater than would be expected solely from the increase in the total polarisation.

Consideration of the Published Polarisation Data on the Monosubstituted Benzenes.

The figures that have been published for the polarisation of fluoro-, chloro-, bromo-, iodo- and nitro-benzene are very numerous and a comprehensive survey would be a difficult task. It is necessary for the purpose of the succeeding sections of this chapter to have an accurate knowledge of the values of the dipole moments of the above-mentioned benzene derivatives in order that calculated values may be obtained for the moments of the substituted diphenyls. With this aim in view a survey was carried out along the lines to be described below.

The work of obtaining values of the dipole moments of the monosubstituted benzenes was divided into three sections. Firstly, in the cases of fluorobenzene, chlorobenzene and bromobenzene the values to be used have been arrived at after a selective study of the data in the literature. The figures were maintained at manageable proportions by ignoring all measurements in solvents other than benzene and by restricting consideration to those measurements made at or near 25°. This led to values identical with those recalculated by Everard and Sutton (10) and recorded below in Table 2. Secondly, in the case of nitrobenzene a highly comprehensive survey of the published data was carried out by Smith and Cleverdon (11) and the recalculated value at which they arrived, the value to be used here, is recorded in Table 2. Finally, the dipole moment of iodobenzene has been redetermined as part of the present investigation and the value obtained is found to be in good agreement with that derived from the measurements of Tiganik (12) though this is rather lower than the one due to Saxby, quoted by Everard and Sutton (loc.cit.). Tiganik's data on recalculation led to a value of 1.39D.

<u>Table 2.</u>

Fluorobenzene	μ = 1.48D
Chlorobenzene	1.60D
Bromobenzene	1.57D
Iodobenzene	1.40D
Nitrobenzene	4.01D

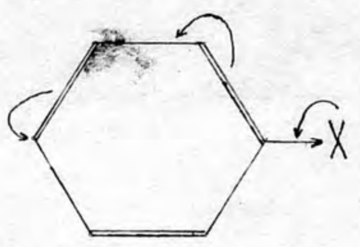
The figures in Table 2. are those in which all the calculated values for the dipole moments of the substituted diphenyls in the later sections of this chapter are based.

Section 11.

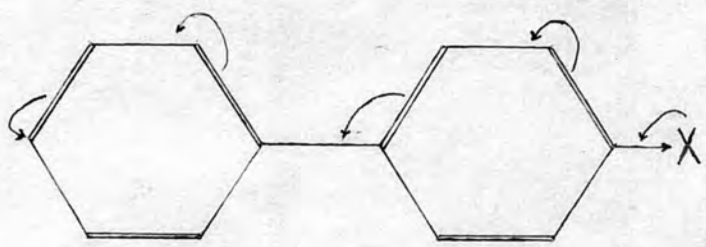
The Monosubstituted Derivatives of Diphenyl.

Le Fèvre and Le Fèvre (3) reviewing the subject of electronic displacements within the diphenyl nucleus pointed out that from the work of Le Fèvre and Turner (13) and of Gull and Turner (14) on the nitration of nitrodiphenyls it appeared that the diphenyl structure exhibited the features of general inductive influences that were transmitted right through the molecule but of tautomeric displacements that were so reduced at the bridge bond that they exerted no effects observable by substitution reactions in the attached ring. They were of the opinion that the development of the latter effects in this nucleus might be inferred from a study of the mesomerism of various diphenyl derivatives, since the mesomeric and tautomeric effects operate by the same mechanism and the presence of one may be taken as evidence for the possibility of the other.

The mesomeric effect in an aromatic nucleus is a permanent electronic rearrangement occurring by the mechanism of the tautomeric effect and hence the mesomeric state of a monohalogenobenzene and a similarly substituted diphenyl may be represented by the curved arrows shown in diagrams (A) and (B).



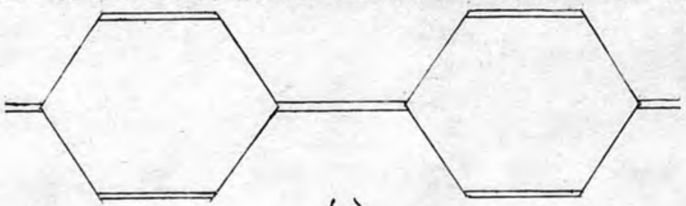
(A)



(B)

It is evident therefore that, X being halogen, the observed moment will consist of the moment of the C-X link plus all the induced moments arising from the interaction of the C-X moment with the polarisable atoms constituting the remainder of the molecule minus the somewhat smaller permanent moments resulting from the mesomeric effect. The contribution of this last-named effect is difficult to estimate, but its existence is held to explain why the halogenobenzenes have smaller moments than the corresponding tert-butyl halides in which no such reversed moments are operative (15). Thus, if the process illustrated in (B) were to occur to any extent, the 4-halogenodiphenyls should show greater reversed polarities than the related benzene compounds and the observed dipole moments would be expected to be smaller than those of the benzene derivatives by approximately the amount of these changes in the mesomeric effect.

The experimental data of Le Fèvre and Le Fèvre did not bear out the above and this, they proposed, was due to either the moments induced in the unsubstituted phenyl nucleus by the C-X moment outweighing the mesomeric moment, or the non-transmission of the mesomeric effect across the 1,1'-bond. The latter suggestion is discounted by the fact that the X-ray examination of diphenyl provides evidence that it is degenerate, with contributions from structures of the type (C).



(C)

Mesomeric effects can therefore occur in diphenyl itself and it would appear unlikely that they would be absent in its derivatives. As a consequence of this they calculated the subsidiary moments induced in the molecules by the principal moment and their results will be considered together with those obtained by the present author later in this section.

More recently Everard and Sutton (10) have discussed in detail the various interactions between a substituent group and an aryl radical to which it is linked. These comprise

(a) the inductive effect arising through polarisation of the radical by the electric field of the substituent at present regarded as the resultant of two components

  (i) the 'Classical' inductive effect, I_C, a purely electrostatic process influencing both σ and π electrons, and

  (ii) the 'Non-classical' inductive effect, I_N leading to changes of π -bond order;

(b) the mesomeric effect arising through the tendency towards formation of a π-bond between the substituent and the carbon atoms to which it is linked, and causing a modification in the π-bonds present in the radical.

It has been shown by Frank (16) that the I_C effect decreases as the inverse cube of the distance from the dipole and is thus of relatively short range; but the non-classical effect influences the whole of a conjugated system, and hence it becomes very closely associated with the mesomeric effect, although, like the I_C effect it may either reinforce or oppose this effect. As these changes in π-electron distribution have a reciprocal effect in modifying the σ-bonds between the carbon atom and the substituent group and those between one carbon atom and another the whole problem is seen to be of a complex nature.

Classical Inductive Effects.

Due to the fact that the measurements upon diphenyl derivatives have been made in solution, and consequently the values of the dipole moments deduced from them are modified by an appreciable and unknown solvent effect, no exact correlation between theory and observation is to be expected. It is, however, of interest in the first instance to determine the extent to which the observed moments can be interpreted on the basis of the classical inductive effect.

According to the theory developed by Smallwood and Herzfeld (17) and by Frank (16) the moment, μ, of a substituent will induce moments μ_x and μ_y respectively parallel to and at right angles to the inducing moment, the values of the induced moments being given by

$$\mu_x = \frac{\alpha(\epsilon + 2).E_x}{3} \quad \text{and} \quad \mu_y = \frac{\alpha(\epsilon + 2).E_y}{3}$$

where α is the polarisability of the polarisable system,

ϵ is the dielectric constant of the medium

and E_x, E_y are the components of the polarising field respectively parallel to and perpendicular to the inducing moment.

E_x and E_y are given by the expressions

$$E_x = \frac{3\cos^2\theta - 1}{\epsilon r^3}\mu \quad \text{and} \quad E_y = \frac{3\cos\theta \ \sin\theta}{\epsilon r^3}\mu$$

where r is the distance between the dipole and the polarisable centre and θ is the angle between u and r.

Thus

$$\mu_x = \frac{\alpha(\epsilon + 2)}{3} \cdot \frac{3\cos^2\theta - 1}{\epsilon r^3} \cdot \mu \qquad (1)$$

and

$$\mu_y = \frac{\alpha(\epsilon + 2)}{3} \cdot \frac{3\cos\theta \sin\theta}{\epsilon r^3} \cdot \mu \qquad (2)$$

Following the method by which Hampson and Weissberger applied this theory to naphthalene compounds (18) and to the isomeric monochlorodiphenyls (7) and Le Fèvre and Le Fèvre (3) used it in the case of a few derivatives of diphenyl, as mentioned above, a monosubstituted diphenyl molecule may be regarded as the corresponding derivative of benzene to which an additional polarisable group, namely a benzene ring, has been added. The polarisable centre of this additional grouping may be taken as being at the middle of the unsubstituted ring, whilst α is the polarisability of benzene, i.e. 12.5×10^{-24} in the plane of the ring and 6.25×10^{-24} at right angles to that plane (19); ϵ is the dielectric constant of benzene, 2.27.

The questions which remain to be answered before any calculations can be carried out are those concerned with the value to be assigned to the polarising dipole and its 'point of action'. Hampson and Weissberger used the dipole moment of the corresponding benzene derivative, as did Le Fèvre and Le Fèvre, while Everard and Sutton mention briefly that they used the corresponding group moment. Two difficulties arise in regard to this last procedure. Firstly, the true moment of the $C_{(aromatic)}$-X dipole in the halogenobenzenes cannot be evaluated without certain assumptions since it should include the contribution of the moment due to the mesomeric effect as was mentioned earlier in connection with the work of Le Fèvre and Le Fèvre. Further, the induced dipole produced in the substituted ring must also contribute towards the induced moment in the second ring as the latter is, in effect, in the field of the resultant dipole of the first ring. For these reasons, and on the grounds of simplicity, the dipole moment of the corresponding benzene derivatives has been taken as the inducing dipole in the calculations that follow. The actual values used are those obtained from measurements made with benzene as solvent since it appeared likely that the errors due to the solvent effect may be minimised by this procedure, the benzene and diphenyl derivatives being roughly the same shape and having similar electrical properties. By using the ordinary

$C_{(alkyl)}$-X group moment as was apparently employed by Everard and Sutton (loc.cit.) one gets a slight exaggeration of the effects which will be discussed later. For similar reasons, incalculating the distance r for the halogeno-compounds the dipole has been taken as located at the 'point of contact' of the carbon and halogen atoms, i.e. on the carbon-halogen bond and 0.775A from the carbon nucleus. For the nitro-compounds the dipole has been taken as acting effectively at the centre of the nitrogen atom. The interatomic distances that have been used are

C-C (aromatic)	1.40 A
C-C (centre bond)	1.50 A
C-N	1.45 A

When the two rings are coplanar the inducing field and the induced moment are in the plane of the unsubstituted ring, and hence the value of α for the plane of the ring is applicable. On the other hand when the rings are not coplanar the field has to be resolved in directions parallel to and at right angles to the plane of the unsubstituted ring, and the appropriate values of α used in each case. As the polarisability is less in the direction at right angles to the ring the effect of the induced moment on the resultant moment decreases progressively with increasing angle between the planes of the rings, and becomes a minimum in the right angles position.

The values of r and θ for the various types of diphenyl compounds to be discussed have been calculated in accordance with the above premises, together with the theoretical ratios of the moments of the diphenyl and benzene derivatives calculated for the two extreme positions, that is with the rings (a) coplanar, and (b) in planes at right angles. In deriving calculated moments for comparison with the observed values the moments of the halogenobenzenes and of nitrobenzene used have been those recorded in Table 2.

A further property of interest in this work, and one the evaluation of which is inherent in the method of calculating the dipole moments, is the molecular refraction of each of the compounds investigated. The figures obtained for these will be discussed in connection with positional isomerism and will be compared with the values derived by adding the difference between the molecular refractions of diphenyl, 52.41 c.c. (20), and benzene, 26.21 c.c., to the molecular refractions of the corresponding benzene derivatives. Table 3. contains the values used, based on the figures of Vogel, Cresswell, Jeffrey and Leicester (21) for the substituted benzenes.

Table 3.

Fluorodiphenyl	$[R_D]$ = 52.18 c.c.
Chlorodiphenyl	57.34 c.c.
Bromodiphenyl	60.19 c.c.
Iododiphenyl	65.35 c.c.
Nitrodiphenyl	58.92 c.c.

The 3-Substituted Derivatives of Diphenyl

The 3-halogeno- and 3-nitro-derivatives of diphenyl are considered first since with a substituent in this position the additional mesomeric and non-classical induction effects brought about by the introduction of a second ring would be expected to be a minimum. Using 2.27 as the value of the dielectric constant of the medium and the value of the polarisability, α, quoted above, equations (1) and (2) may be reduced to

$$\mu_x = 7.834 . \frac{3\cos^2\theta - 1}{r^3} . \mu_{PhX} \qquad (3)$$

and

$$\mu_y = 25.50 . \frac{\cos\theta \sin\theta}{r^3} . \mu_{PhX} \qquad (4)$$

If $\bar{\mu}$ is the resultant moment, then

$$\bar{\mu} = \left[(\mu_{PhX} + \mu_x)^2 + \mu_y^2\right]^{\frac{1}{2}} \qquad (5)$$

For the case of the 3- halogenodiphenyls in both the coplanar and right angles position it can be seen from Figures 10 (a) & (b), which are drawn to scale, that

$$r.\cos\varphi = 2.175\cos 60 + 4.30$$

and $$r.\sin\varphi = 2.175\cos 30$$

from which $$\varphi = 19^\circ\ 19'$$

hence $\theta = 40^\circ 41'$ and $r = 5.71$ A

Substitution of these values into equations (3), (4) and (5) leads to the results

$$\mu_x = 0.0305\mu_{PhX}$$

$$\mu_y = 0.0624\mu_{PhX}$$

and $$\bar{\mu} = 1.032\mu_{PhX}$$

FIG. 10A. 3-HALOGENODIPHENYL (RINGS COPLANAR)

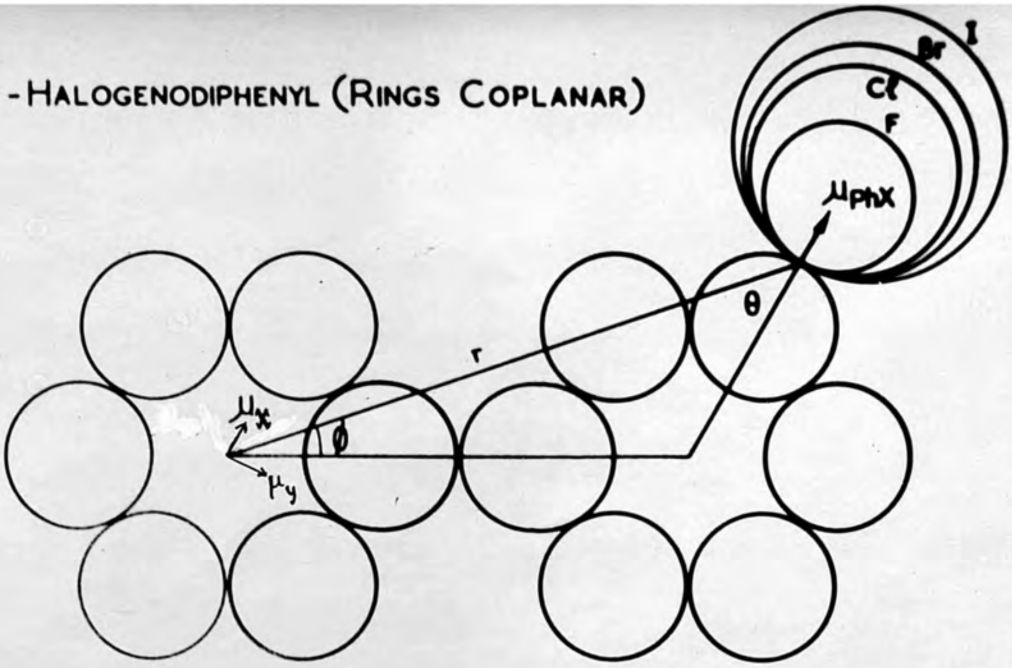


FIG. 10B. 3-HALOGENODIPHENYL (RINGS IN PLANES AT RIGHT ANGLES)

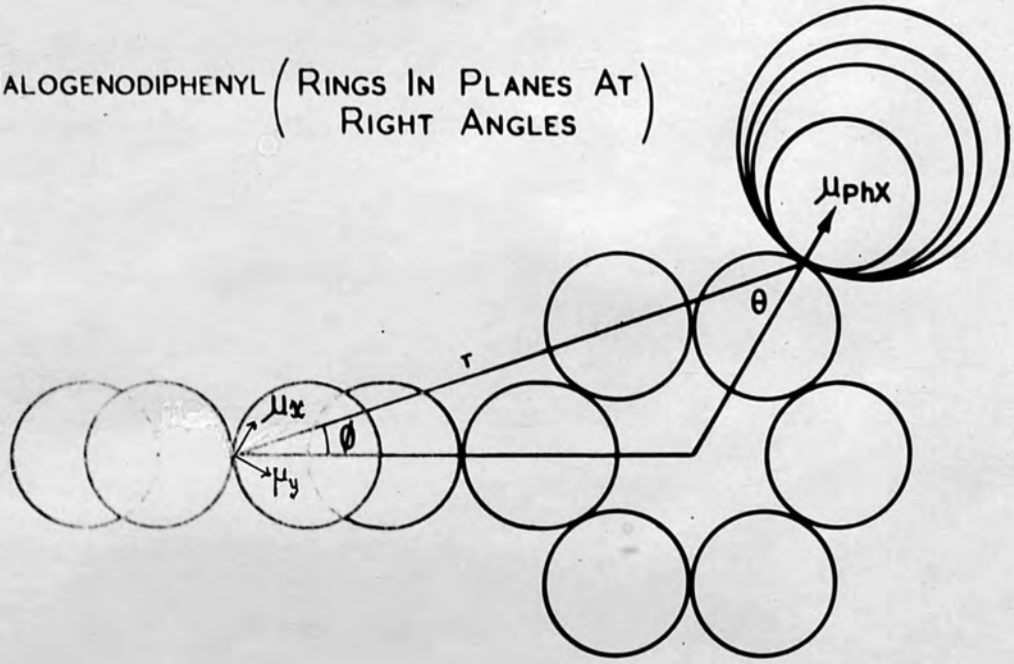
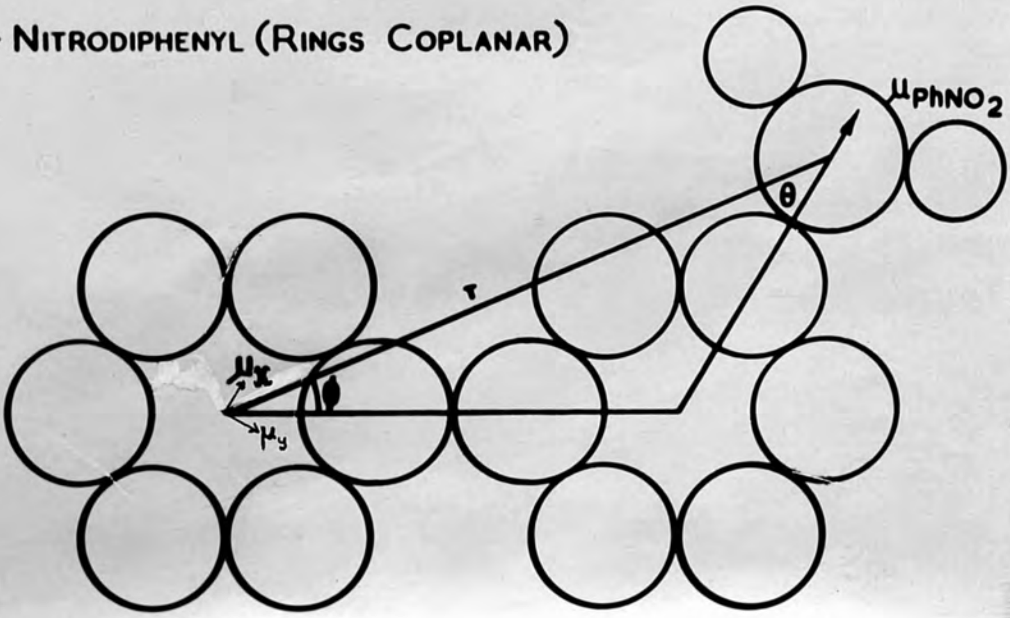


FIG. 10C. 3-NITRODIPHENYL (RINGS COPLANAR)



for the coplanar halogeno-derivatives. Similarly from Figure 10(c) it can be seen that

$$r.\cos\,\phi = 2.87\cos 60 + 4.30$$

and $$r.\sin\,\phi = 2.87\cos 30$$

from which $$\phi = 23^\circ\ 36'$$

hence $\theta = 36^\circ\ 34'$ and $r = 6.25$ A

Substitution of these values into equations (3), (4) and (5) gives

$$\mu_x = 0.0300\ \mu_{PhNO_2}$$

$$\mu_y = 0.0460\ \mu_{PhNO_2}$$

and $$\bar{\mu} = 1.031\ \mu_{PhNO_2}$$

The case in which the planes of the rings are at right angles, as illustrated for the halogeno-derivative by Figure 10(b), is less simple. If

μ_r is the component of the induced moment in the plane at right angles to that of the unsubstituted ring, and

μ_s is the component of the induced moment in the plane of the unsubstituted ring,

then $$\mu_r = \mu_x\cos 30 - \mu_y\cos 60 \qquad (6)$$

and

$$\mu_s = \mu_x\cos 60 + \mu_y\cos 30 \qquad (7)$$

The appropriate value of α can only be brought into the calculation after this resolution has been made, and on doing this one obtains the following equations

$$\mu_r = \frac{1.958}{r^3}\left\{\sqrt{3}(3\cos^2\theta - 1) - 3\cos\theta\sin\theta\right\}\mu_{PhX} \qquad (8)$$

and

$$\mu_s = \frac{3.915}{r^3}\left\{3\cos^2\theta - 1 + \sqrt{3}\cos\theta\sin\theta\right\}\mu_{PhX} \qquad (9)$$

Introduction of the appropriate values of r and θ into these equations gives

$$\mu_r = -0.0024\mu_{PhX}$$

and

$$\mu_s = 0.0693\mu_{PhX}$$

Combination of the values of μ_r and μ_s gives their resultant μ_t which is in the same plane as μ_{PhX} and from this latter pair of values $\bar{\mu}$ may be calculated.

$$\mu_t = (\mu_r^2 + \mu_s^2)^{\frac{1}{2}} \qquad (10)$$

and

$$\bar{\mu} = (\mu_t^2 + \mu_{PhX}^2 + 2\mu_t\mu_{PhX}\cos\gamma)^{\frac{1}{2}} \qquad (11)$$

Substitution of the figures obtained above for μ_r and μ_s into equations (10) and (11) gives

$$\mu_t = 0.0693\mu_{PhX}$$

and

$$\bar{\mu} = 1.034\mu_{PhX}$$

Similarly, for 3-nitrodiphenyl this procedure yields the values

$$\mu_r = 0.0015\mu_{PhNO_2}$$

$$\mu_s = 0.0548\mu_{PhNO_2}$$

$$\mu_t = 0.0548\mu_{PhNO_2}$$

$$\bar{\mu} = 1.030\mu_{PhNO_2}$$

The above results are recorded for convenience in Table 4.

Table 4.

	r (A)	θ	$\bar{\mu}/\mu_{PhX}$ coplanar position	$\bar{\mu}/\mu_{PhX}$ right angles position
3-halogenodiphenyls	5.71	40°41'	1.03_2	1.03_4
3-nitrodiphenyl	6.25	36°34'	1.03_1	1.03_0

whilst the experimental results, including the parameters $\bar{\alpha}$,

$\bar{\beta}$ and $\bar{\nu}$ are to be found in Table 5. together with the calculated values of the molecular refractions.

From the data summarised in Table 4. and Table 5. it is possible to compare the observed and calculated moments and this is done most conveniently in Table 6. The values of the calculated moments are those obtained on the assumption that the planes of the rings are at right angles and for the most part they differ by less than 0.01D from the values obtained on the assumption of coplanar rings.

<u>Table 5.</u>

	$\bar{\alpha}$	$-10^3\bar{\beta}$	$10^3\bar{\nu}$	$P_{2\infty}$	$[R_D]$	$[R_D]$ calc.	μ
3-fluorodiphenyl	1.730	249.0	195	102.0	51.6	52.18	1.57
3-chlorodiphenyl	1.820	284.7	283	112.9	57.6	57.34	1.65
3-bromodiphenyl	1.506	434.5	263	115.1	60.2	60.19	1.64
3-iododiphenyl	1.110	511.9	295	110.2	66.7	65.35	1.46
3-nitrodiphenyl	9.523	333.0	301	405.0	58.7	58.92	4.12

<u>Table 6.</u>

	$\mu_{obs.}$	$\mu_{calc.}$	$\Delta\mu$
3-fluorodiphenyl	1.57	1.53	-0.04
3-chlorodiphenyl	1.65	1.65	0.00
3-bromodiphenyl	1.64	1.62	-0.02
3-iododiphenyl	1.46	1.45	-0.01
3-nitrodiphenyl	4.12	4.13	-0.01

It is readily seen that in each case the observed moment is close to the calculated value and this, it is considered, justifies the method used for computing the classical inductive effect. In view of the uncertainties which beset the use of the Ph-X moment in the calculation together with those due to any solvent effect the above agreement must be considered somewhat fortuitous but, nonetheless, highly satisfactory.

Comparison of the figures in Table 5. with those of previous workers in Table 1. for 3-chloro- and 3-nitrodiphenyl shows that in the case of the chloro-compound the present figure is in good agreement with the redetermined value of Hampson and Weissberger (7) whilst for the 3-nitrodiphenyl the present figure is considerably higher than that obtained by Naeshagen (2), it is difficult to find a reason for this discrepancy.

The most notable figures in Table 6. are those relating to 3-fluorodiphenyl. They will not be discussed at length here but will be considered later in conjunction with those for the positional isomers which will also be shown to be, in varying degrees, anomalous. A comparison of the observed and calculated values of the molecular refraction shows that for the most part the agreement is good particularly since the difference between the results deduced from the refractive index measurements on solutions and those obtained by measurements on the compound in the pure state, if it is a liquid, is often found to be of the order of a cubic centimetre.

One may therefore summarise this section by stating that, in general, the electronic transitions within the molecule of a 3-substituted diphenyl are adequately accounted for on the basis of the classical inductive effect, and may be regarded as substantiating the statement of Everard and

Sutton (10) that the only effect of meta-substitution of a conjugated system into a benzene derivative should be an inductive one, and this would be expected to be small.

The 2-Substituted Derivatives of Diphenyl

Since in the previous part of this section it was shown that the method of calculation of inductive effects is well justified, it will now be applied to the other mono-substituted derivatives of diphenyl. For the 2-halogenodiphenyls it can be seen from Figure 11(a) that

$$r.\cos\varphi = 4.30 + 2.175\cos 60$$

and $$r.\sin\varphi = 2.175\cos 30$$

from which $$\varphi = 30^\circ 28'$$

hence $$\theta = 89^\circ 32' \qquad \text{and } r = 3.73\ \text{A}$$

For the corresponding nitro-compound shown in Figure 11(c)

$$r.\cos\varphi = 4.30 + 2.87\cos 60$$

and $$r.\sin\varphi = 2.87\cos 30$$

thus $$\varphi = 40^\circ 57'$$

while $$\theta = 79^\circ 3' \qquad \text{and } r = 3.79\ \text{A}$$

Considering the case in which the rings are coplanar, substitution of the above figures in equations (3), (4) and (5) leads to the values

$$\mu_x = -0.1509\mu_{PhX}$$

$$\mu_y = 0.0041\mu_{PhX}$$

and $$\bar{\mu} = 0.849\mu_{PhX}$$

for the 2-halogenodiphenyls, and

FIG. 11A. 2 - HALOGENODIPHENYL (RINGS COPLANAR)

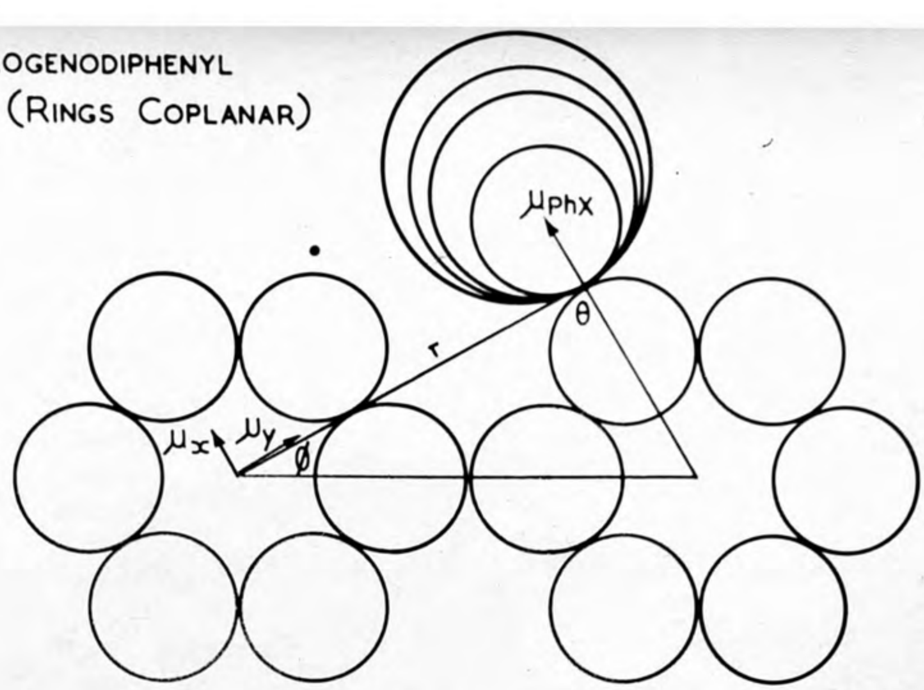


FIG. 11B. 2 - HALOGENODIPHENYL (RINGS IN PLANES AT RIGHT ANGLES)

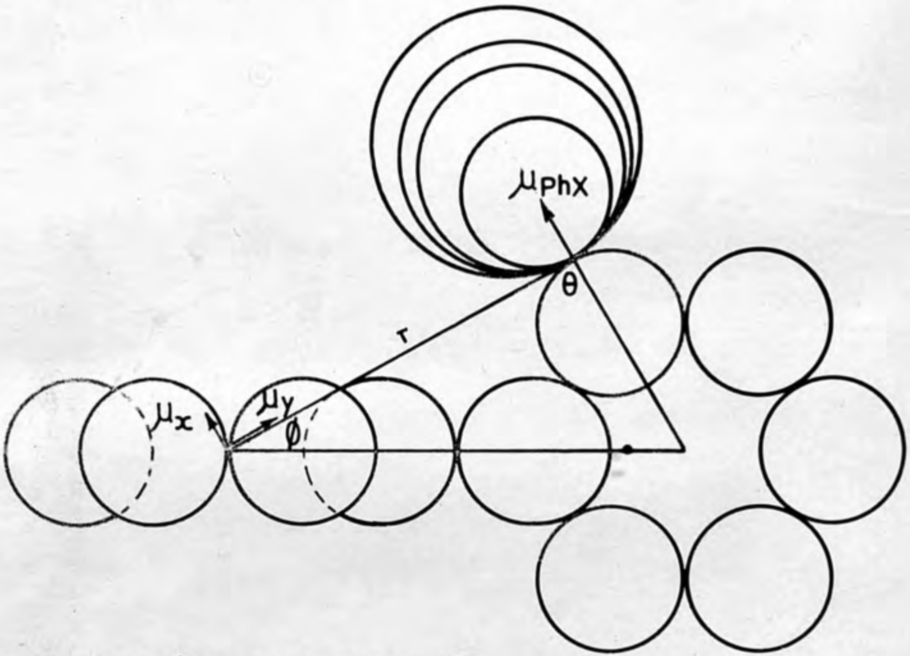
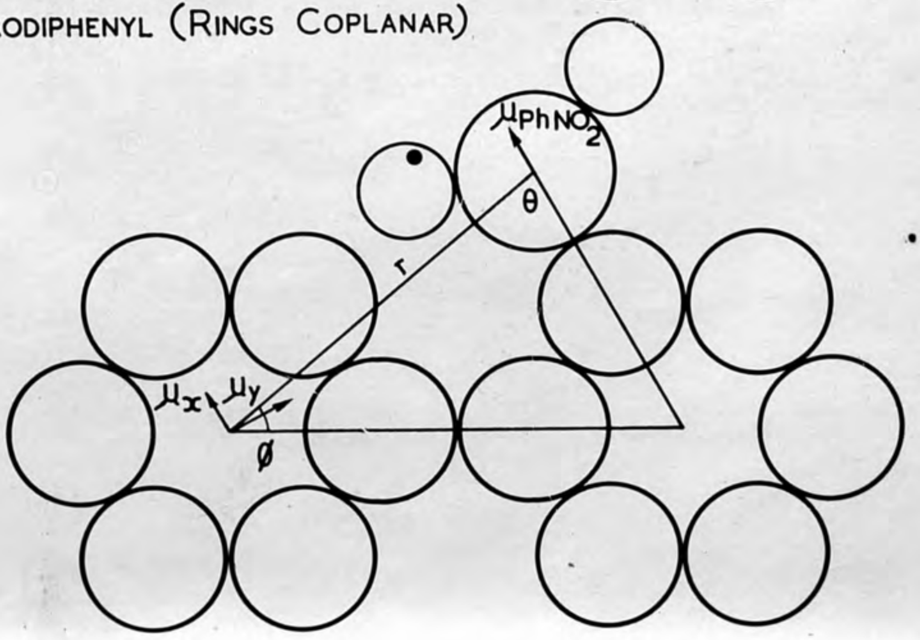


FIG. 11C. 2 - NITRODIPHENYL (RINGS COPLANAR)



$$\mu_x = -0.128\mu_{PhNO_2}$$

$$\mu_y = 0.0803\mu_{PhNO_2}$$

and $$\bar{\mu} = 0.876\mu_{PhNO_2}$$

for 2-nitrodiphenyl.

Consideration of the case in which the planes of the rings are at right angles shows that equations (6) and (7) must be modified, those applicable here being

$$\mu_r = \mu_x\cos 30 + \mu_y\cos 60 \qquad (12)$$

and

$$\mu_s = \mu_y\cos 30 - \mu_x\cos 60 \qquad (13)$$

Thus equations (8) and (9) are replaced in this instance by

$$\mu_r = \frac{1.958}{r^3}\left\{\sqrt{3}(3\cos^2\theta - 1) + 3\cos\theta\sin\theta\right\}\mu_{PhX} \qquad (14)$$

and

$$\mu_s = \frac{3.915}{r^3}\left\{3\sqrt{3}\cos\theta\sin\theta - 3\cos^2\theta + 1\right\}\mu_{PhX} \qquad (15)$$

Introduction of the appropriate values of r and θ into equations (14) and (15) together with equation (10) and the expression

$$\bar{\mu} = (\mu_t^2 + \mu_{PhX}^2 - 2\mu_t\mu_{PhX}\cos\gamma)^{\frac{1}{2}} \qquad (16)$$

in place of equation (11) leads to the values

$$\mu_r = -0.0653\mu_{PhX}$$

$$\mu_s = 0.0755\mu_{PhX}$$

$$\mu_t = 0.0998\mu_{PhX}$$

and $$\bar{\mu} = 0.906\mu_{PhX}$$

for the 2-halogenodiphenyls, and

$$\mu_r = -0.035\mu_{PhNO_2}$$

$$\mu_s = 0.1337\mu_{PhNO_2}$$

$$\mu_t = 0.1383\mu_{PhNO_2}$$

and $$\bar{\mu} = 0.908\mu_{PhNO_2}$$

for the 2-nitrodiphenyl. As in the case of the 3-substituted diphenyls the important figures are tabulated below.

Table 7.

	r	θ	μ/μ_{PhX} coplanar	μ/μ_{PhX} rt. angles
2-halogenodiphenyls	3.73	89°32'	0.84_9	0.90_6
2-nitrodiphenyl	3.79	79°3'	0.87_6	0.90_8

The polarisation data obtained in the present work for the 2-substituted diphenyls is summarised in Table 8. and the comparison of the calculated and observed moments constitutes Table 9.

Table 8.

	α	$-10^3\beta$	$10^3\gamma$	$P_{2\infty}$	$[R_D]$	μ
2-fluorodiphenyl	1.346	251.4	196	89.4	51.6	1.36
2-chlorodiphenyl	1.409	280.8	256	98.5	57.2	1.42
2-bromodiphenyl	1.279	415.9	248	106.7	60.8	1.50
2-iododiphenyl	0.897	511.9	284	100.0	67.1	1.27
2-nitrodiphenyl	7.720	323.7	285	338.0	58.8	3.70

Table 9.

	μ (obs.)	μ calc. coplanar	$\Delta\mu$	μ calc. rt. angles	$\Delta\mu$
2-fluorodiphenyl	1.36	1.26	-0.10	1.34	-0.02
2-chlorodiphenyl	1.42	1.36	-0.06	1.45	0.03
2-bromodiphenyl	1.50	1.33	-0.17	1.42	-0.08
2-iododiphenyl	1.27	1.19	-0.08	1.27	0.00
2-nitrodiphenyl	3.70	3.51	-0.19	3.64	-0.06

Comparison of the results recorded in Table 8. with those already published, Table 1., for 2-chloro- and 2-nitrodiphenyl shows that the present value for the chloro-compound is in good agreement with those obtained by Hampson and Weissberger (7) and by Naeshagen (2) whilst the present value for the nitro-compound is considerably lower than those found by Naeshagen (2), Le Fèvre and Le Fèvre (3) and by Lumbroso (4). Of the compounds measured here this shows the greatest deviation from the results of earlier workers. It may be pointed out that the presence of the 4-isomer, which is difficult to separate from the product of the nitration of diphenyl, in the sample used would cause the observed result to be too high.

From the figures recorded in Table 9. it may be concluded that in general the 2-substituted diphenyls have an angle between the planes of their rings which is close to 90°. There are, however, several anomalies which must be dealt with individually. The iodo-compound would appear to have a structure in which the planes of the rings are at right angles and this may be said to fit well with the conception of an iodine atom of considerable bulk. The chloro-derivative, containing a smaller substituent, one would expect to have a structure somewhat nearer to a planar configuration; the figures show that the observed moment is between the values calculated for the coplanar and right angles positions, but it is nearer to the figure obtained for the latter condition. By analogy it may be expected that the moment of the 2-fluorodiphenyl would be between the two calculated values and in all probability closer to its corresponding coplanar value than is the chloro-compound. This, however, is not found to be the case;

the observed value is seen to be greater than that calculated for the right angles position. Further consideration of this point, again, will be deferred for the present.

The observed value for the moment of 2-nitrodiphenyl is also seen to be greater than that calculated for the right angles position of the two rings. This is not so anomalous as is the case of the fluoro-derivative since the mesomeric effect due to the nitro-group acts in the opposite sense to that due to a halogen and therefore tends to increase the resultant moment. From Figure 11(c). it is seen that steric factors make it appear unlikely that 2- nitrodiphenyl would remain coplanar. One possibility is that the nitro-group may rotate about the C-N linkage. This, however, may be discounted since any appreciable rotation of the group out of the plane of the ring to which it is attached would prevent the possibility of π-bond formation and the associated mesomeric effects thus reducing the resultant moment, but this is contrary to the observed result. One must assume that the most probable state of this molecule is one in which the plane of the nitro-group is slightly inclined to the plane of the ring to which it is attached and also that the planes of the two rings are inclined to one another, the angle between these planes being insufficient to prevent π-overlap.

The most important point arising from Table 9. is that the value of the observed moment for 2-bromodiphenyl is considerably in excess of the calculated values. This is made to seem more anomalous by the fact that the value obtained for 2-iododiphenyl is well in agreement with the calculated value. A possible source of error, which would cause an increase in the observed moment, would be the presence of 4-bromodiphenyl due to the use of impure 2-aminodiphenyl in the preparation. This was eliminated by the use of bromo-compound derived from 2-aminodiphenyl that had been subjected to considerable purification before use.

The non-classical inductive effect mentioned earlier opposes the mesomeric effect in the halogens, enhancing the resultant moment, and the presence of a large I_N effect in 2-bromodiphenyl may possibly be a partial explanation of the high moment of that compound. The work of Guy (22), however, indicates that the π-overlap across the central bond of diphenyl diminishes rapidly as the angle between the planes of the rings increases above $\pi/4$ and that it becomes zero when this angle reaches $3\pi/8$. Therefore, if the bulk of the substituent bromine atom is sufficiently large, as appears likely, then the angle between the planes of the rings in 2-bromodiphenyl will be great enough to reduce the mesomeric and non-classical inductive effects. It is suggested therefore that restriction of the mesomeric effect would reduce the tendency for electrons to pass into the ring from the C-Br bond thus causing an increase in the primary dipole, it being assumed that, after all, the non-classical inductive effect will be by comparison of secondary importance. On the basis of this explanation one would expect 2-iododiphenyl to exhibit a similar elevation of the observed moment above the calculated values. That this is not the case would appear to indicate that the mesomeric moment due to a substituent iodine atom is considerably smaller than that associated with a bromine atom similarly situated.

Comparison of the observed values for the molecular refractions with the calculated figures in Table 3. shows that, as with the isomeric 3-substituted diphenyls, those obtained for the chloro-, bromo- and nitro-derivatives are in good agreement with the calculated figures. The value for the fluoro-compound is lower than calculated whilst that for the iodo-compound is higher than calculated, but in neither case is the discrepancy sufficient to warrant special attention.

The 4-Substituted Derivatives of Diphenyl.

As can be seen from Figures 12(a), (b) and (c) the calculation of inductive effects for the 4-substituted diphenyls is much simplified by the fact that $\theta = 0^{\circ}$ and also that the magnitude of the effect is constant, in a given derivative, and independent of the angle between the planes of the rings. For the halogen-derivatives, Figures 12 (a) and (b), $r = 6.475$A whilst for the nitro-derivative $r = 7.17$ A and, μ_y being zero, substitution in equation (3) gives the corresponding values of μ_x as $0.0578\mu_{PhX}$ and $0.0425\mu_{PhNO_2}$, and these, by application of equation (7), lead to the values of the resultant moment indicated

FIG. 12A. 4-HALOGENODIPHENYL (RINGS COPLANAR)

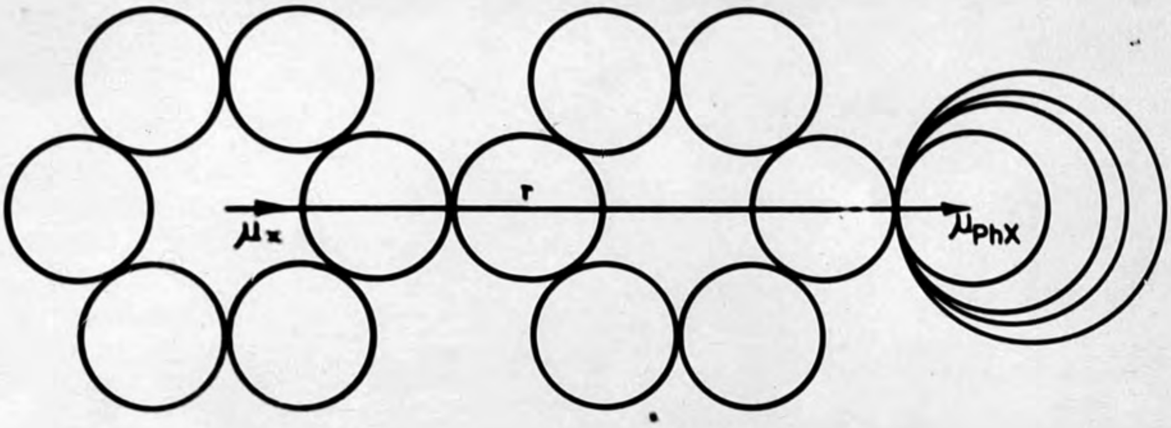


FIG. 12B. 4-HALOGENODIPHENYL (RINGS IN PLANES AT RIGHT ANGLES)

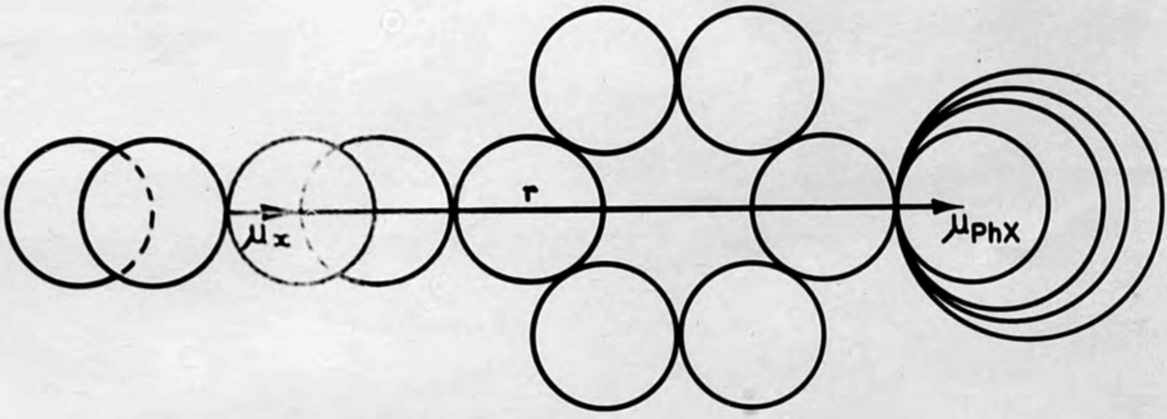
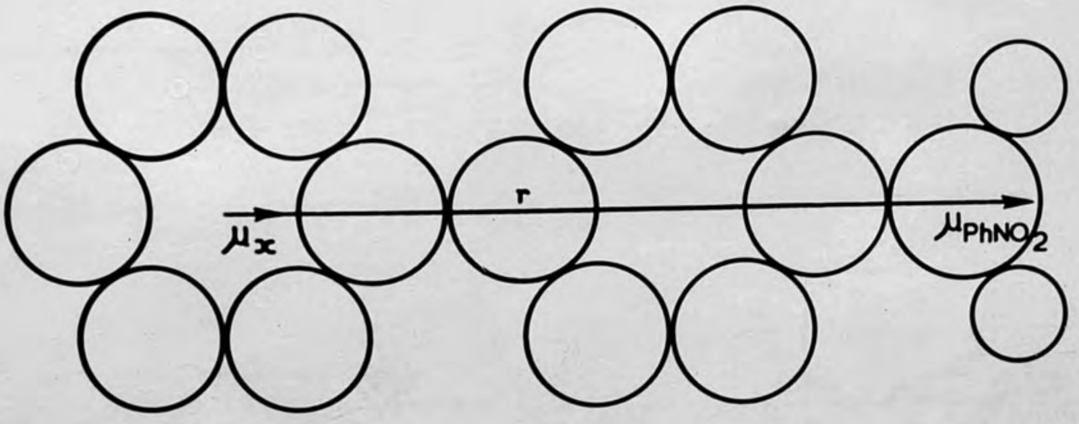


FIG 12C. 4-NITRODIPHENYL (RINGS COPLANAR)



in Table 10.

Table 10.

	r	θ	$\bar{\mu}/\mu_{PhX}$
4-halogenodiphenyls	6.475	0	1.05_8
4-nitrodiphenyl	7.17	0	1.04_2

Tables 11. and 12. contain respectively a summary of the polarisation data for the 4-substituted diphenyl measured here and a comparison of the observed and calculated moments.

Table 11.

	$\bar{\alpha}$	$-10^3\beta$	$10^3\bar{\nu}$	$P_{2\infty}$	$[R_D]$	μ
4-fluorodiphenyl	1.589	248.4	210	97.4	52.1	1.49
4-chlorodiphenyl	1.850	284.6	286	114.0	57.8	1.66
4-bromodiphenyl	1.539	434.3	267	116.8	60.3	1.66
4-iododiphenyl	1.110	531.3	312	109.7	67.0	1.45
4-nitrodiphenyl	10.67	336.7	333	447.7	59.7	4.36

Table 12.

	μ(obs.)	μ(calc.)	Δμ
4-fluorodiphenyl	1.49	1.57	-0.08
4-chlorodiphenyl	1.66	1.69	-0.03
4-bromodiphenyl	1.66	1.66	0.00
4-iododiphenyl	1.45	1.48	-0.03
4-nitrodiphenyl	4.36	4.18	-0.18

The experimental results recorded above for the fluoro- and bromo-compounds are seen to be in good agreement with those of the previous workers summarised in Table 1. The value now obtained for the chloro-derivative is slightly higher than those obtained previously while for 4-nitrodiphenyl the figure now reported is distinctly higher than those due to Naeshagen (2) and Le Fevre and Le Fèvre (3) but somewhat lower than that recorded by Everard, Kumar and Sutton (5), this last mentioned value being derived from measurements on only three solutions.

For the most part the observed values of the moments differ from those calculated on the theory of inductive effects in a manner which is readily explicable on the basis of the mesomeric effect. The para-position of the substituent relative to the second ring is very favourable to mesomerism and the low values of the observed moments of the halogen-diphenyls would be expected from a consideration of the direction of their mesomeric moments. On the other hand the mesomeric effect due to a nitro-group, as stated earlier, will tend to enhance the resultant moment since it acts in the same sense as does the inductive effect and in the opposite sense to that associated with the halogens. This, it is seen, is in agreement with the observed result.

It is of interest to note that, for the most part, the observed values of the molecular refractions of the 4-substituted diphenyls are slightly higher than those of the corresponding 2-, and 3-substituted isomers, and this may be taken as further support for the above explanations of their dipole moments, it being assumed that the amount of double bond character introduced into the central bond by the mesomeric effects in the 4-substituted isomers is responsible for this increase.

To return to the divergences shown by the three isomeric monofluorodiphenyls one can see that the 4-substituted isomer is the least anomalous and can be explained along the lines set out above. In the case of 3-fluorodiphenyl the discrepancy between the theoretical and experimental values of the moment is not large and, if not due to the inadequacy of the theoretical treatment, may in all probability be ascribed to the maintenance within the substituted ring of mesomeric effects of similar magnitude to those in fluorobenzene rather than of the larger values one would expect in the more extensively conjugated diphenyl system. Also, the mesomeric effect due to a fluorine atom being assumed larger than that associated with the other halogens in the circumstances under consideration, the above state of affairs would not be expected to be observable to such a marked extent in the remaining 3-halogenodiphenyls.

The high figure obtained for the moment of 2-fluorodiphenyl may not be explained in the same manner as that of the corresponding bromo-derivative since the bulk of the substituent fluorine atom is not sufficient to prevent rotation into the plane of the unsubstituted ring. Further one would expect the primary dipole to be reduced by the mesomeric effect. However, the direction of the resultant mesomeric moment would be along the axis of the central bond and in a sense such that vector addition would show an enhanced resultant moment. Here again it must be stated that the mesomeric effects due to a fluorine atom are assumed large in comparison with those due to the remainder of the halogens. Thus the effect discussed would not be expected to manifest itself in the case of the chloro-derivative. It is stated in conclusion that all the explanations that have been put forward in this section are of necessity only tentative since firstly, the theory of induced moments used is in all probability inadequate, and secondly, the treatment of the effects involving π-electron shifts has, throughout, been purely qualitative.

Section III.

The 2,2'-Disubstituted Derivatives of Diphenyl

The theory of inductive effects used in Section II. has also been applied to the 2,2'-disubstituted diphenyls in the cis and trans configurations and for the case in which the planes of the rings are at right angles. The simplest case is that in which the substituents are in the wholly trans position, Figure 13(b), as it is readily shown that the resultant moment is zero. For the wholly cis configuration of the molecule, Figure 13(a), resolution in two directions at right angles within the plane of the rings may be carried out. If

A is the resultant moment along the axis of the central bond, and

B is the resultant moment at right angles to the axis of the central bond, then

$$A = \mu_x \cos 60 - \mu_y \cos 30 + \mu_{PhX} \cos 60 - \mu_x \cos 60 + \mu_y \cos 30 - \mu_{PhX} \cos 6$$

$$= 0$$

and

$$B = 2\left\{ \mu_{PhX} \cos 30 + \mu_x \cos 30 + \mu_y \cos 60 \right\}$$

$$= \sqrt{3}\,(\mu_{PhX} + \mu_x) + \mu_y$$

$$= \bar{\mu}$$

FIG. 13A. 2,2′-DIHALOGENODIPHENYL (CIS CONFIGURATION)

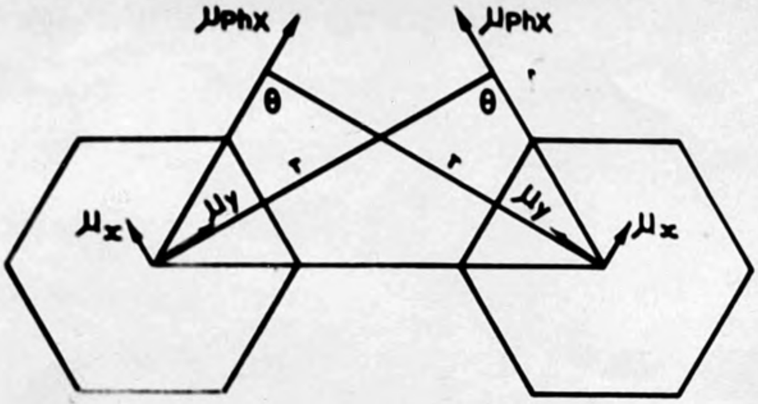


FIG. 13B. 2,2′-DIHALOGENODIPHENYL (TRANS CONFIGURATION)

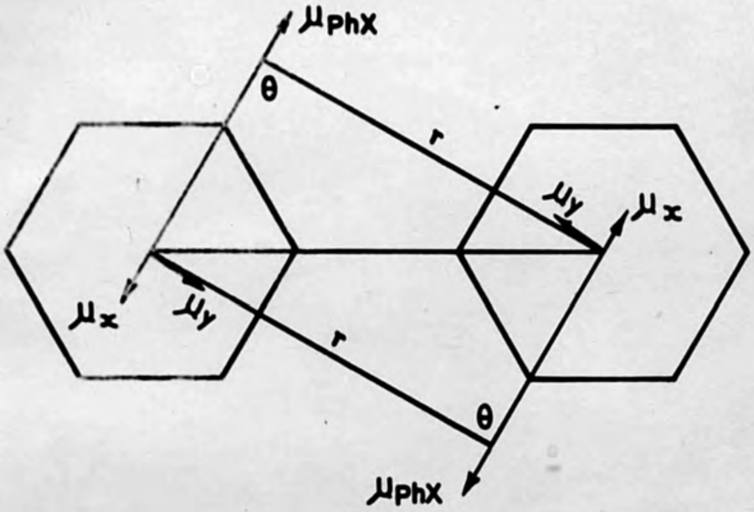
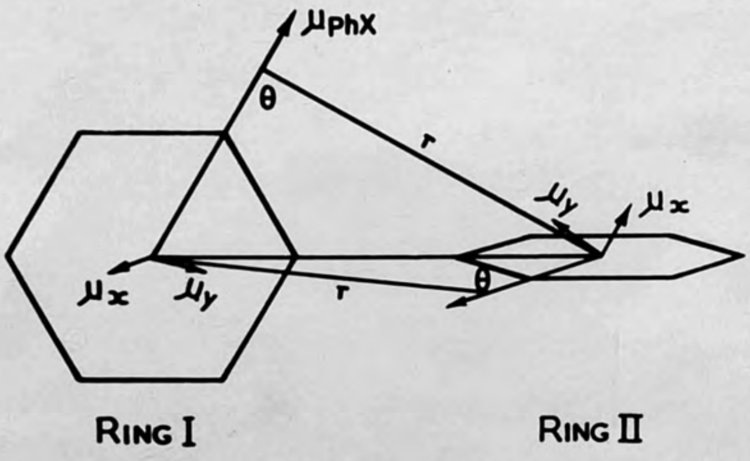


FIG. 13C. 2,2′-DIHALOGENODIPHENYL (RINGS IN PLANES AT RIGHT ANGLES)



Substitution of the values of μ_x and μ_y obtained in the calculations on the 2-substituted diphenyls in the previous section gives for the dihalogeno-compounds

$$\bar{\mu} = 0.849\sqrt{3}\mu_{PhX} + 0.0041\mu_{PhX}$$

$$= 1.475\mu_{PhX}$$

and for the dinitro-compound

$$\bar{\mu} = 0.872\sqrt{3}.\mu_{PhNO_2} + 0.080\mu_{PhNO_2}$$

$$= 1.590\mu_{PhNO_2}$$

For all but the difluoro-derivative the cis position is impossible for steric reasons.

In the case where the planes of the rings are at right angles, Figure 13(c), the calculation is slightly more complex.

For the forces in the plane of ring 1.

$$A_1 = \mu_{PhX}\cos 60 + \mu_x\cos 60 - \mu_y\cos 30$$

and

$$B_1 = \mu_{PhX}\cos 30 + \mu_x\cos 30 + \mu_y\cos 60$$

For the forces in the plane of ring 2.

$$A_2 = \mu_{phX}\cos 60 + \mu_x\cos 60 - \mu_y\cos 30$$

and

$$B_2 = \mu_{PhX}\cos 30 + \mu_x\cos 30 + \mu_y\cos 60$$

But A_1 and A_2 cancel while B_1 and B_2 fortify one another

Hence

$$\bar{\mu} = \left\{ B_1^2 + B_2^2 \right\}^{\frac{1}{2}}$$

$$= \sqrt{2}.B_1$$

All the forces in B_1 and B_2 are in planes at right angles to those of the rings in which the induction is being brought about and therefore the value of the polarisability, α , to be used is 6.25×10^{-24}. Thus the values of μ_x and μ_y to be used in this substitution are half the values used in the calculations for the molecule having the cis configuration above. Hence for the halogeno-derivatives

$$B_1 = \frac{1}{2}\left\{\sqrt{3}\,(\mu_{PhX} + \mu_x) + \mu_y\right\}$$

$$= \frac{\mu_{PhX}}{2}\,(0.925\sqrt{3} + 0.002)$$

$$= 0.802\mu_{PhX}$$

$$\text{and } \bar{\mu} = 1.134\mu_{PhX}$$

while for the nitro-derivative

$$B_1 = \frac{\mu_{PhNO_2}}{2}\,(0.936\sqrt{3} + 0.040)$$

$$= 0.831\mu_{PhNO_2}$$

$$\text{and } \bar{\mu} = 1.175\mu_{PhNO_2}$$

Tables 13 and 14 contain respectively a summary of the polarisation data obtained in the present investigation for a few 2,2'-disubstituted diphenyls and a comparison of the observed moments with those calculated as shown above.

Table 13

	$\bar{\alpha}$	$-10^3\bar{\beta}$	$10^3\bar{\nu}$	$P_{2\infty}$	$[R_D]$	μ
2,2'-difluorodiphenyl	2.120	320.9	127	122.5	50.5	1.88
2,2'-dichlorodiphenyl	2.095	358.7	231	140.1	61.2	1.97
2,2'-dibromodiphenyl	1.400	561.4	222	136.4	66.5	1.87
2,2'-dinitrodiphenyl	11.785	430.9	244	593.3	62.5	5.10

Table 14

	μ obs.	μ calc. cis	μ calc. rt. angles
2,2'-difluorodiphenyl	1.88	2.18	1.68
2,2'-dichlorodiphenyl	1.97	2.35	1.81
2,2'-dibromodiphenyl	1.87	2.32	1.78
2,2'-dinitrodiphenyl	5.10	6.38	4.71

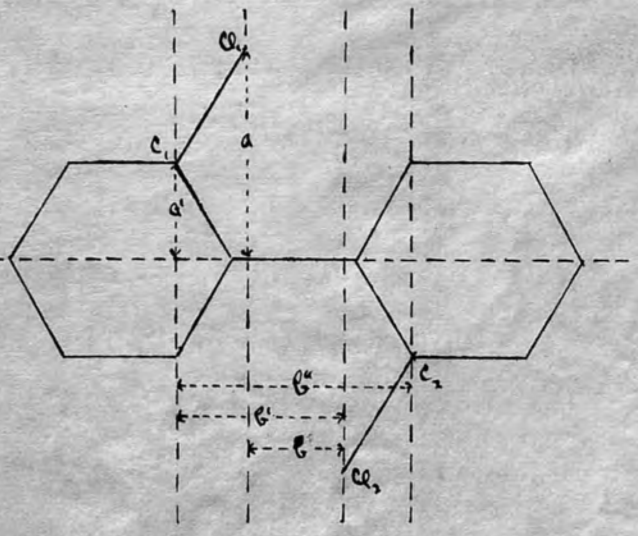
The figures obtained in the present work for 2,2'-dichlorodiphenyl agree well with those obtained on recalculation of the figures of Hampson and Weissberger (7) as do those for the dinitro-compound with the value of Bretscher (8) and that derived by recalculation of the results due to Le Fevre and Vine (9). Further, from Table 14. it is seen that in each case the observed figure is between the calculated value for the cis configuration and that for the case in which the planes of the rings are at right angles.

Hampson and Weissberger (7) have discussed the case of 2,2'-dichlorodiphenyl at length and have evaluated the forces which they considered determined the configuration of the molecule. They concluded from their calculations that since the electrostatic attraction and repulsion forces largely compensate each other, the configuration is determined predominantly by the London dispersion forces between the chlorine atoms. This, in their opinion, was the reason for the high moment of 2,2'-dichlorodiphenyl in comparison with that of the 3,3'-isomer. The general method used was, to calculate the sum of the potentials. Σv, due to the electrostatic and quantum mechanical forces for various values of the angle between the planes of the rings, ψ , and to construct from these Boltzmann terms $e^{-\frac{\Sigma v}{kT}}$, giving the probabilites of the molecules existing in the different configurations. The dipole moment, μ, was then calculated from the formula

$$\mu = 2\mu' \sqrt{\frac{\int_0^{\pi} e^{-\frac{\Sigma v}{kT}} \cdot \cos^2 \frac{\psi}{2} \cdot d\psi}{\int_0^{\pi} e^{-\frac{\Sigma v}{kT}} \cdot d\psi}} \quad (1)$$

where μ' is the component of each of the constituent C-Cl moments perpendicular to the axis of the central bond, and ψ is taken as zero in the coplanar cis position.

In computing the electrostatic potentials, Hampson and Weissberger regarded the dipole as formed by positive and negative charges of magnitude ϵ at the centres of the constituent atoms, ϵ being equal to μ/d, where μ is the moment and d is the distance between the atomic centres. Hence the electrostatic potential is given by $\sum \left(\frac{\epsilon_i \epsilon_j}{r_{ij}} \right)$ where r_{ij} is the distance between the points of charge ϵ_i and ϵ_j and varies with the angle of rotation



(D)

Then, from diagram (D)

$$r = (b^2 + 4a^2 \sin^2 \psi/2)^{\frac{1}{2}}$$

$$r' = (b'^2 + (a - a')^2 + 4aa' \sin^2 \psi/2)^{\frac{1}{2}}$$

and $$r'' = (b''^2 + 4a'^2 \sin^2 \psi/2)^{\frac{1}{2}}$$

where r, r' and r" are the variable distances between Cl_1 and Cl_2, Cl_1 and C_2 and between C_1 and C_2 respectively.

The total electrostatic potential, U, for each angle is

$$\epsilon^2 \left\{ \frac{1}{r} + \frac{1}{r''} - \frac{2}{r'} \right\}$$

Comparison of the figures deduced by this method with those obtained by Smyth, Dornte and Wilson (23) shows that there is good agreement, the two plots of electrostatic potential against ψ following each other closely.

The London potential, L, for chlorine was taken as $115 \times 10^{-60}/r^6$, terms involving higher powers of r, which become important only when the atoms approach very close to each other, being neglected.

Hampson and Weissberger's calculations showed that the electrostatic potentials, which favour the trans configuration, are largely over-compensated by the London potentials and that the configuration of the molecule depends almost entirely upon the latter. Since these decrease with the sixth power of r they produce a considerable preference for the potisions with small values of ψ, the probabilities of the various configurations being given by the numerical values of $e^{-\frac{(U - L)}{kT}}$. Their figures indicated that the smaller the angle ψ, the greater is the probability of the configuration, within the limits set by steric factors. For $\psi = 35^\circ$ the Cl-Cl distance is that of the two chlorine atoms in a chlorine molecule i.e. is impossible; for $\psi = 60^o$ it has a value equal to that for the two chlorine atoms in methylene chloride in which molecule there still appears to be a slight repulsion between the chlorine atoms. Thus configurations having a smaller value of ψ can have only a low probability and the probability function must show a maximum where the repulsion forces, electrostatic and steric, are in equilibrium with the London attraction forces.

These authors calculated the equilibrium distance by what, in their opinion, was the least hypothetical method. They regarded the repulsion potential as a rigid barrier and found by trial and error the angle at which the probability curve must be cut by a line parallel to the probability axis to obtain the experimental value of the moment from equation (1). This angle was found to be 62^o, corresponding to a distance of 3.0 A between the centres of the chlorine atoms, which is in good agreement with the value 2.98 A got by following the suggestion due to Sidgwick (24) of adding 0.5 A to the radius of the covalently bound atoms e.g. the Cl-Cl distance in methylene chloride mentioned above.

An alternative method of calculation used was to multiply the probability function by an exponentially increasing repulsion term of the form $e^{-\frac{be^{-r/\rho}}{kT}}$ which is derived from the repulsion law for ions due to Born and Mayer (25) where b is a constant characteristic of the ion in question and ρ was found for the alkali halides to have a mean value of 0.345 A. Hampson and Weissberger were of the opinion that this law could be assumed to hold for covalently bound atoms and application of the method gave a probability curve with a peak at 62°. It was considered, however, that the uncertainty of the calculations did not justify the evaluation of a theoretical moment. In addition no allowance was made for induction effects, which these authors considered would be small although at the same time such effects would favour configurations with small values of ψ.

The calculations in the first part of this section would seem to indicate that the contribution to the moment due to inductive effects is by no means as small as Hampson and Weissberger thought; for example in the case of a molecule in the cis configuration the value of the moment neglecting inductive effects would be $\sqrt{3}.\mu_{PhX}$ i.e. $1.73\mu_{PhX}$, while the value calculated earlier assuming the presence of inductive effects is $1.47\mu_{PhX}$. Hence the value of ψ derived by these authors, namely 62°, for the probable configuration of 2,2'-dichlorodiphenyl may be considered to require modification.

Lumbroso (4) considered, in addition to the effects enumerated by Hampson and Weissberger, the action of the Pauli repulsion forces which become significant at short distances and may be regarded as an expression of the impenetrability of the electron orbits. He, also, was of the opinion that the induction effects were of little importance. From Hampson and Weissberger's experimental results he derived the value $\psi_{\text{observed}} = 67°$.

Recent work by Bastiansen (26) on electron diffraction measurements leads to a mean value of ψ for 2,2'-dichlorodiphenyl of 74°; for 2,2'-dibromodiphenyl the value is 75°.

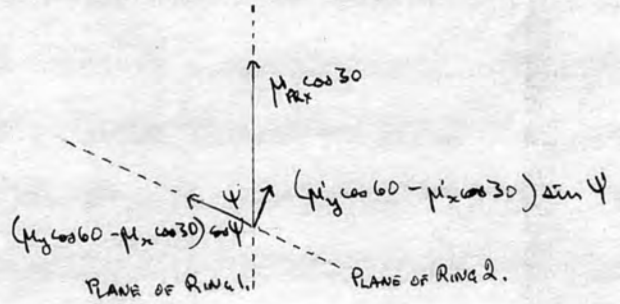
Although it is not to be inferred that the planes of the two benzene rings remain at a fixed angle to one another - a truer picture would undoubtedly include a twisting vibration of low frequency about the central bond - it is of some interest to calculate the approximate value of the mean inclination of the two planes from the observed dipole moment values. If the values of ψ reported by Bastiansen are accepted then it would appear unlikely in view of the work of Guy (22) that any π-orbital overlap can take place across the central bond and it may therefore be implied that any mesomeric effects will be of little importance. In view of this the mean inclination of the planes of the two rings may be obtained by extending the theory of inductive effects used earlier in order to derive a general expression relating the resultant moment $\bar{\mu}$ to the angle between the planes of the rings ψ. This may be carried out as follows:-

Since the molecule is symmetrical about a plane perpendicular to the axis of the central bond and cutting it centrally, then the parts of the moments resolved along this axis will have zero resultant and may be neglected.

Considering the moments associated with the primary dipole in ring 1. and resolving these at right angles to the axis of the central bond, the resultant in this direction is

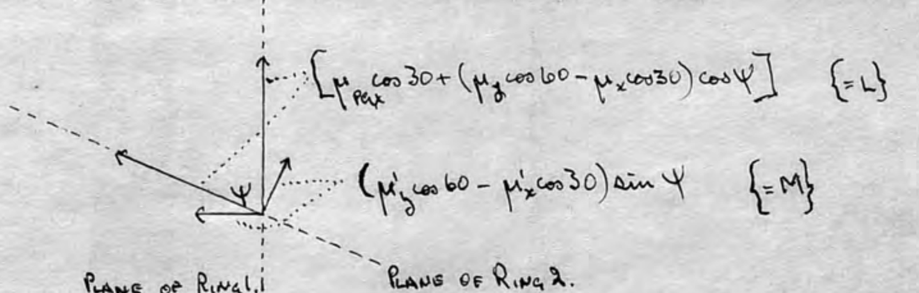
$$\mu_{phX}\cos 30 + (\mu_y)\cos 60 - (\mu_x)\cos 30$$

where (μ_x) and (μ_y) indicate that no values can be assigned to μ_x and μ_y until these have been further resolved into and at right angles to the plane of ring 2.
Then the state existing after carrying out this resolution, since the angle between the planes of the rings is ψ, may be represented by diagram (E)



(E)

in which μ_x and μ_y are the values calculated on the basis of $\alpha = 12.5 \times 10^{-24}$, while μ_x' and μ_y' are the values calculated on the basis of $\alpha = 6.25 \times 10^{-24}$. Similarly in the case of the primary dipole in ring 2. one finds an identical group of moments though inclined at an angle ψ to those due to the primary dipole in ring 1. Combination of the two groups of moments leads to the state represented by diagram (F)



(F)

from which it may be seen that the resultant moment is given by

$$\bar{\mu} = 2L\cos\psi/2 + 2M\cos(90 - \psi + \psi/2)$$
$$= 2L\cos\psi/2 + 2M\sin\psi/2$$

Introducing the values of L and M into this equation one gets

$$\bar{\mu} = 2\left[\left\{\mu_{PhX}\cos 30 + (\mu_y\cos 60 - \mu_x\cos 30)\cos\psi\right\}\cos\psi/2 + (\mu_y'\cos 60 - \mu_x'\cos 30)\sin\psi\,\sin\psi/2\right]$$

But μ_x, μ_y are direct functions of α, hence $\mu_x = 2\mu_x'$ and $\mu_y = 2\mu_y'$

Therefore

$$\bar{\mu} = 2\left\{\mu_{PhX}\cos 30\cos\psi/2 + (\mu_y\cos 60 - \mu_x\cos 30)(\cos\psi\cos\psi/2 + \tfrac{1}{2}\sin\psi\,\sin\psi/2)\right\}$$

By conversion of the functions of ψ into functions of $\psi/2$ and by substitution of the numerical values of cos30° and cos60° the above equation reduces to

$$\underline{\bar{\mu} = \left\{\sqrt{3}.\mu_{PhX} + (\mu_y - \sqrt{3}.\mu_x)\cos^2\psi/2\right\}\cos\psi/2}$$

which in the case of the dihalogenoderivatives may be shown to be

$$\bar{\mu} = (1.732 - 0.257\cos^2\psi/2)\cos\psi/2$$

while for the dinitroderivative it becomes

$$\bar{\mu} = (1.732 - 0.142\cos^2\psi/2)\cos\psi/2$$

and both these latter equations may be shown to give values identical with those derived earlier in this section for the special cases in which $\psi = 0^{o}$ and $\psi = 90^{o}$.

Substitution of the experimental figures for $\bar{\mu}$ into the equations derived above leads to the mean values of the angle between the planes of the two benzene rings recorded in Table 15.

Table 15.

	ψ
2,2'-difluorodiphenyl	71°
2,2'-dichlorodiphenyl	77°
2,2'-dibromodiphenyl	83°
2,2'-dinitrodiphenyl	79°

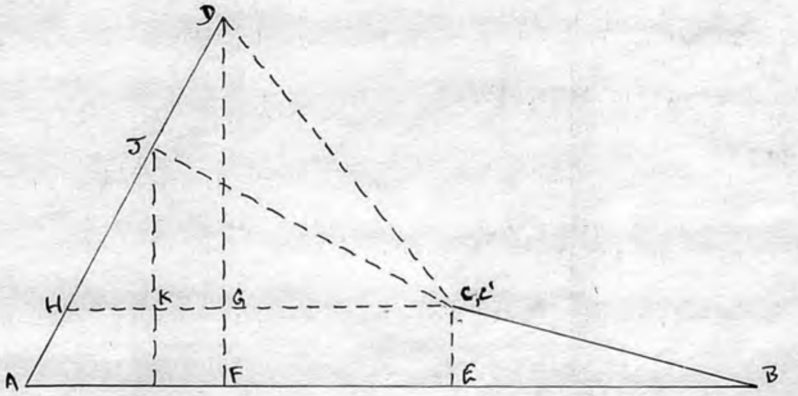
However, it is still necessary to consider the effect upon the values of ψ recorded in Table 15. of the moment induced at one polar substituent due to the presence of the other, a factor which is not accounted for in the treatment given above. This necessitates a knowledge of the polarisability of the polar substituent, of the distance between the inducing dipole and the polarisable centre, and also of the angle between the direction of the inducing dipole and the radius vector from its point of action to the polarisable centre. The difference between the polarisability of the halogen atom or nitro-group and that of hydrogen may be obtained approximately from the bond refractions,

e.g. $[R_D]_{C-Br} = 9.39\text{c.c.}$ and $(R_D)_{C-H} = 1.68\text{c.c.}$

hence $[R_D]\ (Br) - (H) = 7.71\text{c.c.}$

$$\text{from which } \alpha(Br) - (H) = \frac{7.71}{\frac{4}{3}\pi N} = 3.05 \times 10^{-24}$$

Similarly, the polarisability for chlorine was found to be 1.91×10^{-24} and that for the nitro-group 2.24×10^{-24}. The polarisability of fluorine differs only slightly from that of hydrogen and therefore the calculation for 2,2'-difluorodiphenyl requires no correction for this effect. The values of the bond refractions used in these calculations were those of Vogel et alia (21). The polarisable centre of the substituent halogens has been taken as at the centre of the atom whilst in the case of the nitro-group it has been assumed to be 0.5A past the centre of the nitrogen atom along the axis of the C-N bond. For the remainder, the calculations reduce to problems in solid geometry which are illustrated below by the case of 2,2'-dibromodiphenyl.



(G)

Let A be the centre of benzene nucleus 1. containing the dipole at D and B the centre of nucleus 2. with the polarisable centre of the halogen at C. Let C' be the projection of C into the plane of ring 1. and ψ the angle between the planes of the rings. Let $D\hat{J}C$, $D\hat{F}A$ and $C'\hat{E}B$ be right angles.

Then, substituting the values of the bond lengths and atomic radii,

$AB = 1.40+1.50+1.40 = 4.30$, $AD = 1.40+0.775 = 2.175$,

$BC = 1.40+0.775+1.11 = 3.285$, $CE = BC\cos 30^\circ = 2.845$,

$AF = AD\cos 60^\circ = 1.0875$, $DF = AD\cos 30^\circ = 1.883$,

$FE = GC = AB-(AF+BE) = 1.57$, $C'E = CE\cos\psi = 2.845\cos\psi$,

$CC' = CE\sin\psi = 2.845\sin\psi$, $DG = DF-C'E = 1.883-2.845\cos\psi$,

$HG = CE\tan 30^\circ = 1.087-1.645\cos\psi$,

$$HC' = HG+FE = 2.675-1.645\cos\psi ,$$

$$HD = HG\operatorname{cosec}30^\circ = 2.174-3.290\cos\psi,$$

$$DC^2 = DG^2+C'G^2+C'C^2 = 14.105-10.714\cos\psi,$$

and $HC^2 = C'H^2+C'C^2 = 15.154-8.742\cos\psi-5.388\cos^2\psi .$

Let $CDH = \theta$

Then $\cos\theta = \frac{CD^2 + DH^2 - HC^2}{2CD.DH}$

while $\frac{\mu_x}{\mu} = \frac{3.05\times4.27}{3 \times 2.27}.\frac{(3\cos^2\theta - 1)}{CD^3} = 1.912. \frac{(3\cos^2\theta - 1)}{CD^3}$

and $\frac{\mu_y}{\mu} = 1.912. \frac{3\sin\theta\cos\theta}{CD^3}$

Further $DJ = CD\cos\theta$, $JH = DH-DJ$,

$JK = JH\cos30^\circ$ and $JC = CD\sin\theta$.

Hence the contribution of μ_x in the resultant dipole is

$$1.732\mu_x.\cos\psi/2 \;;$$

the contribution of μ_y along JK is $\frac{JK}{JC}\mu_y$ and along CC' is $\frac{CC'}{JC}\mu_y$ from which the contribution of u_y in the resultant dipole is $\frac{2JK}{JC}\mu_y.\cos\psi/2 - \frac{2CC'}{JC}\mu_y.\sin\psi/2.$

Thus the magnitude of these effects may be calculated for given values of ψ and the results used to correct the figures obtained earlier assuming no mutual interaction of the substituents. This has been carried out for the dichloro-, dibromo- and dinitro-derivatives at numerous inclinations of the planes of the rings and the values of ψ giving the best agreement with the experimentally observed moments are recorded in Table 16.

Table 16.

	ψ	Inter nuclear distance (A)	v.d.Waals radii x2 (A)	Covalent radii x2 (A)
2,2'-difluorodiphenyl	71°	3.23	2.70	1.44
2,2'-dichlorodiphenyl	71°	3.35	3.60	1.98
2,2'-dibromodiphenyl	72°	3.50	3.90	2.22
2,2'-dinitrodiphenyl	72°	3.25	3.00	1.40

The modifications in the interplanar angles introduced by correction for the mutual interaction of the substituents show that such effects are not negligible as was assumed by Hampson and Weissberger (7) in their calculations on 2,2'-dichlorodiphenyl. It may also be noted that the values of the internuclear distances of the substituents calculated from these modified values of ψ are of the same order as the sums of the van der Waals radii (27) of the atoms concerned; the necessary figures are listed above for comparison together with those obtained by doubling the covalent atomic radii. In the case of the dinitro-derivative the figures refer to the distance between the nitrogen nuclei.

The values of ψ given in Table 16. are in remarkably close agreement with the mean interplanar angles, 74°±5° and 75°±5° respectively, deduced by Bastiansen (26) for 2,2'-dichloro- and 2,2'-dibromodiphenyl from electron diffraction measurements upon the vapours. They are also identical with the interplanar angles of 72° reported by Smare (28) for crystalline 2,2'-dichlorobenzidine and of 71° found by Fowweather and Hargreaves (29) for 2,2'-dimethylbenzidine hydrochloride. Thus it is evident that the mean interplanar angle for these compounds in the gaseous state, as studied by Bastiansen, and in solution, as studied here, is essentially equal to the fixed angle observed in the crystal, the substient groups in each case having a cis disposition. The explanation for this slightly preferred cis orientation therefore seems to arise through forces within the substituted diphenyl molecule itself, possibly of the type suggested by Hampson and Weissberger (7) and mentioned earlier in this section, namely London dispersion forces acting between the substituent groups.

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