MOLECULAR POLARISATION STUDIES IN RELATION TO MESOMERISM IN AROMATIC COMPOUNDS

by

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SUMMARY

The dipole moments of a number of substituted anilines, in both benzene and dioxan, have been evaluated from measurements of the dielectric constants, densities and refractive indices of dilute solutions. In selecting the compounds for study attention was paid to the desirability of comparing, on the one hand, the effects of *o-p* and *m*-directing substituents and, on the other hand, the effects of the positions of the groups on the deviations from the moments to be expected from the simple vector addition theory. Hence, the dipole moments of *m*- and *p*-nitro- and bromo-, 2:4- and 3:5-dinitro- and dibromo- and 2:4:6-trinitroaniline, *p*-nitro- and 2:4-dinitromethylaniline and 2-methyl-4-nitroaniline have been measured in both solvents.

The results have been interpreted in terms of the mesomeric and inductive effects of the substituents. In the absence of substituents in positions *ortho* to the amino-group the difference between the apparent moments of the amines in dioxan and benzene solutions increased progressively with increase in the interaction moment. The presence of methyl groups, bromine atoms or nitro-groups in both positions *ortho* to the amino-group decreased the dioxan increment although there appeared to be no appreciable interference when there was one nitro-group in such a position and only slight inhibition of the mesomeric effect when there was one bromine atom in the *ortho*-position. The presence of one nitro-group in the *ortho*-position to a methylamino-group caused a decrease in the dioxan increment. All these results are attributable to steric effects in the molecules.

CONTENTS

INTRODUCTION

The first measurements recorded for the dipole moment of an aromatic amine were in 1928 when Estermann (1) published the results he obtained for the moments of aniline in benzene solution and diphenylamine in the solid state and Bretscher (2) published his results for 4:4'-diaminodiphenyl. They were followed intermittently by a few measurements on various aromatic amines but chiefly on aniline itself. There was considerable disagreement in the moments reported by various workers for both aniline and the other amines. This was partially due to working at different temperatures and in various solvents but some discrepancies also arose in the actual methods of calculation.

It was inferred from the available results that the value of the dipole moment of aniline in hydrocarbon solvents was approximately equal to, or slightly greater than, that for the gas phase but this was much less than the moment in ether and 1:4-dioxan solutions. In 1941, Vassiliev and Syrkin (3) attributed the high values obtained in dioxan solutions to the formation of complexes through hydrogen bonding between an amino-hydrogen atom and an oxygen of the dioxan molecule.

If this view was correct, there should be a decrease in the interaction polarisation as the amino-hydrogen atoms of the aniline molecule are progressively replaced by methyl groups, the hydrogen atoms of which are less likely to engage in hydrogen bonding. As there were no suitable data available to test this hypothesis, Few and Smith (4) measured the dipole moments of aniline, methylaniline and dimethylamine. They found that the apparent molecular polarisation of aniline in dioxan (95.11 c.c.) was much greater than in benzene solution (78.35 c.c.). The difference in the molecular polarisations in the two solvents was smaller for methylaniline (13.52 c.c.) and quite small in the case of dimethylaniline where the difference was only 3.73 c.c.

The various results obtained indicated that an appreciable increase in molecular polarisation due to hydrogen bonding only occurred when at least one of the species involved had a highly polarisable electronic system. For the arylamines this polarisation was most likely to occur through an increase in the mesomeric effect of the amino-group, which in turn implies that the molecules must be able to adopt a structure in which the amino-hydrogen atoms approach coplanarity with the aromatic ring.

This aroused particular interest in the amines for which steric inhibition of resonance may occur. Birtles and Hampson (5) and Ingham and Hampson (6) found that the dipole moments of aminodurene and mesidine in benzene were 1.39 and 1.40 respectively, values appreciably less than for aniline. On the other hand, the moments of bromodurene and bromobenzene were almost identical, a circumstance which led Ingham and Hampson to infer that it was the steric effect of the *ortho*-methyl groups in hindering the formation of resonance structures involving N=C double bonds which caused the moments of aminodurene and mesidine to be less than that of aniline.

Few and Smith (7) had observed that the dipole moment of 2:4:6-tribromoaniline (1.69D) in benzene was considerably greater than that of aniline (1.51 D) whilst the apparent value in dioxan solution is much greater than that in benzene, suggesting that the hydrogen bonding to the amino-hydrogen atom results in an increased mesomeric effect. Smith (8) found that the moments of mesidine, aminodurene and methylmesidine in benzene and dioxan were lower than the values for aniline and methylaniline. The results indicated that mesomerism was inhibited appreciably with mesidine and aminodurene and to a considerable extent with methylmesidine.

The present investigation is chiefly concerned with the measurement of the apparent dipole moments of various pairs of aromatic amines, in both solvents, which, on the simple vector theory, should have equal dipole moments but of which the mesomeric effects are different.

Previous evidence had shown that the difference between the moments of aromatic amines in benzene and dioxan solutions was indicative of the electron mobility in the molecules; hydrogen bonding appeared to increase the mesomeric effect of the amine group. This suggests that the presence, in the aromatic ring, of groups which enhance this mesomeric effect should favour the effect due to dioxan. The difference between the moments in the two solvents should be much less in the presence of groups which have little effect on, or tend to counteract the mesomeric effect of the amine group.

It would be expected, from first principles, that substitution of a nitro-group in the ortho or para position in the aromatic ring would act in conjugation with and therefore enhance the mesomeric effect of an amino group, whereas in the meta position it would only have a small effect. The apparent enhancement of the moment in dioxan solution would be expected to follow an order similar to that in benzene solution. At the same time, when any substituents were present in the ortho position, steric inhibition of mesomerism remained a possibility. On general grounds, when amino groups and bromine atoms occupy positions ortho or para to one another their mesomeric effects would be expected to have a tendency to oppose each other slightly. Evidence obtained from p-chloroaniline and 2:4:6-tribromoaniline suggested that this effect was more than overcome by other effects, of which a modification in the inductive effect of the halogen atoms was probably the main factor. Further investigation of such compounds in the two solvents appeared to be necessary, therefore, to help in elucidating this problem.

Hence, in the present investigation, the dipole moments of a series of nitroanilines and a corresponding series of bromoanilines have been measured, both in benzene and in dioxan solution, and the results have been interpreted in terms of the mesomeric and inductive effects of the substituents.

CHAPTER I

EXPERIMENTAL METHODS

Section I

Apparatus

The determination of the dipole moments of the compounds studied here has been based on the Clausius-Mosotti-Debye theory. The use of Debye's extension of this theory to calculate the molecular polarisation and the dipole moment of a polar compound from studies of its dilute solutions in a non-polar solvent requires measurements of the dielectric constants, refractive indices and densities of solutions of graded, moderately low concentrations. The apparatus necessary for the determination of these quantities will be described in this section.

Determination of Dielectric Constants

The apparatus used for the measurement of dielectric constants was designed by Few, Smith and Witten (1) and built by A.V. Few (2). Subsequent changes have involved only the form of the power supply. The apparatus was based on the heterodyne-beat principle and, provided that the dielectric constants of the liquids concerned came within the range 2 to 3, it permitted their measurement relative to the dielectric constant of a standard liquid with an accuracy of about ± 0.0001.

Circuit diagrams of the apparatus are shown in Figures (1) and (2) and the components used are listed in Table (1). The apparatus consisted of a crystal-controlled oscillator, operating at a frequency of 10^6 cycles per second, and a variable-frequency oscillator, containing in its tuned circuit two ordinary variable condensers and, at choice, either the dielectric cell or the precision condenser with which the latter was matched. As the precision condenser used had a capacity range of 300 µµF, 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, was about 100 µµF. To ensure full use of the scale of the precision condenser, the inductance was designed to give resonance at a frequence of 10^6 cycles per second with a total capacity of about 450 - 500 µµF in the circuit. This figure allows 100 - 150 µµF for the minimum values of the capacitance of the adjustment condensers, lead capacities, etc. By substituting these quantities in the equation,

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

the required value of the inductance was about 50 microhenries. High quality short-wave tuning condensers were used, and the inductances were made of 24 s.w.g. enamelled copper wire closely wound on Paxolin formers.

All tendency for "locking-in" between the oscillators was eliminated by using electron coupling to mix the two high frequency oscillations (vide Groves (3)). The quartz controlled oscillator and the variable

TABLE I

List of Components

V_1	Cossor V.9	V_3	Raytheon 6.SA.7
V_2	Marconi S.24	V_4	Osram Z.21
L_1	30 turns of 24 S.W.G., 2 in. diameter, close wound.		
L_2	7 turns " " " " "		
L_3	34 turns " " " " "		
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	2 μF - 1000 volts		
C_7, C_9, C_{11}, C_{12}, C_{13}	1 μF - 350 volts		
C_8	1 μF - 800 volts		
C_{10}	0.25 μF - 450 volts		
C_{14}, C_{15}	2 μμF trimmers		
R_1, R_2	1 megohm	R_5	150 ohms
R_3, R_4	0.1 megohm	R_6	2 megohms
R_7	10,000 ohms + 50,000 ohms variable		
A_1	0 - 10 moving coil milliameter		
A_2	0 - 200 moving coil microameter		
J	jack for earphones	P	socket for screened cable
Q	quartz crystal, approximately 1 megacycle		

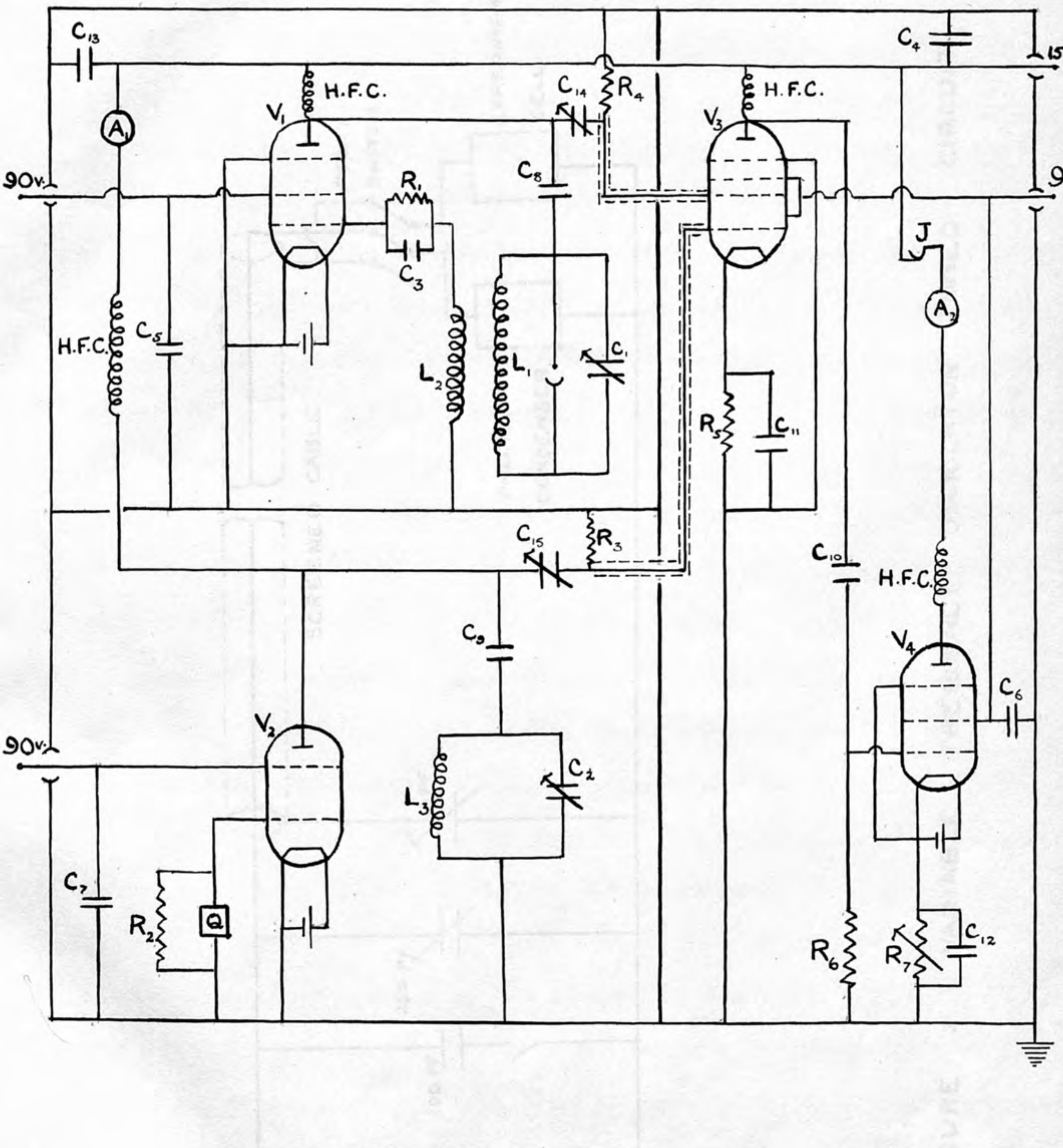


FIGURE I. CIRCUIT DIAGRAM OF HETERODYNE BEAT APPARATUS

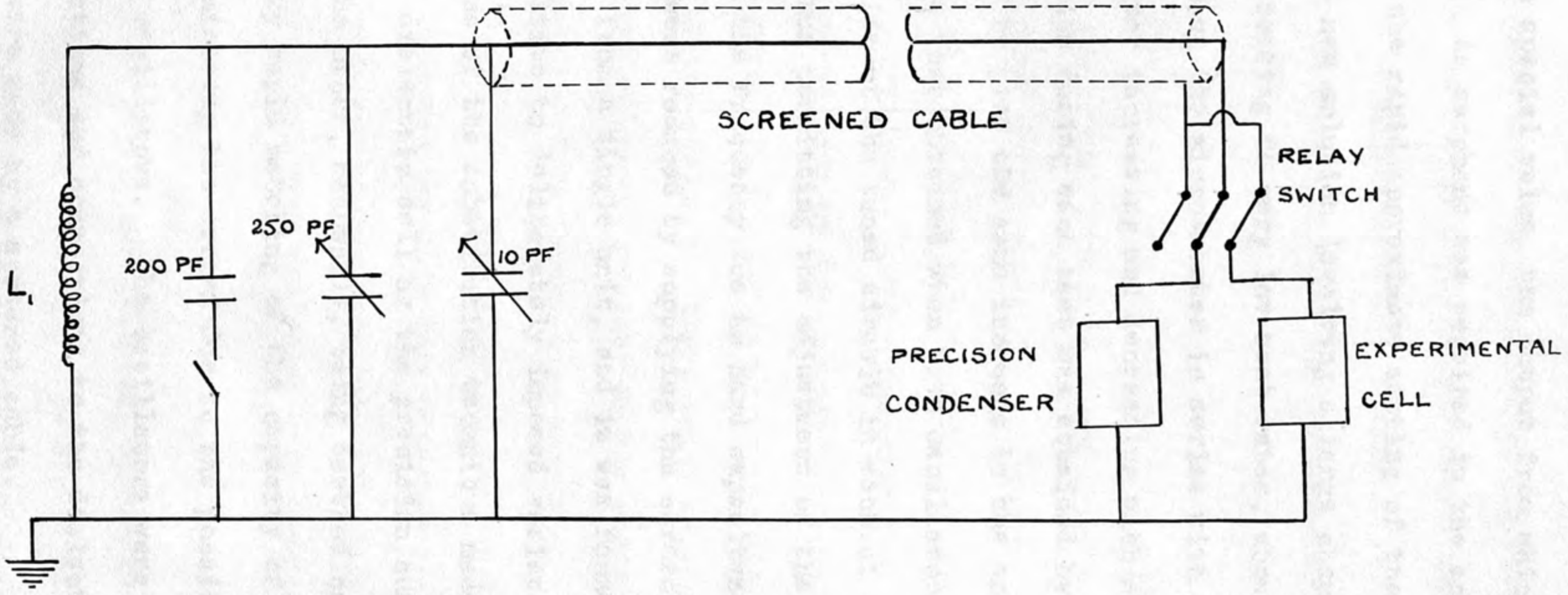


FIGURE 2. VARIABLE FREQUENCY OSCILLATOR TUNED CIRCUIT

oscillator were, therefore, connected through condensers to separate grids of a special valve, the output from which was fed to an anode bend detector. An earphone was required in the anode circuit of the detector valve for the 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 and decreasing with each beat. Maximum change of deflection during each beat was attained by adjusting each oscillator separately to give the same increase in the anode current of the detector valve above that obtained when both oscillators were switched off.

One side of the tuned circuit in each of the two oscillators was earthed, thus permitting the adjustment of the tuning condensers without changes in the frequency due to hand capacitance. Variations of frequency were reduced by supplying the screening grid and anode potentials from a single unit, and it was found that the beat frequency was insensitive to deliberately imposed variations of these potentials.

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 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 a screened cable.

Low tension supplies for each valve were drawn from accumulators. 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 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

As the relay unit can be operated by a bell-push situated at a 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 by switching the test condenser and the precision condenser alternately into the circuit indicated that the capacity associated with the relay unit remained constant during use.

Precision Condenser

A Sullivan N.P.L. certificated, direct drive, precision variable air condenser, having a minimum capacity of 65 $\mu\mu F$ and a maximum capacity of 365 $\mu\mu F$, was used. 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-fiftieth of a scale division by estimation, such a division corresponding to approximately 0.008 $\mu\mu$F.

Using a dielectric cell with a capacity of 100 $\mu\mu$F 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 within the limits with which the condenser could be read, and it was adjustable 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. By adjusting the trimming condensers in the variable frequency oscillator, the oscillators were matched to zero beats. 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 manner, the whole scale of the condenser was calibrated. By repeating readings at several points of the scale, the calibration was found to be satisfactory within the limits of the accuracy with which the scale could be read. The results obtained are shown in Figure (3).

Although in actual measurements the capacity of the precision condenser was always adjusted so that when it was in the circuit the beat frequency was as nearly as possible 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

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

differentiation with respect to C (L remaining constant) gives

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

dividing (2) by (1)

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

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)

$$\frac{df}{10^6} = \frac{-0.01 \times 10^{-12}}{2 \times 500 \times 10^{-12}}$$

i.e. df = 10 c.p.s.

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

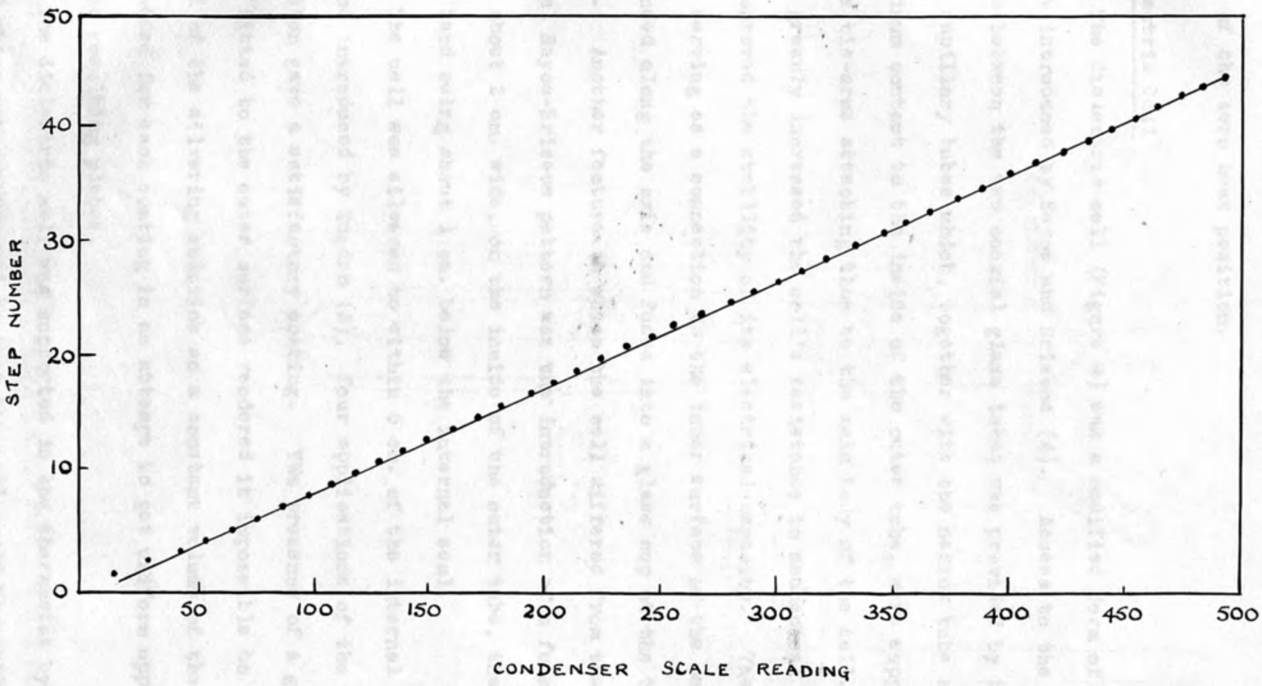


FIGURE 3. CALIBRATION OF PRECISION CONDENSER SCALE

five cycles per second, always assuming that the beats are on the same side of the zero beat position.

Dielectric Cell

The dielectric cell (Figure 4) was a modified form of the type first introduced by Sayce and Briscoe (4). Access to the annular space between the two coaxial glass tubes was provided by two 3 mm. bore capillary tubes which, together with the narrow tube carrying a platinum contact to the inside of the outer tube, were supported by glass tie-arms attaching them to the main body of the cell. These arms greatly increased the cell's resistance to mechanical strain and so 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. Another feature in which the cell differed from the conventional Sayce-Briscoe pattern was the introduction of a fused-on gold band about 2 cm. wide, on the inside of the outer tube, the top of this band being about 1 cm. below the internal seal.

The cell was silvered to within 5 cm. of the internal seal by the method introduced by Sugden (5); four applications of the silvering solution gave a satisfactory coating. The presence of a gold-leaf ring fitted to the outer surface rendered it impossible to see the level of the silvering solution so a constant volume of the solution was added for each coating in an attempt to get uniform upper edges to the resulting plates.

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

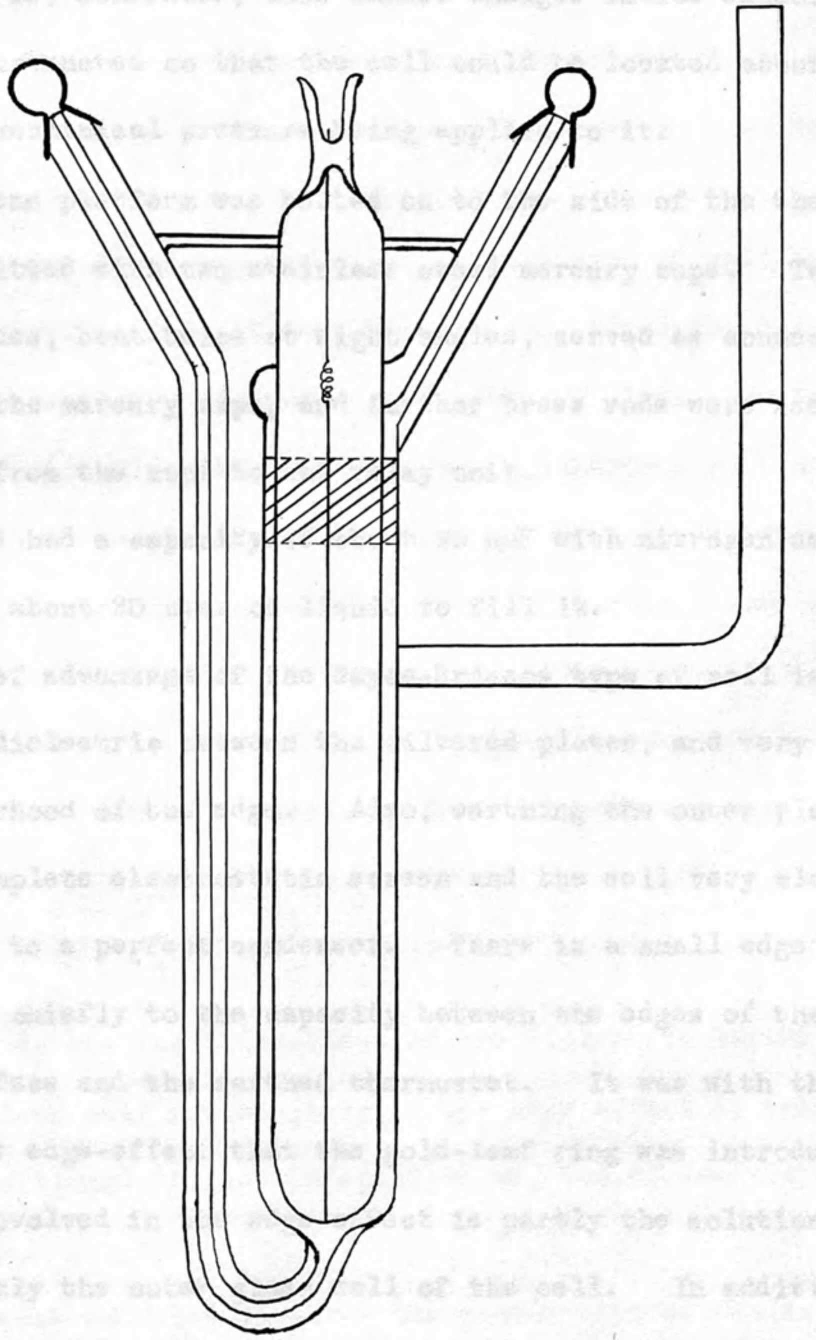


FIGURE 4. DIELECTRIC CELL

and removed. It was important to ensure that the cell was not strained by the stand as, otherwise, this caused changes in its capacity. The stand was constructed so that the cell could be located accurately, but without any mechanical pressure being applied to it.

A Distrene platform was bolted on to 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 the cups to the relay unit.

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

The chief advantage of the Sayce-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 very closely approximates to a perfect condenser. There is a small edge effect which is due chiefly to the capacity between the edges of the inner silvered surface and the earthed thermostat. It was with the idea of reducing this edge-effect that the gold-leaf 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. Again, the dielectric is mixed, involving the air space between the wire and the inner glass cell wall, the solution and the two glass walls. This effect was minimised by using a very thin platinum connecting wire passing axially up the centre of the cell. Calculation showed that the capacity of this wire to the outer plate and to the thermostat is small (0.3 µµF) and that its maximum variation with change of the dielectric constant of the medium in the cell from 1 to 3 was only 0.005 µµF and so could 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 investigation 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, is related to the dielectric constant of the liquid, ϵ_1, and to that of the outer wall, ϵ_2, by the 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 the 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 so that the edge correction was small. This 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 closely fitted the outer wall of the cell. It was about 3 cm. 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 water in the thermostat, and the capacity again determined. This value was slightly higher than in the former case, the difference corresponding to the capacity between the inner silvered surface and the 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 5) 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 similar in general design to that used in this investigation but 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 showed that the edge correction was almost exactly cancelled by the correction to be applied due to the use of $\epsilon = 1$ for the dielectric constant of nitrogen in the calculation of results, with the result that the dielectric constants calculated on this basis were

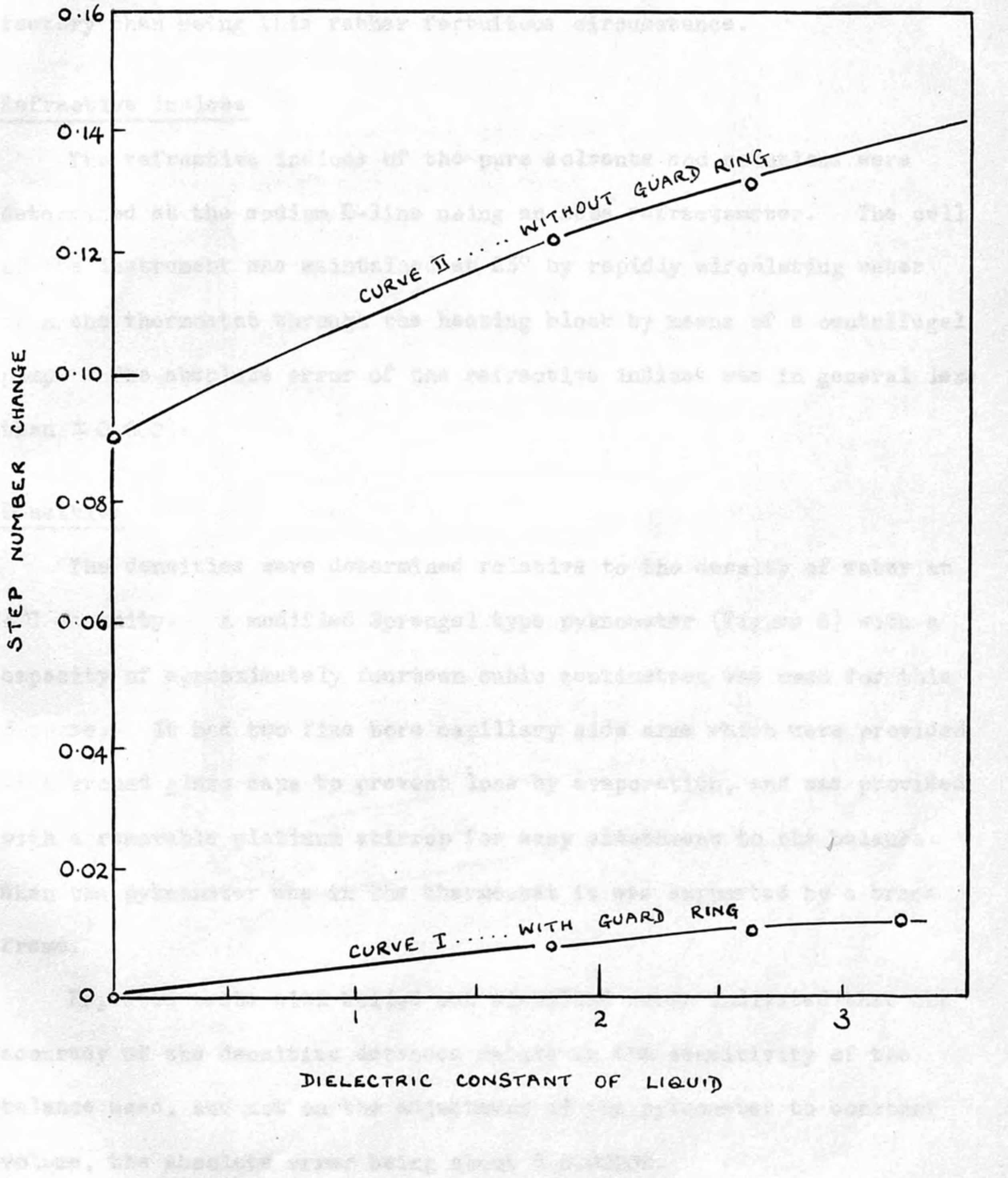


FIGURE 5. DIELECTRIC CELL EDGE CORRECTION

correct within the limits of experimental error. The reduction of the edge effect by means of a guard ring, however, seems rather more satisfactory than using this rather fortuitous circumstance.

Refractive Indices

The refractive indices of the pure solvents 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 less than ± 0.0001.

Densities

The densities were determined relative to the density of water at 4°C as unity. A modified Sprengel type pyknometer (Figure 6) with a capacity of approximately fourteen cubic centimetres was used for this purpose. It had two fine bore capillary side arms which were provided with ground glass caps to prevent loss by evaporation, and was provided with a removable platinum stirrup for easy attachment to the balance. When the pyknometer was 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 mainly 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

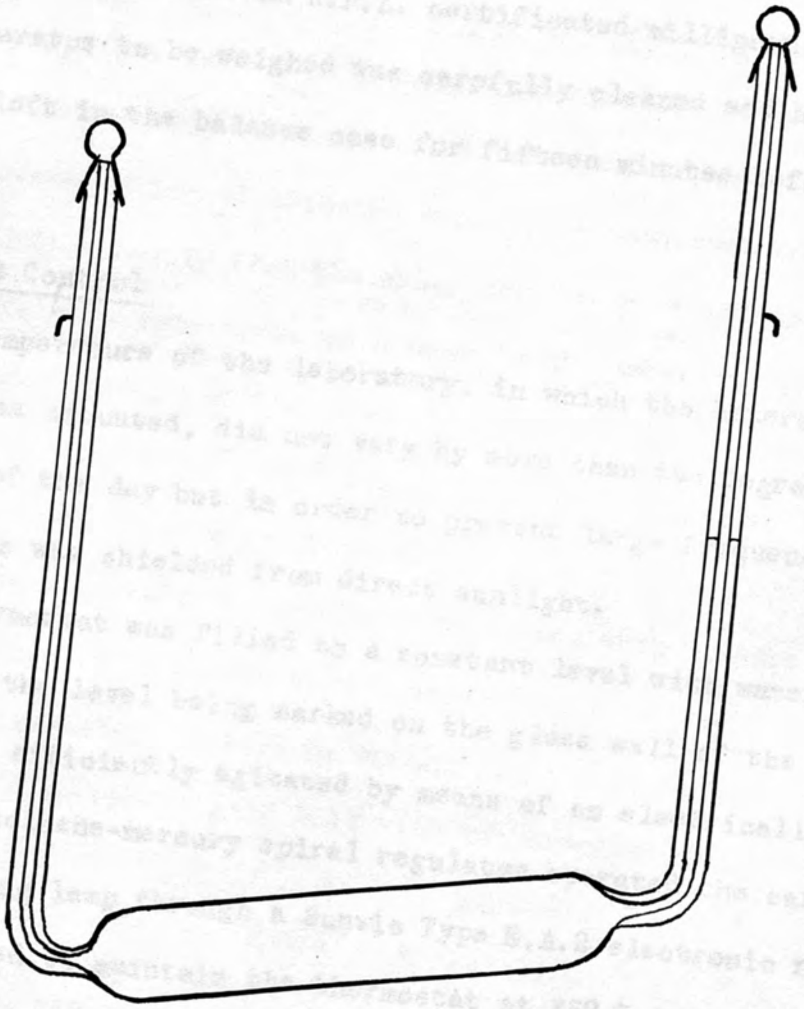


FIGURE 6. PYKNOMETER

solutions and for the determination of the densities. It had a sensitivity of 2.2 divisions per milligram throughout the range used, so that the weighings were accurate to 0.1 milligrams. The weights were calibrated against an N.P.L. certificated milligram rider. All glass apparatus to be weighed was carefully cleaned and handled with silk and left in the balance case for fifteen 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. The water was efficiently agitated by means 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 $25^{\circ} \pm 0.002^{\circ}$. The temperature registered by the Beckmann thermometer showed no detectable variation when it was moved to different points in the thermostat. The thermometer had previously been calibrated by comparison with an N.P.L. certificated thermometer.

Section II

Method of Calculation of the Dielectric Constants

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

Two reference substances were used in the determination of the 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 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,

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

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

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

From (1) and (2)

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

From (1) and (3)

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

Then

$$\frac{\epsilon_S - \epsilon_N}{\epsilon_B - \epsilon_N} = \frac{R_S - R_N}{R_B - R_N} \quad . \; . \; . \; . \; . \; . \; . \quad 6.$$

and

$$\epsilon_S = \frac{R_S - R_N}{R_B - R_N}(\epsilon_B - \epsilon_N) + \epsilon_N \quad . \; . \; . \; . \quad 7.$$

The dielectric constants can be calculated from equation (7) from the readings R_S, R_B and R_N and the known values of ϵ_S and ϵ_N.

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, $\quad 2.5905_0$ and $\quad 2.9085_0$,

whereas if the dielectric constant of nitrogen is assumed to be unity, the corresponding values of ϵ_S are

2.2725, $\quad 2.5906_3$ and $\quad 2.9087_5$.

The error introduced is

zero, $\quad +0.0001_3$ and $+0.0002_5$.

The values for the solutions are slightly higher in this case, than those 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 edge correction of the cell.

Since the present measurements have been completed a revised value of the dielectric constant of benzene at 25° has been published by

Hartshorn, Parry and Essen (8), viz. 2.2741. Although the assumption of this value increases the actual values of the dielectric constants it has only a very small effect on the value deduced for the dielectric constant increment, $\Delta\epsilon$. Thus the new value leads to a difference of 0.0016 for an increment of 1.2745 or 0.12% in the dielectric increment, and hence in the value of α deduced. This is illustrated by the calculation of the dipole moment of m-nitroaniline in Chapter II which has been deduced on both bases.

Evaluation of the Edge Correction

Using the graph of the edge correction (Figure 5, 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

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

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	$+ 0.0001_3$	$- 0.0000_3$	$+ 0.0001_0$
2.71	$+ 0.0002_5$	$- 0.0000_5$	+ 0.0002

Thus, if the dielectric constant of nitrogen is assumed to be unity and the edge correction of the cell is ignored, the resulting dielectric constants, up to values of $\epsilon = 2.6$, are free from both errors within the accuracy permitted by the scale of the precision condenser, i.e. within ±0.0001.

Section III

Method of Calculation of the Molecular Polarisations and Dipole Moments

The molecular polarisation of a polar compound is the sum of two terms, the orientation polarisation, P_μ, due to the permanent moment of the molecule and the distortion polarisation, P_D, which arises from the displacement of the electrons and the atomic nuclei by the applied electric field. It was first shown by Debye (9) that in the case of a polar compound the Clausius-Mosotti equation required a further term due to the presence of the permanent dipole and the equation deduced by Debye was

$$P_2 = P_D + P_\mu = \frac{4\pi N\alpha}{3} + \frac{4\pi N\mu^2}{9KT} \quad . \quad . \quad . \quad . \quad . \quad . \quad 1.$$

The derivation of this equation involved the assumption that the molecules are sufficiently far apart to prevent any interaction between them, therefore restricting the use of the equation to gases at low pressures. Debye pointed out that on the analogy of the Kinetic behaviour of a solute in dilute solution, the equation derived for the molecular polarisation of a substance in the ideal gas state should be applicable to the case of a polar solute at low concentration in a non-polar solvent, provided that there is no specific mutual interaction. This involves the assumption that for a two component system the dielectric polarisation can be regarded as additive for the two different types of molecules. Thus for a single molecular species the Clausius-Mosotti-Debye theory leads to the expression

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi Z \gamma$$

where Z is the number of molecules present per unit volume and γ is their polarisability. Hence for two molecular species of polarisability, γ_1 and γ_2

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi (Z_1\gamma_1 + Z_2\gamma_2)$$

and therefore the specific polarisation of the mixture p is given by

$$p = \frac{\epsilon - 1}{\epsilon + 2} .v = \frac{4}{3}\pi (Z_1 v \gamma_1 + Z_2 v \gamma_2)$$

where v is the specific volume of the solution.

If the molecules of the two components have masses m_1 and m_2, then z_1v and z_2v, the numbers of molecules of the two types per gram of solution are equal to w_1/m_1 and w_2/m_2 where w_1 and w_2 are the weight fractions of the components in the solution, so

$$p = \frac{\epsilon - 1}{\epsilon + 2} .v = \frac{4}{3}\pi \left(\frac{w_1\gamma_1}{m_1} + \frac{w_2\gamma_2}{m_2}\right)$$

Now if there were one pure component, say 1, alone, $z_1vm_1 = 1$, and hence its specific polarisation p_1 is given by $\frac{4\pi}{3} \cdot \frac{\gamma_1}{m_1}$.

Hence

$$p = p_1w_1 + p_2w_2 .$$

Only at very low concentrations of a polar solute in a non-polar solvent, however, will there be any approach to conditions which will justify the assumption inherent in the Debye theory that the dipoles are too far apart to undergo any mutual interaction. It does not suffice therefore to determine p_1 for the solvent and p for one solution in order to obtain a value of p_2 which represents the dielectric behaviour of isolated solute molecules, but it is necessary to make measurements on a series of solutions of graded, moderately low, concentrations, and to extrapolate the results to zero concentration. Under such conditions the value of p_2 should have the same significance as for a dilute gas

$$p_2 = \frac{4}{3}\pi\frac{\gamma_2}{m_2}$$

or $$P_2 = M_2 p_2 = \frac{4}{3}\pi\cdot\frac{M}{m}\cdot\gamma_2 = \frac{4}{3}\pi N\gamma_2$$

where P_2 is the molecular polarisation of the solute and γ_2 is the polarisability of the molecule arising from both distortion and orientation of the molecule, i.e. $\gamma_E + \gamma_A + \gamma_u$. But on the Debye theory $\gamma_\mu = \mu^2/3kT$ and hence

$$P_2 = \frac{4}{3}\pi N\left(\gamma_E + \gamma_A + \frac{\mu^2}{3kT}\right)$$

Therefore if the value of P_2 can be determined and also the quantity $\frac{4}{3}\pi N\ (\gamma_E + \gamma_A)$, i.e. P_{E+A}, μ can be calculated. In this work it has been assumed that P_{E+A} can be represented sufficiently closely by the molecular refraction of the compound for the sodium D line. This is most satisfactorily determined by using a method analogous to that for the molecular polarisation, assuming that

$$r = r_1 w_1 + r_2 w_2$$

where r is the specific refraction of the solution.

Throughout this work the results have been interpreted on the basis of this Debye theory. It is known that this does not take into account the change in the effective dipole moment of a molecule arising through the presence of a polarisable solvent. Other theories such as that of Onsager have been suggested to take account of the effect of the solvent but so far none has been suggested which is capable of doing this with certainty. The fact that the moments as derived by the Debye theory show, under suitable conditions, vector additivity features superior to those derived from other theories, is a strong factor in favour of their use in the present context.

The polarisation of the solution, P_{12}, is then equal to the polarisation contributions of the solvent and solute.

$$P_{12} = P_1 f_1 + P_2 f_2 = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \times \frac{M_1 f_1 + M_2 f_2}{d_{12}} \quad . \; . \; . \; . \quad 2.$$

The subscripts 1, 2 and 12 refer to the solvent, solute and solution respectively. Assuming that the polarisation of the solvent remains constant over the range studied, the molecular polarisation of the solute can be calculated from this equation. 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.

The molecular polarisation at infinite dilution, $P_{2\infty}$, may be determined by two methods.

The first method involves a graphical extrapolation of the curve produced by plotting the calculated molecular polarisation at each concentration against the weight fraction of the solute present. Sugden (10) has shown that the calculation of P_2 from equation (2) can be simplified by the use of specific polarisations. Since the molecular polarisation P_2, is the product of the specific polarisation,

p_2, and the molecular weight M_2 of the solute, it follows from equation (2)

$$P_{12} = P_1 f_1 - P_2 f_2$$

that

$$p_{12} = p_1 w_1 - p_2 w_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 3.$$

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

Also,

$$p_{12} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot v_{12} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 4.$$

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

$$w_1 = 1 - w_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 5.$$

Then, from (3) and (5),

$$p_2 = p_1 + \frac{p_{12} - p_1}{w_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 6.$$

and therefore

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

The values of P_2, calculated by equation (7), are plotted against the weight fraction of the solute present and the curve extrapolated to $W_2 = 0$.

This method of calculation involves two disadvantages. Since the calculation of P_2 at a particular concentration involves the difference between the two terms p_{12} and p_1, which are very nearly equal, the percentage error in P_2 increases as w_2 decreases. The manner in which P_2 varies with the concentration of the solute present is unknown so the extrapolation is also uncertain in many cases.

The other method available was used in this investigation and is due to Smith and Cleverdon (11). The dielectric constant of the solution is assumed to vary with the weight fraction of the solute present according to the relationship:

$$\epsilon_{12} = \epsilon_1 + \alpha w_2 + \alpha' w_2^2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad 8.$$

where α and α' are constants. In the case of very dilute solutions where w_2 is small w_2^2 is negligible and therefore ϵ is almost linear with w_2. The value of α, in these cases, was determined by plotting a graph of $\Delta\epsilon$ against w_2, the gradient giving α.

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

$$v_{12} = v_1 + \beta w_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad 9.$$

where β is a constant.

The value of β was determined by the relation,

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

thus placing less weight on the values of $(v_{12} - v_1)$ at low concentrations where the possible error in $(v_{12} - v_1)/w_2$ is large. The value of β calculated at each concentration was found to be constant within the limits of experimental error.

The molecular polarisation at infinite dilution was calculated from the values of α and β, using the equation derived by Halverstat and Kumler (12)

$$P_2 = M_2 p_2 = M_2 \left[\frac{3 \alpha v_1}{(\epsilon_1 + 2)} + (v_1 + \beta) \frac{\epsilon - 1}{\epsilon + 2} \right] \quad . \ . \quad 10.$$

This equation can be derived by the combination of equation (4) with equations (6), (8) and (9) and differentiating the resulting 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.

Actually, the value of $P_{2\infty}$ found from graphical extrapolation of the P_2 - w_2 curve to $w_2 = 0$, and the value of $P_{2\infty}$ obtained by linear extrapolation of the graph P_2 against $(\epsilon_{12} - 1)/(\epsilon_{12} + 2)$, the volume polarisation, to $(\epsilon_1 - 1)/(\epsilon_1 + 2)$, the volume polarisation of the solvent, are in good agreement with the value of $P_{2\infty}$ obtained from the parameters but there is a greater degree of uncertainty.

The molecular refraction for the sodium D line was calculated similarly from the relationship,

$$[R_D]_2 = M_2 r_2 = M_2\left[\frac{3\gamma v_1}{(n_1^2+2)^2} + (v_1+\beta)\cdot\frac{n_1^2-1}{n_1^2+2}\right]$$

where n_1 is the refractive index of the pure solvent for the sodium D line and γ is the mean value of $\frac{\Delta n^2}{w_2}$ over the concentration range studied.

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 substitution of the values of the distortion and molecular polarisations in the equation:

$$P_\mu = P_{2\infty} - P_D = \frac{4\pi N\mu^2}{9kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad 11.$$

The distortion polarisation is itself composed of two terms, the electronic and atomic polarisations. It was shown by Maxwell (13) that $\epsilon = n^2_\infty$ for a non-polar substance. Substitution of the value of n^2_∞ into the Lorentz-Lorenz molecular refraction equation leads to a value of the molecular refraction which is identical to the molecular polarisation calculated from the Clausius-Mosotti equation.

Thus,

$$\left[R_\infty\right] = P_D = P_A + P_E \quad \ldots \ldots \ldots \ldots \ldots \quad 12.$$

In the case of a polar compound, the molecular refraction calculated for light of long wave-length (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, the total distortion polarisation can be calculated by observations of the refractive index in the infra-red region of the spectrum. This method is not practically applicable, due to the difficulty in observing 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 (14) has indicated that this value of the electronic polarisation is generally 1 - 2 cc. greater than the value obtained by extrapolation of the refractive indices to infinite wave-length using a one-term Sellmeier equation. In general the atomic polarisation is small, usually not more than 5 cc. Jenkins (15) 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. As the atomic polarisation is associated with the bending vibrations of dipolar bonds there is no direct relationship between this and the overall dipole moment of a molecule. Much less is there any direct proportionality with the electron polarisation. Since it depends on the displacement of such polar bonds with respect to one another in the field it is impossible to allot P_A values to groups. Therefore the total distortion polarisation is usually assumed to be equal to R_D, the molecular refraction calculated for light at the wave-length of the sodium D line. As most of the compounds studied here had fairly high dipole moments this assumption causes no great error, as it does, in fact, make a small allowance for P_A. On the other hand, when interpreting the results for picryl chloride and picramide, where the atomic polarisation is likely to be exceptionally high, the moment has also been calculated using a value of $P_E + P_A$ based on the value of P for 1:3:5-trinitrobenzene, which contains a similar series of balanced dipoles.

There seems to be no clear relationship between dipole moment and atomic polarisation, and P_A values cannot be allotted to groups. The procedure used in the present work is to make no allowance for P_A. The total distortion polarisation is assumed to be equal to R_D, the molecular refraction calculated for light at the wave-length of the sodium D-line.

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

i.e.
$$\left[R_D\right] = M_2 r_2 = M_2 \left[r_1 + \frac{r_{12} - r_1}{w_2} \right] \quad . \; . \; . \; . \; . \; . \quad 13.$$

where $$r_{12} = \frac{n_{12}^2 - 1}{n_{12}^2 + 2}\, v_{12} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 14.$$

and $$r_1 = \frac{n_1^2 - 1}{n_1^2 + 2} \cdot v_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 15.$$

It was assumed that n_{12}^2 varied linearly with the weight fraction according to the relationship:

$$n_{12}^2 = n_1^2 + \gamma w_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad 16.$$

Combination of equations (9), (13), (14), (15) and (16) in a manner similar to that of Halverstat and Kumler for obtaining the molecular polarisation at $w_2 = 0$ leads to the equation:

$$\left[R_D\right] = M_2 \left[\frac{3\, v_1 \gamma}{(n_1^2 + 2)^2} + (v_1 + \beta)\, \frac{n_1^2 - 1}{n_1^2 + 2} \right] \quad . \; . \; . \quad 17.$$

where the parameter γ is obtained from the expression

$$\gamma = \frac{\sum (n_{12}^2 - n_1^2)}{\sum w_2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad 18.$$

This method has the advantage that less reliance is placed on the values of $(n_{12}^2 - n_1^2)$ at low concentrations where possible experimental errors are high.

The dipole moment is then calculated using equation (11)

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

hence $$\mu = \sqrt{\frac{9kT}{4\pi N} \cdot P_\mu} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 19.$$

$$\mu = 0.22124 \sqrt{P_\mu} \text{ at } 25^\circ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad 20.$$

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

It is evident that neglecting atomic polarisation causes a corresponding error 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 1.5, the error introduced is small. For larger molecules, particularly those with large opposed dipoles, however, the error is greater, especially when the molecular dipole moment is rather low.

Observational Errors

The accuracy with which P_2 can be determined depends, not only on the accuracy of the dielectric constant and specific volume determinations, but also upon the concentration of the solutions studied, 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)

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

as p_1 is constant,

$$\Delta p_2 = \frac{\Delta p_{12}}{w_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 21.$$

from (4)

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

partial differentiation with respect to ϵ_{12} gives,

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

partial differentiation with respect to v gives,

$$\frac{\partial p_{12}}{\partial v_{12}} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 23.$$

from equation (21), using equations (22) and (23),

$$\Delta p_2 = \frac{1}{w_2}\left[\frac{3v_{12} \cdot \Delta\epsilon_{12}}{(\epsilon_{12} + 2)^2} + \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \Delta v_{12}\right] \quad . \; . \; . \quad 24.$$

If the error in the dielectric constants is ± 0.0001, and in the specific volumes is ± 0.00002, then at the average values of $\epsilon_{12} = 2.4$, and $v_{12} = 1.0$, the corresponding errors in p_2 are as follows:

at $w_2 = 0.005$ $\quad p_2 = \pm\ 0.6\%$
at $w_2 = 0.01$ $\quad p_2 = \pm\ 0.3\%$

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 permissible in most cases when the concentrations studied cover a reasonable range, the error should not be greater than ± 0.2%, and in some cases is probably less than this. Some of the compounds which have been studied here, however, proved to be only sparingly soluble in benzene or dioxan: in these cases the results may unavoidably be of rather lower accuracy.

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 an analogous procedure to that used to determine the error in p_2, the error in $[R_D]$ can be calculated from equation (14),

i.e.

$$\Delta r_2 = \frac{1}{w_2}\left[\frac{6nv_{12} \cdot \Delta n}{(n^2 + 2)^2} + \frac{n^2 - 1}{n^2 + 2} \cdot \Delta v_{12}\right] \quad . \; . \; . \quad 25.$$

If the error in the refractive indices is ± 0.0001 and the error in the specific volume is, as before, ± 0.00002, then at the average values of $n = 1.47$ and $v = 1.0$, the corresponding errors in r_2 are as follows:

at $w_2 = 0.005$ $\Delta r = \pm 1.1\%$

at $w_2 = 0.01$ $\Delta r = \pm 0.6\%$

The error in the mean value of $\left[R_D\right]$ computed by equations (17) and (18), where less reliance is placed on the values of $(n_{12}^2 - n_1^2)$ for dilute solutions, is probably not greater than ± 0.2%.

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

To render the results as strictly comparable as possible a standard technique of measurement was adopted, so that any errors introduced were of a similar order of magnitude for each set of measurements. The whole of the measurements in one series were usually completed in a single day.

Preparation of the Solutions

The solutions were prepared in 100 c.c. ground glass stoppered flasks, which were graduated in 10 c.c. increments so that an approximately known volume of solvent could be rapidly introduced. The flasks were cleaned before each series of measurements with an alcohol-nitric acid mixture and washed thoroughly with distilled water. They were dried overnight in an electrically heated oven controlled at 120° and, after cooling in a desiccator, 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 introduced rapidly into the flasks which were again weighed accurately to 0.1 mg. The solvent was added directly from its container by blowing it over with dry nitrogen from a cylinder. The volume of liquid transferred was readily controlled by a screw clip and a mercury escape valve in the nitrogen supply tube.

A sample of the solvent was transferred to another 100 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 preparation 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 into the flasks by means of a dropper, and solid solutes, in a finely powdered condition, were introduced through a dry short-necked funnel.

Determination of the Dielectric Constants

Owing to the high dielectric constant of water, the dielectric constants of the solvent and 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 and heterodyne beat apparatus were switched on and allowed to warm up for an hour before any measurements were taken. The dielectric cell was dried by passing nitrogen through it for the same time. 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 precision condenser was 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 taken; 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, in which case they were repeated until a constant value was obtained.

The cell was removed from the thermostat, dried on the outside, and then filled with pure solvent by means of a transference apparatus similar to that used previously; the delivery tube had been made to fit inside the side arm of the cell in order to prevent 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 placed in the thermostat and the readings taken. This procedure was repeated with the remaining solutions and finally the nitrogen and pure solvent readings were repeated. 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.

Determination of the Densities

The pyknometer was dried by passing nitrogen, from a cylinder, through it for an hour. The outside of the pyknometer was cleaned with silk and it was weighed accurately to 0.1 mg. It was then filled with the solvent by the application of suction from a water pump, and placed in the thermostat for twenty minutes. Whilst still in the thermostat, the pyknometer was adjusted to the constant volume mark by applying a filter paper to one arm 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 three times with the first of the solutions, filled with this solution and then the above procedure repeated. The other 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 and wiped dry. The above operations were repeated for each of the solutions in turn.

CHAPTER II

EXPERIMENTAL RESULTS

Section I

Preparation and Purification of Materials

Some of the materials used were purchased and purified before use, whereas others were prepared specially for these measurements. Considerable attention was paid to the exclusion of moisture from both the solutes and the solvents. All solids were stored under nitrogen in tightly stoppered bottles and finally left in an evacuated desiccator for twenty-four hours immediately before use. Liquid solutes were vacuum distilled within two days of making measurements on them and then stored under nitrogen in a sealed tube. Solvents were distilled the day before use and stored under nitrogen in a desiccator until required.

The physical constants of the materials, together with the values obtained by other investigators, are recorded at the end of each method of purification. Unless otherwise stated, boiling points have been corrected to one atmosphere pressure.

Benzene

"Crystallisable" grade benzene was purified by the method used by Few and Smith (1). It was shaken with concentrated sulphuric acid and washed twice with water, twice with 5% aqueous potassium hydroxide and finally four times with water. The benzene was then roughly dried over calcium chloride and fractionally crystallised until it formed a glassy crystalline mass on freezing, before drying over phosphorous pentoxide for a fortnight. The benzene was distilled from this reagent, collecting the middle fraction which was of constant boiling point to within 0.02° in each case.

Boiling point 79.85°
$d_4^{25} = 0.87368 \pm 0.00003$
$n_D^{25} = 1.4979 \pm 0.0001$

Few and Smith (1) give:

Boiling point 79.7°
$d_4^{25} = 0.87368 \pm 0.00003$
$n_D^{25} = 1.4981 \pm 0.0001$

Littlejohn and Smith (2) give:

Boiling point 79.8°
$d_4^{25} = 0.87368 \pm 0.00003$
$n_D^{25} = 1.4980 \pm 0.0001$

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

Jenkins and Sutton (3) give $d_4^{25} = 0.8736$

1:4-Dioxan

Commercial dioxan was boiled with sodium under reflux for five or six hours, until the sodium remained bright and then the dioxan was distilled. This process was repeated with the distillate. The middle fraction which was of constant boiling point to within 0.02° in each case was collected.

Boiling point 101.0°

$n_D^{25} = 1.4199 \pm 0.0002$

Few and Smith (1) give:

Boiling point 100.9°

$d_4^{25} = 1.02793 \pm 0.00006$

$n_D^{25} = 1.4200 \pm 0.0001$

2:4-Dinitroaniline

2:4-Dinitroaniline was prepared by the method of Wells and Allen (4). 60G. of 2:4-dinitrochlorobenzene and 21.6g. of ammonium acetate were heated under reflux, in a bolt-head flask, half immersed in an oil bath which was maintained at 170° for seven hours. During this heating ammonia was bubbled through the reaction mixture at the rate of three to four bubbles per second. The product was boiled with 100 ml. of water and filtered. The 2:4-dinitroaniline was extracted from the residue with boiling alcohol. Water was added to the extract until the solution became slightly turbid. The solution was then heated until this turbidity disappeared and allowed to cool overnight, after which it was filtered and the residue dried. The 2:4-dinitroaniline was recrystallised from aqueous alcohol until a constant melting point was attained.

Yield = 27 g. = 50%
m.p. 178°

Wells and Allen (4) give m.p. 180°
Willgerodt (5) gives m.p. 182° - 183°
Blanskma (6) gives m.p. 186°

2:4:6-Trinitroaniline

Picryl chloride was prepared by Brady and Horton's (7) method. 50 G. of dry picric acid were heated with 100 g. of phosphorus pentachloride, under reflux, on a water-bath until the violent action subsided. The product was poured into water and rapidly collected. The crude picryl chloride was air-dried, washed with ether and recrystallised from benzene and alcohol (1:3).

Yield = 20 g. = 40%
m.p. 82°-82.5°

Picramide was prepared from the picryl chloride by the method of Le Fevre, Moir and Turner (8).

Ammonia was passed through a solution of 20 g. of picryl chloride in 100 ml. of boiling nitrobenzene for four hours. The mixture was cooled and the resulting solid recrystallised to constant melting point from glacial acetic acid. The product contained some ammonium chloride. This was removed by Soxhlet extraction, using dioxan as solvent.

Yield = 7.5 g. = 42%
m.p. 189°

Le Fevre, Moir and Turner (8) give m.p. 187° - 188°
Meisenheimer and Patzig (9) give m.p. 188°
Jaeger (10) gives m.p. 190°

m-Nitroaniline

Sodium polysulphide solution was prepared by boiling 40 g. of sodium sulphide in 150 ml. of water with 10 g. of sulphur until the solution became clear. 25 G. of m-dinitrobenzene were heated in 200 ml. of water until the water boiled gently. The sodium polysulphide solution was added dropwise, while the mixture was stirred mechanically. The mixture was boiled for twenty minutes after the final addition, then cooled and filtered. The product was washed with cold water and recrystallised from water to constant melting point.

m.p. 112.4°

Sidgwick and Rubie (11) give m.p. 114.6°

Berliner and May (12) give m.p. 112.5°

3:5-Dinitroaniline

All attempts to prepare 3:5 dinitroaniline according to the method of Nicolet (13) yielded 5-nitro-1:3-diaminobenzene, m.p. 143°. 3:5-dinitroaniline was obtained using a modification of this method.

A solution of ammonium polysulphide was prepared by passing hydrogen sulphide into a solution of 150 ml. of 95% alcohol and 75 ml. of 0.880 ammonia until the weight increased by 6.3 g. This solution was added dropwise to a solution of 15 g. of 2:4:6-trinitrobenzene in 450 ml. of boiling alcohol and the heating continued for one hour after the addition was complete. The mixture was filtered to remove sulphur and the alcohol distilled off. The residue was extracted thoroughly with hot water and the extract concentrated until crystallisation began and then cooled in ice-water. The 3:5-dinitroaniline was recrystallised from water until constant melting point was attained.

Yield = 6.5 g. = 50%

m.p. 161°

Nicolet (13) gives m.p. 155°- 156°

Curtius and Riedel (14) give m.p. 161°

van Duin (15) gives m.p. 162°

p-Nitroaniline

Commercial "pure" p-nitroaniline was recrystallised from water to constant melting point.

m.p. 148.9°

Berliner and May (12) give m.p. 147.8°

2:4-Dibromoaniline

2:4-Dibromoaniline was prepared according to the method of Chattaway and Clemo (16).

53.5 G. of p-bromoacetanilide and 20.5 g. of fused and finely powdered sodium acetate were suspended in sufficient glacial acetic acid to make a thick paste. 40 G. of bromine, dissolved in nine times its volume of glacial acetic acid, were added slowly and the mixture heated for six hours on a water bath, whilst excluding the presence of water from the reaction mixture. On diluting the cooled product with water, aceto-2:4-dibromoanilide separated. This was immediately filtered and crystallised from alcohol.

Yield = 28 g. = 38%

m.p. aceto-2:4-dibromoanilide 144°

Chattaway and Clemo (16) give m.p. 146°

The anilide was dissolved in boiling alcohol mixed with about one eighth of its bulk of concentrated hydrochloric acid and boiled under reflux for nine hours. The alcohol was distilled off in a current of steam. A slight excess of sodium hydroxide was added to the cooled residue and the amine was filtered off and redistilled in steam to remove any colouration. The 2:4-dibromoaniline was recrystallised from aqueous alcohol to constant melting point.

Yield = 19 g. = 95%
m.p. 79.5°

Chattaway and Clemo (16) give m.p. 78° - 79°
Griess (17) gives m.p. 79.5°

m-Bromoaniline

m-Bromonitrobenzene was prepared according to the method of Johnson and Gauerke (18).

A 2 l. flask was fitted with a separating funnel, a polythene-sealed electrical stirrer and a reflux condenser, the upper end of which carried an outlet tube dipping under soda-lime. 135 G. of freshly distilled dry nitrobenzene were introduced into the flask and the latter heated on an oil-bath at 135° to 140°. 13 G. of reduced iron powder and 281 g. of bromine, that had been dried by shaking with an equal volume of concentrated sulphuric acid, were added in the following way: 4 g. of the reduced iron were added to the stirred nitrobenzene and then 30 ml. of the bromine were added dropwise at such a rate that the bromine vapour did not traverse the condenser. The mixture was heated for an hour before a similar portion of iron and bromine was added and then for another hour before and after the final addition. The product was poured into 750 ml. of water containing 25 ml. of saturated sodium bisulphite solution. The product was steam distilled and the distillate filtered and steam distilled again to remove a purple colouration.

Yield = 70 g. = 35%

m.p. $51^{\circ} - 52^{\circ}$

The m-bromonitrobenzene was reduced to m-bromoaniline following the method of Mathieson and Newbery (19).

50 G. of m-bromonitrobenzene in 150 ml. of alcohol were boiled with 24 ml. of a $12\frac{1}{2}\%$ solution of calcium chloride. After removal from the steam-bath, 20 g. of reduced iron were added at such a rate that the heat of reaction kept the solution boiling gently. After the final addition, the mixture was heated on a water-bath for thirty minutes before distilling off the alcohol. The residue was made strongly alkaline with sodium hydroxide solution and steam distilled. The m-bromoaniline was extracted with ether and dried over potassium carbonate. The ether was distilled off and the m-bromoaniline purified by successive vacuum distillations at 15 mm.

Yield = 24 g. = 57%

b.p. $120^{\circ}/15$ mm.

3:5-Dibromoaniline

3:5-Dibromoaniline was prepared from p-nitroaniline through the intermediates, 2:6-dibromo-4-nitroaniline and 3:5-dibromo-1-nitrobenzene which were obtained by the method of Meyer, Meyer and Jaeger (20).

2:6-Dibromo-4-nitroaniline

31 Ml. of bromine were added dropwise to 40 g. of p-nitroaniline

in methyl alcohol solution. The slightly soluble, yellow, dibromonitroaniline was filtered, washed with water and dried.

Yield = 61 g. = 79%

m.p. 202°

3:5-Dibromo-1-nitrobenzene

61 G. of 2:6-dibromo-4-nitroaniline were suspended in 305 ml. of alcohol. 61 G. of concentrated sulphuric acid and about 14.5 g. of finely powdered sodium nitrite were added to the liquid in small amounts. The liquid was boiled, with frequent shaking, until there was no longer a smell of acetaldehyde. On cooling, the mixture solidified and was filtered, washed with water and steam distilled. The distillate was filtered but the solid product appeared to be a mixture. It was boiled with excess sulphuric acid and sodium nitrite in alcohol until there was no further reaction, then cooled, filtered and steam distilled.

Yield = 32 g. = 56%

m.p. 104°

3:5-Dibromoaniline

3:5-Dibromoaniline was prepared by the reduction of 3:5-dibromo-1-nitrobenzene with iron filings and concentrated hydrochloric acid in methanol.

20 G. of iron filings were added, in four portions at five minute intervals, to 32 g. of 3:5-dibromo-1-nitrobenzene in 55 ml. of boiling methyl alcohol and 1.1 ml. of concentrated hydrochloric acid. The mixture was boiled and stirred vigorously for two hours, then made alkaline with sodium hydroxide and steam distilled. The solid product that was filtered off was apparently a mixture. The reduction was

repeated, with this solid product, under the same conditions as before. The mixture was made alkaline and steam distilled. The solid product was filtered off and recrystallised from petroleum ether, boiling point 40° - 60°, until constant melting point was attained. Pure 3:5-dibromoaniline was obtained after the second reduction.

Yield = 17 g. = 59.5%

m.p. 55.1°

Vorlander and Siebert (21) give m.p. 57°

Senear et al. (22) give m.p. 47.5° - 50.5°

p-Bromoaniline

p-Bromoaniline was prepared by the bromination of acetanilide followed by acid hydrolysis.

p-Bromoacetanilide

A solution containing 18.8 ml. of bromine in 37 ml. of glacial acetic acid was added dropwise to 50 g. of acetanilide dissolved in approximately 250 ml. of acetic acid. The mixture was allowed to stand for thirty minutes and then poured into 2 l. of water. The precipitate was filtered, washed with water and recrystallised from aqueous alcohol.

Yield = 72 g. = 91%

m.p. 167°

p-Bromoaniline

36 G. of p-bromoacetanilide were dissolved in 70 ml. of boiling water. 44 ml. of concentrated hydrochloric acid were added slowly to the solution which was boiled under reflux for forty minutes. The solution was diluted with 300 ml. of water and distilled until about

200 ml. of distillate were collected. The residue was poured into ice-water and made just alkaline with 5% aqueous sodium hydroxide. The precipitate was filtered, washed with cold water and recrystallised, from cyclohexane, until constant melting point was attained.

Yield = 22 g. = 76%

m.p. 63.5°

Remmers (23) gives m.p. 63.5°

Hubner (24) gives m.p. 63° - 64°

2:4-Dinitromethylaniline

2:4-Dinitromethylaniline was prepared according to the method of Glazer, Hughes, Ingold, James, Jones and Roberts (25).

9.4 G. of 33% methylamine in alcoholic solution were added to a solution of 20.25 g. of 2:4-dinitro-1-chlorobenzene in alcohol. The product was filtered and recrystallised, to constant melting point, from aqueous acetone.

Yield = 18.3 g. = 93%

m.p. 178.7°

Glazer, Hughes, Ingold, James, Jones and Roberts (25) give m.p. 177°

Leymann (26) gives m.p. 178°

p-Nitromethylaniline

p-Nitromethylaniline (B.D.H.) was recrystallised from aqueous alcohol until a constant melting point was attained.

m.p. 152.2°

Blanskma (27) gives m.p. 151°

Meldola and Salmon (28) give m.p. 152°

Section II

Tables of Experimental Results

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

1.	2:4-Dinitroaniline in Benzene
2.	2:4-Dinitroaniline in Dioxan
3.	2:4:6-Trinitroaniline in Benzene
4.	2:4:6-Trinitroaniline in Dioxan
5.	m-Nitroaniline in Benzene
6.	m-Nitroaniline in Dioxan
7.	3:5-Dinitroaniline in Benzene
8.	3:5-Dinitroaniline in Dioxan
9.	p-Nitroaniline in Benzene
10.	p-Nitroaniline in Dioxan
11.	2:4-Dibromoaniline in Benzene
12.	2:4-Dibromoaniline in Dioxan
13.	m-Bromoaniline in Benzene
14.	m-Bromoaniline in Dioxan
15.	3:5-Dibromoaniline in Benzene
16.	3:5-Dibromoaniline in Dioxan
17.	p-Bromoaniline in Benzene
18.	p-Bromoaniline in Dioxan
19.	2:4-Dinitromethylaniline in Benzene
20.	2:4-Dinitromethylaniline in Dioxan

21. p-Nitromethylaniline in Benzene

22. p-Nitromethylaniline in Dioxan

23. 2-Methyl-4-nitroaniline in Benzene

24. 2-Methyl-4-nitroaniline in Dioxan

25. 2:4:6-Trinitro-1-chlorobenzene in Dioxan

26. m-Nitroaniline in Benzene (calculated from $\epsilon_s = 2.2741$)

1. 2:4-DINITROANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14459	0.34090	—
0.01653	2.2761	1.14452	0.34155	782.51
0.04155	2.2808	1.14442	0.34241	727.95
0.06312	2.2858	1.14427	0.34330	758.71
0.08335	2.2898	1.14420	0.34402	747.90
0.09910	2.2928	1.14410	0.34455	736.89
0.12835	2.2990	1.14390	0.34564	738.70

$\Delta\epsilon/w_2$	$\Delta v/w_2$
21.77	-0.4234
19.98	-0.4091
21.07	-0.5070
20.76	-0.4679
20.48	-0.4945
20.65	-0.5376

$\alpha = 20.62$ $\beta = -0.4945$ $R_D = 43.6$

$P_{2\infty} = 745.75$ $P_\mu = 702.15$

$\mu = 5.869$

2. 2:4-DINITROANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2132	0.97305	0.28019	—
0.1472	2.2563	0.97256	0.28706	905.97
0.2472	2.2857	0.97219	0.29165	900.26
0.3658	2.3203	0.97177	0.29698	891.84
0.5203	2.3655	0.97122	0.30379	881.93
0.6684	2.4085	0.97073	0.31014	871.86
0.8055	2.4482	0.97026	0.31589	862.92

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4200	2.01640	—	—	—
1.4202	2.01697	0.3872	29.28	-0.3328
1.4203	2.01725	0.3439	29.33	-0.3479
1.4207	2.01839	0.5440	29.28	-0.3499
1.4210	2.01924	0.5458	29.27	-0.3517
1.4212	2.01981	0.5101	29.21	-0.3471
1.4217	2.02123	0.5996	29.17	-0.3464

$\alpha = 29.26$ $\beta = -0.3474$ $\gamma = 0.5246$

$P_{2\infty} = 914.15$ $R_D = 45.76$ $P_\mu = 868.39$

$\mu = 6.527$

3. 2:4:6-TRINITROANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14458	0.34090	—
0.1214	2.2775	1.14388	0.34163	214.94
0.2333	2.2828	1.14324	0.34243	227.37
0.2763	2.2841	1.14297	0.34259	217.30
0.3679	2.2883	1.14243	0.34321	221.00
0.4770	2.2929	1.14184	0.34389	220.79
0.5880	2.2981	1.14118	0.34466	223.64

$\Delta\epsilon/w_2$	$\Delta v/w_2$
4.119	-0.5766
4.415	-0.5744
4.199	-0.5827
4.295	-0.5844
4.277	-0.5744
4.354	-0.5782

$\alpha = 4.277$ $\beta = -0.5785$ $R_D = 50.1$

$P_{2\infty} = 221.99$ $P_\mu = 171.89$

$\mu = 2.904$

4. 2:4:6-TRINITROANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2576	0.97465	0.28789	—
0.1210	2.2649	0.97417	0.28892	259.86
0.2377	2.2731	0.97370	0.29010	277.77
0.3496	2.2800	0.97322	0.29106	272.53
0.4536	2.2867	0.97284	0.29201	272.88
0.6613	2.3001	0.97197	0.29387	271.96

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4197	2.01555	—	—	—
1.41985	2.01597	0.3554	6.033	-0.3967
1.4200	2.01640	0.3997	6.521	-0.3996
1.4202	2.01697	0.4062	6.407	-0.4090
1.4204	2.01754	0.4387	6.415	-0.3990
1.4209	2.01896	0.5157	6.427	-0.4052

$\alpha = 6.385$ $\beta = 0.4031$ $\gamma = 0.4498$

$P_{2\infty} = 273.46$ $R_D = 51.18$ $P_\mu = 222.28$

$\mu = 3.302$

5. m-NITROANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14459	0.34090	—
0.1481	2.3006	1.14405	0.34597	519.93
0.2716	2.3247	1.14358	0.35027	523.60
0.4154	2.3523	1.14303	0.35513	520.25
0.5324	2.3753	1.14256	0.35913	520.04
0.6361	2.3957	1.14212	0.36260	518.28
0.7416	2.4158	1.14167	0.36603	518.30

$\Delta\epsilon/w_2$	$\Delta v/w_2$
18.97	-0.3646
19.22	-0.3718
19.21	-0.3756
19.31	-0.3812
19.37	-0.3883
19.32	-0.3938

$\alpha = 19.12$

$\beta = -0.3835$

$R_D = 37.1$

$P_{2\infty} = 528.09$

$P_\mu = 490.99$

$\mu = 4.910$

6. m-NITROANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2169	0.97322	0.28085	—
0.5884	2.3647	0.97193	0.30390	579.88
1.1338	2.5076	0.97071	0.32466	572.55
1.7381	2.6620	0.96940	0.34559	553.27
2.3073	2.8126	0.96821	0.36466	540.51
2.8900	2.9684	0.96690	0.38307	527.34
5.5876	3.7173	0.96106	0.45677	481.59

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4200	2.01640	—	—	—
1.4209	2.01896	0.4445	25.11	-0.2192
1.4219	2.02180	0.4763	25.64	-0.2214
1.4230	2.02493	0.4908	25.61	-0.2199
1.4240	2.02778	0.4932	25.82	-0.2171
1.4250	2.03063	0.4924	26.00	-0.2187
1.4298	2.04433	0.4999	26.85	-0.2176

$\alpha = 25.07$ $\beta = -0.2186$ $\gamma = 0.4920$

$P_{2\infty} = 599.48$ $R_D = 38.67$ $P_\mu = 560.81$

$\mu = 5.245$

7. 3:5-DINITROANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14453	0.34088	—
0.02174	2.2761	1.14442	0.34152	601.52
0.03992	2.2793	1.14433	0.34210	622.07
0.07184	2.2852	1.14417	0.34315	641.06
0.1137	2.2931	1.14396	0.34457	656.73
0.1776	2.3048	1.14363	0.34664	656.34
0.2158	2.3116	1.14344	0.34784	653.04

$\Delta\epsilon/w_2$	$\Delta v/w_2$
16.56	-0.5060
17.03	-0.5010
17.68	-0.5011
18.12	-0.5013
18.19	-0.5068
18.12	-0.5051

$\alpha = 18.00$ $\beta = -0.5042$ $R_D = 43.6$

$P_{2\infty} = 654.94$ $P_\mu = 611.34$

$\mu = 5.473$

8.

3:5-DINITROANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2411	0.97384	0.28498	—
0.1172	2.2700	0.97347	0.28953	763.12
0.2093	2.2921	0.97314	0.29296	750.39
0.3692	2.3318	0.97263	0.29903	749.07
0.4781	2.3578	0.97229	0.30295	740.48
0.6852	2.4084	0.97167	0.31043	732.35
1.2689	2.5487	0.96975	0.33017	704.36

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4196	2.01526	—	—	—
1.41975	2.01569	0.3669	24.66	-0.3157
1.41985	2.01597	0.3392	24.37	-0.3344
1.4200	2.01640	0.3088	24.57	-0.3277
1.4201	2.01668	0.2971	24.41	-0.3242
1.4205	2.01782	0.3736	24.42	-0.3167
1.4212	2.01981	0.3586	24.24	-0.3278

$\alpha = 24.34$ $\beta = -0.3248$ $\gamma = 0.3456$

$P_{2\infty} = 758.75$ $R_D = 41.52$ $P_\mu = 717.23$

$\mu = 5.931$

9. p-NITROANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14460	0.34090	—
0.06217	2.2915	1.14437	0.34439	822.46
0.1113	2.3068	1.14415	0.34717	825.30
0.1716		1.14389	0.35026	
0.2025	2.3354	1.14377	0.35231	825.35
0.2612	2.3538	1.14357	0.35559	823.90
0.3336	2.3768	1.14322	0.35948	816.37

$\Delta\epsilon/w_2$	$\Delta v/w_2$
30.56	-0.3700
30.81	-0.4043
	-0.4138
31.06	-0.4099
31.13	-0.3943
31.26	-0.4137

$\alpha = 30.62$

$\beta = -0.4053$

$R_D = 37.1$

$P_{2\infty} = 826.00$

$P_\mu = 788.90$

$\mu = 6.221$

10. p-NITROANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2120	0.97304	0.27999	—
0.6259	2.4799	0.97152	0.32093	947.66
1.1971	2.7289	0.97015	0.35469	900.58
1.8488	3.0183	0.96857	0.38955	857.20
2.4847	3.3065	0.96701	0.42032	818.76
3.7102	3.8820	0.96418	0.47243	755.09

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4200	2.01640	—	—	—
1.4215	2.02066	0.6806	42.80	-0.2429
1.4229	2.02464	0.6883	43.18	-0.2414
1.4244	2.02892	0.6772	43.61	-0.2418
1.4261	2.03376	0.6987	44.05	-0.2427
1.4292	2.04261	0.7064	45.01	-0.2388

$\alpha = 42.35$ $\beta = -0.2409$ $\gamma = 0.6953$

$P_{2\infty} = 991.59$ $R_D = 42.97$ $P_\mu = 948.62$

$\mu = 6.822$

11. 2:4-DIBROMOANILINE IN BENZENE.

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14458	0.34090	—
0.4388	2.2868	1.14172	0.34272	189.63
0.8734	2.3012	1.13889	0.34454	190.13
1.2675	2.3144	1.13631	0.34618	190.08
1.5007	2.3226	1.13480	0.34722	191.23
2.3899	2.3530	1.12897	0.35091	190.65
3.0807	2.3762	1.12446	0.35361	189.08

n_D	n_D	n_D/w_2	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4979	2.24370	—	—	—
1.49815	2.24445	0.1709	3.259	-0.6518
1.49835	2.24505	0.1546	3.286	-0.6515
1.4987	2.24610	0.1893	3.306	-0.6525
1.4988	2.24640	0.1799	3.338	-0.6517
1.49925	2.24775	0.1695	3.368	-0.6532
1.4999	2.24970	0.1948	3.366	-0.6531

$\alpha = 3.245$

$\beta = -0.6526$

$\gamma = 0.1806$

$P_{2\infty} = 189.94$

$R_D = 44.82$

$P_\mu = 145.12$

$\mu = 2.668$

12. 2:4-DIBROMOANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2327	0.97360	0.28354	—
0.2412	2.2442	0.97241	0.28506	229.29
0.4653	2.2551	0.97132	0.28650	230.79
0.7255	2.2678	0.97003	0.28816	230.93
0.9416	2.2785	0.96901	0.28956	231.59
1.3499	2.2989	0.96701	0.29218	231.77
2.5606	2.3592	0.96112	0.29968	229.32

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.41985	2.01597	—	—	—
1.4201	2.01668	0.2529	4.768	-0.4892
1.4203	2.01725	0.2751	4.814	-0.4879
1.42065	2.01825	0.3143	4.838	-0.4907
1.4208	2.01867	0.2867	4.864	-0.4864
1.4214	2.02038	0.3267	4.904	-0.4874
1.4229	2.02464	0.3386	4.940	-0.4870

$\alpha = 4.76$ $\beta = -0.4856$ $\gamma = 0.3175$

$P_{2\infty} = 230.40$ $R_D = 45.41$ $P_\mu = 184.99$

$\mu = 3.012$

13. m-BROMOANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14462	0.34091	—
0.5453	2.2984	1.14178	0.34489	182.82
1.1485	2.3271	1.13860	0.34920	181.20
2.1855	2.3768	1.13312	0.35362	180.72
2.7200	2.4031	1.13035	0.36020	180.65
3.5843	2.4453	1.12581	0.36603	179.21

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4977	2.24311	—	—	—
1.4981	2.24430	0.2182	4.750	-0.5208
1.4986	2.24558	0.2150	4.754	-0.5242
1.4994	2.24820	0.2329	4.772	-0.5262
1.4998	2.24940	0.2313	4.801	-0.5246
1.5002	2.25060	0.2090	4.821	-0.5248

$\alpha = 4.724$ $\beta = -0.5247$ $\gamma = 0.2233$

$P_{2\infty} = 184.64$ $R_D = 38.57$ $P_\mu = 146.07$

$\mu = 2.676$

14. m-BROMOANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2081	0.97304	0.27935	—
0.4723	2.2404	0.97133	0.28413	222.17
1.0489	2.2801	0.96932	0.28991	221.26
1.5168	2.3152	0.96764	0.29450	219.89
1.9210	2.3408	0.96622	0.29845	219.10
2.4336	2.3768	0.96439	0.30337	217.86
3.0376	2.4198	0.96226	0.30911	216.60

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4201	2.01668	—	—	—
1.4207	2.01839	0.3621	6.838	-0.3621
1.4215	2.02066	0.3794	6.864	-0.3547
1.4221	2.02237	0.3751	6.882	-0.3560
1.4227	2.02408	0.3852	6.908	-0.3550
1.4232	2.02550	0.3624	6.932	-0.3554
1.4242	2.02835	0.3809	6.969	-0.3549

$\alpha = 6.815$ $\beta = -0.3552$ $\gamma = 0.3755$

$P_{2\infty} = 223.78$ $R_D = 38.59$ $P_\mu = 185.19$

$\mu = 3.014$

15. 3:5-DIBROMOANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14455	0.34089	—
0.4847	2.2928	1.14139	0.34374	233.09
0.9687	2.3133	1.13823	0.34656	232.42
1.5503	2.3384	1.13442	0.34997	232.52
2.1582	2.3641	1.13035	0.35332	230.07
2.9390	2.3982	1.12527	0.35773	229.33
3.6569	2.4293	1.12061	0.36161	227.73

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4979	2.24370	—	—	—
1.4982	2.24460	0.1857	4.188	-0.6519
1.4985	2.24550	0.1858	4.212	-0.6524
1.4989	2.24670	0.1935	4.251	-0.6534
1.4993	2.24790	0.1946	4.244	-0.6580
1.5000	2.25000	0.2144	4.277	-0.6560
1.5007	2.25210	0.2297	4.288	-0.6547

$\alpha = 4.222$ $\beta = -0.6554$ $\gamma = 0.2090$

$P_{2\infty} = 235.85$ $R_D = 46.00$ $P_\mu = 189.85$

$\mu = 3.052$

16. 3:5-DIBROMOANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2378	0.97377	0.28442	—
0.3518	2.2601	0.97206	0.28753	293.21
0.7223	2.2830	0.97028	0.29065	287.81
1.0220	2.3016	0.96882	0.29315	285.73
1.4682	2.3296	0.96669	0.29687	284.16
1.5138	2.3321	0.96644	0.29718	282.89
1.9836	2.3624	0.96415	0.30111	282.51

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4198	2.01569	—	—	—
1.4201	2.01668	0.2814	6.339	-0.4861
1.4205	2.01782	0.2945	6.258	-0.4832
1.4209	2.01896	0.3199	6.243	-0.4843
1.4212	2.01981	0.2806	6.253	-0.4822
1.4214	2.02038	0.3098	6.229	-0.4842
1.4220	2.02208	0.3223	6.282	-0.4850

$\alpha = 6.252$ $\beta = -0.4840$ $\gamma = 0.3057$

$P_{2\infty} = 291.10$ $R_D = 44.98$ $P_\mu = 246.12$

$\mu = 3.475$

17.

p-BROMOANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14457	0.34089	—
0.4137	2.2971	1.14244	0.34485	223.32
0.8649	2.3236	1.14003	0.34900	219.96
1.2547	2.3474	1.13798	0.35270	220.57
1.6885	2.3735	1.13567	0.35666	219.32
2.3484	2.4135	1.13220	0.36261	217.76
3.3782	2.4771	1.12695	0.37181	216.10

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4978	2.24340	—	—	—
1.49805	2.24415	0.1813	5.946	-0.5149
1.49835	2.24505	0.1908	5.908	-0.5249
1.4988	2.24640	0.2391	5.970	-0.5252
1.4990	2.24700	0.2132	5.982	-0.5271
1.4995	2.24850	0.2172	6.004	-0.5267
1.5003	2.25090	0.2220	6.056	-0.5216

$\alpha = 5.915$ $\beta = -0.5242$ $\gamma = 0.2171$

$P_{2\infty} = 223.20$ $R_D = 38.39$ $P_\mu = 184.81$

$\mu = 3.011$

18. p-BROMOANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2352	0.97368	0.28397	—
0.6200	2.2884	0.97148	0.29187	268.05
1.2231	2.3407	0.96929	0.29938	265.60
1.8509	2.3949	0.96707	0.30694	262.35
2.4778	2.4503	0.96482	0.31442	260.27
3.1159	2.5073	0.96258	0.32190	258.27
4.0471	2.5911	0.95925	0.33244	254.89

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4194	2.01470	—	—	—
1.4203	2.01725	0.4113	8.580	-0.3548
1.4212	2.01981	0.4178	8.625	-0.3589
1.4221	2.02237	0.4144	8.624	-0.3571
1.4230	2.02493	0.4129	8.676	-0.3576
1.4239	2.02749	0.4105	8.734	-0.3562
1.4253	2.03148	0.4146	8.792	-0.3566

$\alpha = 8.542$ $\beta = -0.3569$ $\gamma = 0.4134$

$P_{2\infty} = 270.26$ $R_D = 39.71$ $P_\mu = 230.55$

$\mu = 3.363$

19. 2:4-DINITROMETHYLANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14495	0.34101	—
0.03527	2.2800	1.14480	0.34237	827.45
0.06149	2.2858	1.14468	0.34342	839.93
0.1174	2.2981	1.14444	0.34564	844.75
0.1614	2.3088	1.14422	0.34756	867.32
0.2060	2.3188	1.14404	0.34935	865.41

$\Delta\epsilon/w_2$	$\Delta v/w_2$
21.26	-0.4253
21.62	-0.4391
21.81	-0.4344
22.49	-0.4523
22.48	-0.4417

$\alpha = 22.2$ $\beta = -0.4375$ $R_D = 48.7$

$P_{2\infty} = 865.05$ $P_{\mu} = 816.35$

$\mu = 6.332$

20.

2:4-DINITROMETHYLANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2185	0.97315	0.28109	—
0.06835	2.2366	0.97294	0.28399	891.90
0.1809	2.2683	0.97263	0.28901	918.56
0.2472	2.2840	0.97242	0.29145	881.66
0.3094	2.3046	0.97222	0.29465	919.46
0.4029	2.3299	0.97192	0.29852	910.29

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4201	2.01668	—	—	—
1.4202	2.01697	0.4243	26.48	-0.3072
1.4204	2.01758	0.4975	27.53	-0.2875
1.4205	2.01782	0.4617	26.50	-0.2957
1.4207	2.01839	0.5527	27.83	-0.3006
1.4209	2.01896	0.5659	27.65	-0.3053

$\alpha = 27.65$ $\beta = -0.2996$ $\gamma = 0.5230$

$P_{2\infty} = 932.64$ $R_D = 52.27$ $P_\mu = 880.37$

$\mu = 6.572$

21.

p-NITROMETHYLANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14483	0.34097	—
0.05169	2.2898	1.14466	0.34416	990.86
0.0942	2.3042	1.14451	0.34679	991.61
0.1521	2.3236	1.14426	0.35030	985.18
0.2035	2.3405	1.14411	0.35334	976.74
0.2675	2.3618	1.14385	0.35712	970.47
0.3384	2.3858	1.14362	0.36135	968.20

$\Delta\epsilon/w_2$	$\Delta v/w_2$
33.47	-0.3289
33.64	-0.3396
33.60	-0.3748
33.42	-0.3538
33.38	-0.3664
33.48	-0.3576

$\alpha = 33.50$ $\beta = -0.3585$ $R_D = 42.2$

$P_{2\infty} = 994.63$ $P_\mu = 952.43$

$\mu = 6.835$

22. p-NITROMETHYLANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2101	0.97306	0.27968	—
0.1786	2.2843	0.97274	0.29160	1058.02
0.3359	2.3507	0.97241	0.30189	1048.58
0.5372	2.4352	0.97207	0.31456	1030.45
0.6842	2.4968	0.97177	0.32346	1016.12
0.9486	2.6071	0.97126	0.33881	990.97
1.2676	2.7405	0.97073	0.35641	963.54

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4200	2.01640	—	—	—
1.4205	2.01782	0.7951	41.55	-0.1792
1.4209	2.01896	0.7621	41.86	-0.1935
1.4213	2.02009	0.6869	41.90	-0.1843
1.4218	2.02152	0.7483	42.03	-0.1885
1.4223	2.02294	0.6894	41.85	-0.1898
1.4231	2.02521	0.6950	41.84	-0.1838

$\alpha = 41.85$ $\beta = -0.1867$ $\gamma = 0.7120$

$P_{2\infty} = 1083.07$ $R_D = 49.88$ $P_\mu = 1033.19$

$\mu = 7.120$

23. 2-METHYL-4-NITROANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2725	1.14454	0.34088	—
0.0706	2.2934	1.14427	0.34471	877.27
0.1479	2.3155	1.14400	0.34873	859.41
0.2011	2.3319	1.14375	0.35166	867.47
0.3098	2.3642	1.14329	0.35738	862.22
0.5323	2.4318	1.14249	0.36911	858.78
0.6635	2.4749	1.14194	0.37638	868.22

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4980	2.24400	—	—	—
1.49805	2.24415	0.2125	29.60	-0.3824
1.4981	2.24430	0.2028	29.07	-0.3651
1.49815	2.24445	0.2238	29.54	-0.3928
1.49825	2.24475	0.2421	29.60	-0.4035
1.4986	2.24580	0.3382	29.93	-0.3851
1.4987	2.24610	0.3168	30.50	-0.3919

$\alpha = 29.6$ $\beta = -0.3891$ $\gamma = 0.2883$

$P_{2\infty} = 881.37$ $R_D = 42.03$ $P_\mu = 839.34$

$\mu = 6.417$

24.

2-METHYL-4-NITROANILINE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2154	0.97328	0.28062	—
0.6254	2.4664	0.97197	0.31913	979.58
1.1106	2.6529	0.97097	0.34493	923.73
1.7718	2.9432	0.96950	0.38112	905.72
2.2969	3.1501	0.96841	0.40430	861.97
3.5261	3.6727	0.96587	0.45507	795.44

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4200	2.01640	—	—	—
1.4215	2.02066	0.6812	40.15	-0.2095
1.4225	2.02351	0.6403	39.40	-0.2080
1.4242	2.02835	0.6722	41.08	-0.2133
1.4256	2.03234	0.6940	40.69	-0.2120
1.4283	2.04004	0.6704	41.33	-0.2101

$\alpha = 40.53$ $\beta = -0.2103$ $\gamma = 0.6833$

$P_{2\infty} = 1046.75$ $R_D = 48.20$ $P_\mu = 998.55$

$\mu = 6.999$

25.

PICRYL CHLORIDE IN DIOXAN

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2137	0.97316	0.28031	—
0.5473	2.2172	0.97098	0.28025	64.53
1.1024	2.2200	0.96877	0.28007	64.00
1.6111	2.2233	0.96672	0.28002	64.94
2.2809	2.2268	0.96404	0.27981	63.97
2.9237	2.2312	0.96150	0.27978	64.90
4.1321	2.2385	0.95669	0.27955	64.84

n_D	n_D^2	$\Delta n_D^2/w_2$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
1.4200	2.01640	—	—	—
1.4208	2.01867	0.4148	0.640	-0.3983
1.4212	2.01981	0.3093	0.572	-0.3982
1.4220	2.02208	0.3526	0.596	-0.3997
1.4229	2.02464	0.3613	0.574	-0.3998
1.4236	2.02664	0.3502	0.599	-0.3988
1.4251	2.03091	0.3512	0.600	-0.3986

$\alpha = 0.597$ $\beta = -0.3989$ $\gamma = 0.3521$

$P_{2\infty} = 65.25$ $R_D = 51.75$ $P_\mu = 13.50$

$\mu = 0.843$

26. m-NITROANILINE IN BENZENE

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2
0.0000	2.2741	1.14459	0.34120	—
0.1481	2.3022	1.14405	0.34628	520.91
0.2716	2.3264	1.14358	0.35060	525.17
0.4154	2.3540	1.14303	0.35546	521.29
0.5324	2.3771	1.14256	0.35947	521.12
0.6361	2.3974	1.14212	0.36294	519.20
0.7416	2.4176	1.14167	0.36636	515.74

$\Delta\epsilon/w_2$	$\Delta v/w_2$
18.97	-0.3646
19.26	-0.3718
19.23	-0.3756
19.35	-0.3812
19.39	-0.3883
19.35	-0.3938

α = 19.15 β = -0.3835 R_D = 37.1

$P_{2\infty}$ = 528.52 P_{μ} = 491.42

μ = 4.910

CHAPTER III

DISCUSSION OF RESULTS

Section I

Survey of Previous Results

The dipole moment and molecular polarisation of aniline have been studied by many workers at various temperatures and in a number of different solvents. Relatively few measurements have been made on substituted anilines although Few and Smith (1, 2, 3) studied a number of these compounds in both benzene and dioxan solutions.

In the present investigation the dipole moments of m- and p-bromo- and nitro-, 2:4- and 3:5-dibromo- and dinitro- and 2:4:6-trinitroanilines have been measured. A summary of the previous results together with those obtained here is given in the following table.

TABLE I

Dipole Moments of Substituted Anilines

	Previous Investigation			Present Investigation	
	μ_B	(Temp.)	μ_D	μ_B	μ_D
(a) m-Bromoaniline	2.65	(20°)	—	2.68	3.01
(a) p-Bromoaniline	2.99	(20°)	—	3.01	3.36
(b) p-Bromoaniline	2.87	(23°)	—	3.01	3.36
(c) p-Bromoaniline	2.85	(25°)	—	3.01	3.36
(a) m-Nitroaniline	4.94	(40°)	—	4.91	5.245
(d) m-Nitroaniline	5.00	(30°)	5.22	4.91	5.245
(a) p-Nitroaniline	6.4	(70°)	—	6.22	6.82
(e) p-Nitroaniline	—	(30°)	6.68	6.22	6.82
(c) p-Nitroaniline	6.32	(25°)	—	6.22	6.82
(f) p-Nitroaniline	6.17	(25°)	6.81	6.22	6.82
(f) 2:4-Dinitroaniline	—	(25°)	6.48	5.87	6.53
(f) 3:5-Dinitroaniline	—	(25°)	5.91	5.47	5.93
(f) 2:4:6-Trinitroaniline	—	(25°)	3.25	2.90	3.30

(a) Tiganik (4); (b) Bergmann and Tschudnovsky (5);

(c) Le Fèvre and Le Fèvre (6); (d) Davis, Bridge and Svirbely (7);

(e) Kumler and Porter (8); (f) Wassiliew and Syrkin (9).

Wassiliew and Syrkin have measured the dipole moments of a number of the compounds studied here. No extensive comparison of the two sets of results is possible as only the final figures for the moments of the compounds are available from their work. In the case of p-nitroaniline in benzene and of 2:4-dinitroaniline and 2:4:6-trinitroaniline in dioxan Wassiliew and Syrkin's results are 0.05D higher than those found here whereas their figures for p-nitroaniline and 3:5-dinitroaniline in dioxan are, respectively, only 0.01 and 0.02D higher than the values obtained in this investigation.

Tiganik's values for the dipole moments of m- and p-bromoaniline in benzene at 20° are 0.03 and 0.02D lower than those found here, whilst his figure for m-nitroaniline in benzene at 40° is 0.03D higher.

As the nitro-anilines are only very sparingly soluble in benzene, in several cases there was no detectable change in the refractive indices of the solutions over the whole of the concentration range studied. In all the other cases where the concentration range was slightly greater only a rough estimation of the molecular refraction could be obtained experimentally as the shift in refractive index was small and the solutions of the nitro-anilines were intensely coloured. Therefore, in this work, the values of the molecular refractions of the nitro-anilines in benzene solution have been calculated from the bond refractions found by Vogel (10).

In the case of the bromoanilines in benzene it is possible to detect a reasonable change in the refractive indices of the solutions. The molecular refractions calculated from these readings are in good agreement with those calculated from Vogel's bond refractions. Hence, it seems reasonable to calculate the molecular refractions of the nitro-anilines from Vogel's figures. Table II summarises the molecular refractions for a number of substituted anilines found by these two methods.

TABLE II

Molecular Refractions of Substituted Anilines

	Experimental	Calculated
(a) p-Bromoaniline	38.4	38.4
(a) m-Bromoaniline	38.6	38.4
(a) 2:4-Dibromoaniline	44.8	46.2
(a) 3:5-Dibromoaniline	46.0	46.2
(b) 2:4:6-Tribromoaniline	55.5	54.0
(a) 2-Methyl-4-nitroaniline	42.0	42.0
(b) p-Chloroaniline	35.8	35.5
(c) Mesidine	45.0	45.3
(c) Aminodurene	49.6	50.2

(a) Present investigation; (b) Few and Smith (2);

(c) Smith (3).

The values of the refractions used in these calculations were:

$C_6H_6 = 26.2$; $C_6H_5CH_3 = 31.1$; $C_6H_5NH_2 = 30.6$; $C_6H_5Br = 34.0$;

$C_6H_5NO_2 = 32.7$; $C_6H_5Cl = 31.1$.

Section II

Factors influencing the Dipole Moments of Poly-substituted Benzenes

In 1926, J.J. Thomson (11) suggested that the dipole moments of molecules should be the resultants of the vector summation of the characteristic atomic, bond and group moments. It might be expected that the moments of the disubstituted benzenes, for instance, should be calculable by the vector law, which leads to the conditions that

for ortho substituents $\mu = \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2}$

for meta substituents $\mu = \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2}$

for para substituents $\mu = \mu_1 - \mu_2$

where μ_1 and μ_2 are the group moments of the two substituents.

So far as p-disubstituents are concerned this expectation is fulfilled by the halogeno-, cyano- and nitro-groups. Many apparent anomalies arise when the vector theory is applied to the calculation of the dipole moments of aromatic compounds. If the electric moments associated with chemical bonds were constant quantities and dependent only on the difference between the electro-negativities of the atoms bonded, for example, then the dipole moments of the halogenobenzenes, nitrobenzene, aniline, etc. should be equal to those of their aliphatic analogues, but this is not true. Therefore, there must be some other factor operating in these cases.

The various mechanisms by which the introduction of a substituent group may cause a displacement of electrons in the remainder of the molecule are reviewed in this section. These are generally classified according to their origin into inductive and mesomeric effects.

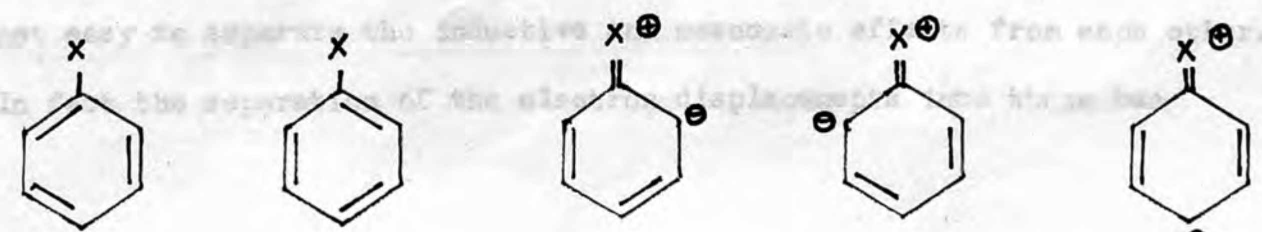
Inductive Effect

All matter in the vicinity of a dipole tends to become polarised. Consequently, a dipole in one bond or group has a polarising effect on the remainder of the molecule. The presence of a dipole in a group in a benzene ring will produce an induced moment in the benzene ring. This will generally be greater than that produced in an alkyl group owing to the greater polarisability of the benzene ring. If this were the only factor concerned, the moments of the aromatic compounds would be expected to be rather greater than those of the aliphatic compounds. As this is true in some cases but not in others there must also be some other factor operating.

Mesomeric Effect

The aromatic ring may be written formally as a conjugated system with alternate single and double bonds.

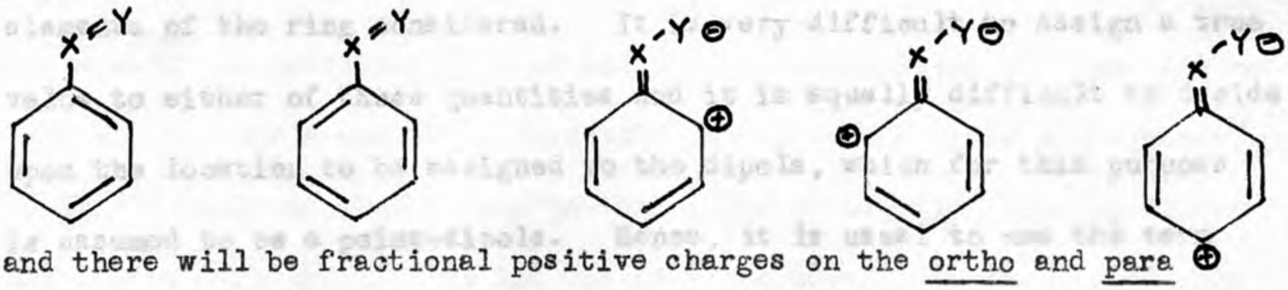
In substituted benzenes when an atom linked directly to the ring has an unshared pair of electrons in its valency shell they can be shared with the carbon atom to which it is attached. This leads to adjustments in the disposition of the electrons so that the structure has contributions from the five structures



The result is that there are fractional negative charges on the carbon atoms in the ortho and para positions in the ring.

If the dipole of substituent X is directed with its negative end away from the ring this mesomeric effect will produce a component of the moment which will oppose the primary moment. Therefore, the moment of the aromatic compound will tend to be less than that of its aliphatic analogue, in this case.

On the other hand, if the atom X, linked to a carbon atom of the ring, is itself also linked to an atom Y by a double or triple bond there is the possibility of a mesomeric effect in the reverse sense. The overall structure will be made up from contributions from the five structures



and there will be fractional positive charges on the ortho and para carbon atoms.

In this case, if the group XY has a moment directed away from the ring the mesomeric effect is in the same sense as this moment and the moment of the aromatic compound will tend to be greater than that of its aliphatic analogue.

It is difficult to evaluate the actual extent to which the differences between the dipole moments of aromatic compounds and their aliphatic analogues are dependent on the mesomeric effect because it is not easy to separate the inductive and mesomeric effects from each other. In fact the separation of the electron displacements into these two effects is rather arbitrary and dependent upon the devices used to express diagrammatically the electron displacements which occur. On the molecular orbital theory, this distinction disappears.

Sutton (12) tried to overcome this difficulty by comparing the moments of substituted benzenes with those of the corresponding tert. butyl compounds. This method does not make full allowance for the fact that the polarisability of benzene is non-isotropic owing to the ease of polarisation of the π-electrons in the plane of the rings. On the other hand, Groves and Sugden (13) attempted a more complete analysis of the inductive effect but, in order to carry this out, it was necessary to make assumptions regarding the dielectric constant of the polarisable material of the ring and also of the medium between the dipole and the elements of the ring considered. It is very difficult to assign a true value to either of these quantities and it is equally difficult to decide upon the location to be assigned to the dipole, which for this purpose is assumed to be a point-dipole. Hence, it is usual to use the term "mesomeric moment" in the sense originally defined by Sutton, i.e. as the vector difference between the moment of an aromatic molecule and that of its aliphatic (preferably tert. butyl) analogue.

All these effects become much more complex when more than one substituent is introduced into the aromatic ring. As each of these effects, which may influence the dipole moment of the compound, will be mentioned in the discussion of the experimental results, they will be summarised briefly here.

Mutual Inductive Effects of Substituent Groups

The dipoles of each substituent group will tend to displace the electrons of the other groups present, i.e. produce induced dipoles in them. Provided that the substituents are some distance apart classical electrostatic theory may be used to calculate rough values of these induced moments. The theory of Smallwood and Herzfeld (14), which has been developed by Frank (15) and by Hampson and Weissberger (16) shows that the components of the induced moment along and at right angles to the axis of the inducing dipole are given by

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

$$\mu_y = \mu\alpha\frac{\epsilon_a + 2}{3\epsilon_b r^3} . 3\sin\theta\cos\theta$$

where α is the polarisability of the polarisable system, r is the distance between the dipole and the polarisable centre of the other substituent, θ is the angle of inclination to the dipole of the line joining these points, and ϵ_a and ϵ_b are the dielectric constants of the polarisable material and the medium intervening between this and the dipole, respectively.

The main difficulties which arise in applying this theory are the same as those encountered in Groves and Sugden's analyses, viz. the location to be assumed for the point dipole and the values to be used for the dielectric constants involved. As no contributions from molecular rotation should be included in the latter their values have been taken here as approximately equal to the dielectric constant of benzene (2.27). Although it seems a rather sweeping assumption to apply these macroscopic considerations to such a problem it has been shown that it does explain satisfactorily the observed moments of such compounds as the mononitro- and monohalogeno- diphenyls (17).

The calculation of the order of magnitude of the mutual inductive effects of two polar groups upon one another may be illustrated by evaluating it for p-bromoaniline. For this purpose both the locations of the point dipoles and the polarisable centres of the substituent groups can be assumed to be near the centres of the nitrogen and bromine atoms, respectively. The N-C, C_{ar} - C_{ar} and C-Br inter-nuclear distances may be taken as 1.45, 1.40, and 1.88A, respectively. By comparison of the molecular refractions of benzene, bromobenzene, and aniline it is deduced that the polarisabilities of the amino group and of the bromine atom exceed that of the hydrogen atom which they replace by 1.80 and 3.05×10^{-24} c.c., respectively. Hence the induced moment, in the direction of the C-Br dipole, produced in the amino group as a result of the presence of the bromine atom is

$$\mu_x = \frac{1.56 \times 1.8 \times 10^{-24} \times 4.27}{3 \times 2.27 \times 6.13^3 \times 10^{-24}} \times 2 = 0.015\underline{\underline{D}}.$$

Similarly the components of the induced moments produced in the bromine atom as a result of the presence of the amino group are

(a) along the axis of the NH_2 dipole

$$\mu_x = \frac{1.53 \times 3.05 \times 10^{-24} \times 4.27}{3 \times 2.27 \times 6.13^3 \times 10^{-24}} (3 \cos 48^\circ - 1) = 0.004\underline{\underline{D}}.$$

(b) at right angles to the NH_2 dipole

$$\mu_y = \frac{1.53 \times 3.05 \times 10^{-24} \times 4.27}{3 \times 2.27 \times 6.13^3 \times 10^{-24}} (3 \sin 48^\circ \cos 48^\circ) = 0.019\underline{\underline{D}}.$$

Now the resultant dipole of the molecule will be inclined at about 24° to both the C-Br and NH$_2$ dipole so the component of the induced moment along the axis of the resultant dipole is

$$0.015 \cos 24^\circ + 0.004 \cos 24^\circ + 0.019 \cos 66^\circ = 0.025\text{D}$$

Owing to the high polarisability of the bromine atom this is the compound which has the highest relative moment arising from mutual induction between the groups. This value, however, is small as compared with the observed enhancement of dipole moment when two groups are *para* to one another. Hence, it does not account for all the difference observed but must be borne in mind when interpreting small differences between calculated and experimental moments.

Other Modifications to Inductive Effect with Two Substituents

Although this method is reasonably satisfactory in conjunction with vector summation in explaining the observed moments of the *p*-halogenotoluenes, for instance, it is less convincing when applied to molecules containing two groups which are *ortho* or *meta* to one another. If the bonds linking the ring carbon atoms to the substituent groups are directed radially from the centre of the ring, the moment of *o*-dinitro- or an *o*-dihalogenobenzene would be expected to be $\sqrt{3}$ times the moment of the corresponding monosubstituted benzene. As shown by the figures in Table III, the observed values are all much less than this. The "effective moments" of the substituents, which are $1/\sqrt{3}$ times the observed moments of the disubstituted compounds are between 8 and 24% lower than in the monosubstituted benzenes.

TABLE III

Moments of o-Disubstituted Benzenes in Benzene Solution

X	$\mu(\text{PhX})$	$\mu(\underline{o}\text{-}C_6H_4X_2)$	$\mu(X_{\text{eff.}})$	Ratio $[\mu(\text{eff.}):\mu(\text{PhX})]$
NO_2	4.01	5.98	3.45	0.90
F	1.48	2.38	1.37	0.92
Cl	1.58	2.33	1.35	0.89
Br	1.56	2.11	1.22	0.83
I	1.40	1.70	0.98	0.76

An increase of the angle between the moment vectors of the two groups cannot be ruled out as a contributory cause of this effect but in-plane displacement of the groups with respect to one another is likely to be much too small to account for the magnitude of the effect observed. For example, the angle between the C-I moment vectors in o-di-iodobenzene would have to be increased from 60° to 105° to account for the moment observed. Out-of-plane bending of the C-X bonds has also been suggested by some electron diffraction measurements. This is unlikely to be great since, if this were the case, it would be expected that the difference between the molecular polarisation and molecular refraction of 1:3:5-tribromo-2:4:6-trinitrobenzene would be much greater than the sum of the corresponding differences for sym-tribromobenzene and sym-trinitrobenzene. This is not true. The improbability of appreciable bending of the bonds is also indicated by the fact that the dipole moments of 2:4:6-tribromo-nitro-benzene and 2:4:6-tribromo-1:3-dinitrobenzene are almost exactly equal (18).

Also, in the absence of adequate data for the dipole moments in the vapour state the solvent effect cannot be ruled out as contributing to the observed difference, but this is improbable, as on general grounds there is no reason why o-dinitrobenzene should show a greater negative solvent effect than nitrobenzene. In m-dinitrobenzene the solvent effect would be expected to be less than in nitrobenzene, as the main components of the induced moments in the solvent molecules will not be directed along the axis of the resultant dipole.

The major effect must arise, therefore, from inductive or mesomeric effects. Smallwood and Herzfeld attributed the whole to the mutual inductive effects of the substituent groups and showed by calculations that the observed moments could be explained roughly on these grounds. In their calculations, however, they made the doubtful assumption that the dielectric constant of the medium between each dipole and the polarisable centre of the centre group is unity. As the distances involved are so short the calculated effect is very critically dependent on the locations assumed for the dipole and the polarisable centre. Reasonable assumptions for these when used in conjunction with a value of 2.27 for the dielectric constants involved lead to calculated depressions of the effective moment of each group which are only about one-third of the observed depressions.

That the whole of this "ortho-effect" is not due to simple induction of moments in each substituent by the dipole of the other is also suggested by the moments of m-disubstituted benzenes. If the simple vector additivity law held their moments would be expected to be equal to those of the corresponding mono-substituted benzenes. The observed values, however, are lower in each case.

TABLE IV

Dipole Moments of m-Disubstituted Benzenes in Benzene

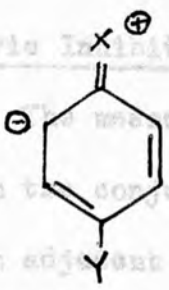
X	$\mu(PhX)$	$\mu(\underline{m}\text{-}C_6H_4X_2)$	Ratio
NO_2	4.01	3.82	0.956
Cl	1.58	1.49	0.943
Br	1.56	1.49	0.954
I	1.40	1.27	0.936

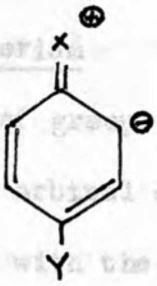
Owing to the fact that the line joining the polarisable centre of one group to the dipole of the other is inclined at about 60° to the axis of this dipole, the moments which are induced at each substituent by the dipole of the other have only a small resultant acting along the axis of the molecular dipole moment. If the dielectric constant of the intervening material is taken as 2.27, this effect accounts for a moment decrease of only 0.02D. in m-dinitrobenzene and about 0.01D. in the halogenobenzenes or only about 10% of the observed decreases. Even Smallwood and Herzfeld's assumption that this dielectric constant is unity would account for decreases of only about 0.05D. and 0.03D. respectively. It is evident, therefore, that another factor is operating here. This cannot be a decrease in the mesomeric effect of each substituent through the presence of the other, since such a decrease would account for the lower moment of m-dinitrobenzene but would be expected to give rise to increased moments in the m-dihalogenobenzenes. The observed effect, therefore, must rather be associated with a non-additivity of the inductive effects of the substituent groups. This is to be expected since the inductive effect is propagated chain-wise through the polarisation of the electrons of each C-C bond, and the introduction of a second substituent interferes with this propagation through the carbon atom to which it is linked.

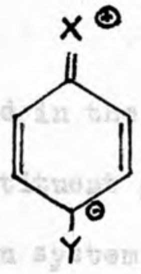
Interaction of Mesomeric Effects

The dipole moments of the p-halogeno-, p-nitro- and p-cyanotoluenes in benzene are all about 0.3 to 0.4D. greater than the values for the corresponding derivatives of benzene. As the induced moments produced in each substituent by the other should be small and the dipole moment of toluene is about 0.37D. with the positive end of the dipole directed away from the ring, the vector law appears to hold fairly well in these compounds. Therefore, it seems reasonable to assume that the vector law is obeyed for other p-substituted toluenes in which the dipole axis of the substituent group is not directed along the axis of the bond linking it to the ring carbon atom. This has been assumed in this work in calculating the angle of inclination of the dipole of the amino-group.

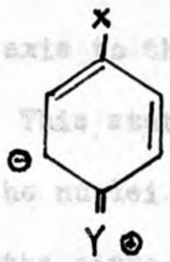
When two different o-p-directing groups, other than methyl, are in positions para to one another, the resulting molecule frequently has a dipole moment which differs appreciably from the value calculated by the vector summation method. In such cases it can reasonably be assumed that there is an interaction between both the inductive and the mesomeric effects of the two groupings. Thus for substituents X and Y, the mesomeric effect of X will tend to give contributions to the state of the molecule from structures such as

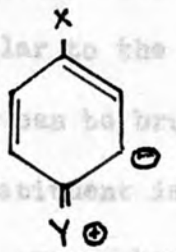


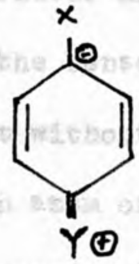




whilst the mesomeric effect of Y will lead to contributions from structures such as

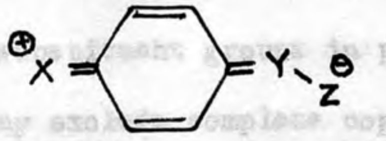






The characteristics of the groups X and Y will govern the predominating structure.

When a m-directing group is substituted in the position para to an o-p-directing group, however, the contributing resonance structures become much more important than with either substituent separately. This is reflected in the large increase in the mesomeric moment of the compound. In these compounds the mesomeric effects of each group tend to set up similar electron distributions in the ionic resonance structures, which are thereby stabilised, as in



,

where X is an o-p-directing group and YZ is a m-directing group. The interaction moment is as great as 1.48D. in the case of p-nitrodimethylaniline.

Steric Inhibition of Mesomerism

The mesomeric effect of groups substituted in the benzene ring arises from the conjugation of an orbital of the substituent group, or of the atom adjacent to the ring, with the π-electron system of the ring. If this adjacent atom is in the first short period, the atomic orbital involved must have considerable p-character. Its overlap with the ring orbitals will increase together with its p-character and the approach of its axis to the perpendicular to the plane of the benzene ring.

This state of affairs can be brought about without any displacement of the nuclei when the substituent is a halogen atom or a cyano-group. For the nitro- or aldehyde group, however, the conjugation necessitates the plane of the substituent group being drawn into or near to the plane of the ring, and hence such structures will be preferred. With amino-, methylamino-, dimethylamino-, hydroxy, and methoxy groups, two configurational changes can be distinguished. In the first place, there will be a tendency towards trigonal hybridisation of the orbitals of the atom adjacent to the ring so that the p-character of the lone-pair orbital will be increased. Secondly, in order to permit this orbital to conjugate with the ring system, the other atoms linked to the nitrogen or oxygen atom will tend to be drawn into or near to the plane of the ring.

The presence of substituent groups in positions <u>ortho</u> to the group under consideration may exclude complete coplanarity on steric grounds so that even if some conjugation with the ring is possible the mesomeric effect should be less than in the absence of the <u>ortho</u> substituents.

On this basis, changes in the "mesomeric moment", in the sense defined by Sutton, when obstructive groups are introduced in the ring, have frequently been used as evidence of the inhibition of mesomerism. The most convincing examples have been the comparisons of the dipole moments of nitromesitylene, 3.67D. (19), and nitrodurene, 3.62D. (20), with that of nitrobenzene, 4.01D., and of the moments of dimethyl-mesidine, 1.03D. (21), and of 2:4:6-tribromo-dimethylaniline, 1.02D. (2), with that of dimethylaniline, 1.58D.

The fact that the moments of the two tri-substituted dimethylanilines are almost equal and are not very different from the moment of trimethylamine, 0.86D., suggests that in these compounds the mesomeric effect of the dimethylamino-group is almost entirely suppressed. For the two nitro-compounds, on the other hand, the obstructing groups are methyl groups in both cases, so a similarity in the inhibition would be expected: here the observed moments are still much higher than for the aliphatic analogue so that it is probable that mesomerism is by no means completely inhibited. This view is supported by the observation that the dipole moment of nitroaminodurene, 4.98D., exceeds the algebraic sum of the moments of nitrodurene and aminodurene, indicating that even in durene compounds there is some interaction between the groups in positions para to one another (21).

In other cases where steric inhibition of mesomerism has been inferred from dipole moment data the position is less clear as the results with similar groups of compounds sometimes appear to be contradictory. For instance, the dipole moments of aminodurene and of mesidine, 1.45D. (3), are less than the moment of aniline, 1.53D., whereas the moment of 2:4:6-tribromoaniline, 1.73D. (2), is appreciably greater. If the lower values of the former compounds are attributable to steric inhibition of resonance, the steric effect of a methyl group would appear to be greater than that of a bromine atom. On the other hand, with the phenolic groups, the moments of durenol, 1.68D. (22), 2:4:6-trichlorophenol, 1.62D., and 2:4:6-tribromophenol, 1.56D. (23), are all greater than the value for phenol, 1.45D, and nearer to the moment of alcohol, 1.69D., indicating that the mesomeric effect is repressed in all cases.

From the discussion of the interaction of the inductive effects in previous sections it is evident that it is rather dangerous to draw definite conclusions regarding the enhancement or inhibition of mesomeric effects when substituents are present in positions meta or especially ortho to one another. Fortunately, however, the present work taken in conjunction with previous results suggests that there is a relationship between the mesomeric effect in aromatic amines and the difference between the apparent dipole moments in benzene and dioxan. Hence such data may be used to reinforce arguments regarding the extent of the mesomeric effect when the direct measurements on benzene solution lead to ambiguous conclusions.

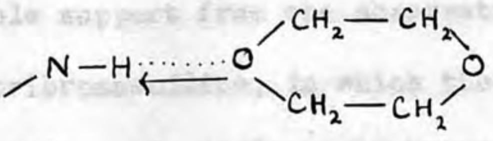
Section III

The Effect on the Apparent Moment of an Amine of using Dioxan as the Solvent

In 1934, Higasi (24) observed that the apparent dipole moment of aniline was 1.67D. in ether although it was only 1.53D. in benzene. In view of the polar nature of the ether molecule this did not appear to be abnormal. In 1941, however, Halverstadt and Kumler (25) found that the moments of aniline and xenylamine in dioxan solution were 1.90 and 2.07D, respectively. Although the figures they obtained later (26) from the same data, but using their method of extrapolation were slightly lower (1.73 and 2.02D., respectively) the differences between the values in the two solvents were still far greater than those usually associated with a solvent effect. Pointing out that Kumler and Porter (8) had observed the moment of p-nitroaniline in dioxan to be 6.68D., whereas Le Fèvre and Le Fèvre (6) had found the value in benzene solution to be 6.32D., Halverstadt and Kumler commented that these were interesting abnormalities, but they offered no explanation.

In the meantime Wassiliew and Syrkin (9) had shown that the apparent dipole moments of aniline, p-nitroaniline and β-naphthylamine were all higher in dioxan than in benzene solution. They attributed this to hydrogen-bonding between the amino-hydrogen atoms and the oxygen atoms of the dioxan molecules. Anziolotti and Curran (27) and Curran (28) also explained the fact that the apparent moments of certain phenols are higher in dioxan than in benzene in a similar manner.

Since Few and Smith (1) found that the moment of methylaniline is also appreciably greater in dioxan than in benzene whereas there is only a small difference between the values for dimethylaniline in the two solvents, there is little doubt that this interpretation is correct. Dioxan itself is probably a non-polar molecule; the difference between its molecular polarisation (26.06 c.c.) and molecular refraction (21.70 c.c.) arising from a rather high atom (vibration) polarisation associated with the presence of the two opposed highly polar ether groupings. Hence the mere fact that an amine molecule and a dioxan molecule come together is not sufficient to account for the observed increase of polarisation, as the dipole moment of the complex would then be the same as that of the amine molecule itself, and its molecular polarisation the sum of the molecular polarisations of the amine and dioxan. It must be inferred, therefore, that there is a displacement of charge associated with the complex formation. This would be expected to involve displacement of electron density from the oxygen atom of a dioxan molecule towards the hydrogen atom to which it is bridge-bonded and hence effectively add a component to the moment along the H-N bond axis:



There is some evidence, however, which suggests that this direct component is small. In the first place, the results obtained with solutions containing n-butyl alcohol and pyridine, in which system similar hydrogen bond formation occurs, indicate that the effective dipole moment of the complex is almost equal to the vector sum of the moments of the alcohol and pyridine molecules (29) whilst that of the complex between n-butyl alcohol and triethylamine, which is formed even more readily, is only slightly above the value of the corresponding vector sum (30). These results refer to the actual moments of the complexes and not to the mean square moment of the molecules present, some of which are complex, as in the measurements on amines, so it seems unlikely that the whole effect observed with the latter arises simply from electron displacements in the N-H.....O system. Secondly, it was found by Few and Smith (2) that the apparent moments of n- and tert.-butylamines were almost the same in dioxan as in benzene. This may mean that there is no hydrogen-bonding between these molecules and dioxan but it seems safer to interpret it as indicating that any hydrogen bonding which occurs does not give rise to an increase in dielectric polarisation.

It seems logical to suppose, therefore, that the main increase in apparent polarisation arises through secondary electron displacements in the amine molecule, which can occur readily with aniline but less readily with aliphatic amines, through the mesomeric mechanism. This view received considerable support from the observation (3) that whilst for aniline and 2:4:6-tribromoaniline, in which there seemed to be no steric inhibition of mesomerism, the differences between the apparent moments in benzene and in dioxan ($\Delta\mu$) are 0.24 and 0.27D., respectively, $\Delta\mu$ is only 0.12D. for both mesidine and aminodurene, where there appears to be such inhibition. Also, $\Delta\mu$ is 0.18D. for methylaniline but for methylmesidine, where the mesomeric effect would be expected to be almost completely repressed, $\Delta\mu$ is only 0.04D., which is almost the same as it is for dimethylaniline where this type of hydrogen-bonding is impossible. Further, for p-nitroaniline, in which the mesomeric effect is much greater than in aniline itself $\Delta\mu$ had been found to be very much greater still and, hence, there appears to be a complete parallelism between the $\Delta\mu$ values and the possibility of mesomeric electron displacement in the amine molecule.

The magnitudes of the observed $\Delta\mu$ values are evidently dependent on two factors:

(a) the extent of association complex formation, and

(b) the increase in the dipole moment of the molecule accompanying such association.

There is, however, good reason to believe that these two factors will show parallel changes, since withdrawal of electron density towards the aromatic ring is likely to tend to stabilise the hydrogen bond to the dioxan molecule. From studies of various systems in which hydrogen-bonding can occur, Hulett, Pegg and Sutton (31) have observed a fairly linear relationship between K, the association constant, and the increase in the moment above that expected from vector additivity. Hence, for the amines it seems fairly certain that an increased $\Delta\mu$ value indicates both an increased tendency for hydrogen-bond complex formation and an increased electronic displacement in the molecules resulting from such bonding.

One of the objects of the present work was to investigate the validity of this view and, if it proved to be justified, to utilise the

$\Delta\mu$ values in interpreting dipole moment data in terms of inductive and mesomeric displacements. In particular it was intended to use these values in checking conclusions which were drawn from consideration of the results obtained for benzene solutions.

Calculation of 'Mesomeric' Moments

The case of the vector analysis of substituted anilines is complicated by the fact that the amino-group is not coplanar with the benzene ring. It is necessary to make some assumption about the direction of the effective moment vector in aniline before a vector analysis of the observed values of the moments of these compounds may be attempted. Marsden and Sutton (52) calculated this angle using a number of compounds but obtained very varied results.

The two methods that seem to give the most satisfactory results will be given here.

The angle of inclination of the aniline dipole to the plane of the benzene ring may be calculated from a comparison of the moments of *p*-phenylene-diamine and aniline. In this case it is necessary to make two assumptions; (a) that the effective moments of the amine are equal in the two compounds, and (b) that both amino-groups in *p*-phenylene-diamine undergo free and independent rotation.

If the first condition holds, the instantaneous value of the moment of a *p*-phenylene-diamine molecule should be given by

$$\mu = 2\mu_A \sin\theta \cos\phi/2$$

where θ is the angle of inclination to the C-N bond of the moment vector in aniline, ϕ is the angle between the planes containing the N-C bonds

Section IV

Calculation of 'Mesomeric' Moments

The case of the vector analysis of substituted anilines is complicated by the fact that the amino-group is not coplanar with the benzene ring. It is necessary to make some assumption about the direction of the effective moment vector in aniline before a vector analysis of the observed values of the moments of these compounds may be attempted. Marsden and Sutton (32) calculated this angle using a number of compounds but obtained very varied results.

The two methods that seem to give the most satisfactory results will be given here.

The angle of inclination of the aniline dipole to the plane of the benzene ring may be calculated from a comparison of the moments of p-phenylene-diamine and aniline. In this case it is necessary to make two assumptions; (a) that the effective moments of the amine are equal in the two compounds, and (b) that both amino-groups in p-phenylene-diamine undergo free and independent rotation.

If the first condition holds, the instantaneous value of the moment of a p-phenylene-diamine molecule should be given by

$$\mu = 2\mu_A \sin\theta \cos\phi/2$$

where θ is the angle of inclination to the C-N bond of the moment vector in aniline, ϕ is the angle between the planes containing the N-C bonds and the axes of the moments and μ_A is the dipole moment of aniline.

The quantity actually determined in making dipole moment measurements is P_μ which depends on the mean value of μ^2. Hence, if there is no preferred orientation and all values of ϕ between 0 and π are equally probable, the observed moment should be the root mean square value of the moments for all values of ϕ i.e. it should be given by:

$$\mu^2 = \frac{1}{\pi}\cdot\int_0^{\pi}(2\mu_A \sin\theta\cos\phi/2)^2 . d\phi$$

$$= 2\mu_A^2 \sin^2\theta$$

$$\therefore\ \mu = \sqrt{2}\ \mu_A \sin\theta$$

Tiganik (4) found that the moment of p-phenylene-diamine in benzene was 1.56D. whereas that of aniline was 1.52D. Substitution of these figures in the equation gives

$$\sin\theta = \frac{1.56}{\sqrt{2} \times 1.53}$$

and hence, $\theta = 42.5^\circ$ or 137.5°

The second method of deriving this angle involves a comparison of the moments of aniline and p-toluidine. The evidence of the relative values of the moments of p-nitrotoluene and nitrobenzene and of p-chlorotoluene and chlorobenzene indicates that the mesomeric effects of the nitro-group and the chlorine atom are not appreciably affected by introducing a methyl group in the para position.

Therefore, the effective moment in the amino-group is assumed to be the same in p-toluidine as in aniline. If this is true the following relationship should hold:

$$\mu^2_{p\text{-}T} = \mu^2_A + \mu^2_T \overset{-}{\oplus} 2\mu_A\mu_T \cos\theta$$

where μ_T and $\mu_{p\text{-}T}$ are the dipole moments of toluene and p-toluidine, respectively.

Using Tiganik's value of 1.31D. for the moment of p-toluidine,

$$1.31^2 = 1.52^2 + 0.39^2 \overset{-}{\oplus} 2 \times 1.52 \times 0.39 \times \cos\theta$$

$$\therefore \cos\theta = 0.6501$$

$$\text{and } \theta = 49.5^\circ$$

The agreement between the values obtained by these two methods is not perfect but is quite reasonable when the assumptions involved are considered, especially as the moment of the methyl group is so small. In determining the angle on which the calculation of the theoretical moments of the amines should be based, more weight was given to the value obtained from p-toluidine as the assumptions involved here seemed less serious. Thus, for the purpose of this investigation, it has been assumed that the aniline dipole is inclined to the plane of the benzene ring at an angle of 48°.

Calculation of "Theoretical" Moments
para and 3:5:Disubstituted Anilines

The moments of the substituents are directed along the C-N bond axis whilst the primary aniline moment is directed at an angle of 48° to this bond. The theoretical resultant moment of the p- or 3:5:disubstituted aniline is given by:

$$\mu^2 = \mu^2_S + \mu^2_A + 2\mu_S\mu_A \cos 48^\circ$$

where μ_S is the dipole moment of the substituted benzene.

The moments of the 3:5-disubstituted anilines may also be calculated from this equation replacing the moment of the mono-substituted benzene by that of the *meta*-disubstituted benzene. In the cases of nitro- and bromo-anilines the latter method gives slightly lower values than the former.

meta- and 2:4-Disubstituted Anilines

The moments of the substituents are directed at 60° to the C-N bond axis whilst the primary aniline moment makes an angle of 48° with this bond but is not necessarily coplanar with it.

Assuming free rotation of the amino-group, the component of the moment along the C-N bond, μ_x, is given by:

$$\mu_x = \tfrac{1}{2}\mu_s + \mu_A \cos 48^\circ$$

and $$\mu_y^2 = \left(\tfrac{\sqrt{3}}{2}\mu_s\right)^2 + \mu_A^2 \sin^2 48^\circ + 2\sqrt{3}\,\mu_s\mu_A \sin 48^\circ \cos\phi$$

where μ_y is the component of the moment at right angles to the C-N bond.

Therefore the mean value of this moment is given by:

$$\mu_y^2 = \tfrac{3}{4}\mu_s^2 + \mu_A^2 \sin^2 48^\circ + \frac{1}{\pi}\int_0^\pi 2\sqrt{3}\,\mu_s\mu_A \sin 48^\circ \cos\phi . d\phi$$

$$= \tfrac{3}{4}\mu_s^2 + \mu_A^2 \sin^2 48^\circ$$

$$\mu^2 = \mu_x^2 + \mu_y^2$$

$$\therefore \mu^2 = \mu_s^2 + \mu_A^2 + \mu_s\mu_A \cos 48^\circ$$

The theoretical moments of the 2:4-disubstituted benzenes may be calculated from this equation by substitution of the moments of either the mono- or *meta*-disubstituted benzenes.

The moments of the monomethylanilines may be evaluated in a similar manner but, in this case, it is assumed that the angle of inclination of the methylaniline dipole to the plane of the benzene ring is $38\frac{1}{2}^\circ$.

The theoretical and observed dipole moments of the substituted anilines are summarised in Table V. In these calculations the following moments have been used:

Aniline	1.53D.	Methylaniline	1.68D.
Nitrobenzene	4.01D.	m-Dinitrobenzene	3.83D.
Bromobenzene	1.56D.	m-Dibromobenzene	1.49D.

Calculation of the 'Mesomeric' Moments

For para and 3:5-disubstituted anilines the resultant moment (observed) is given by:

$$\mu^2 = (\mu_S + \mu_M)^2 + 2(\mu_S + \mu_M)\,\mu_A \cos 48^\circ + \mu_A^2$$

where μ_A is the mesomeric moment.

Similarly, the mesomeric moments of meta- and 2:4-disubstituted derivatives may be evaluated from the equation:

$$\mu^2 = (\mu_S + \mu_M)^2 + \mu_A^2 + \mu_A(\mu_S + \mu_M)\cos 48^\circ$$

TABLE V

Compound	μ (observed)	μ (calculated)		μ (mesomeric)	
		(a)	(b)	(a)	(b)
2:4-Dinitroaniline	5.87	4.75	4.58	1.17	1.35
2:4:6-Trinitroaniline	2.90	1.53		1.44	
m-Nitroaniline	4.91	4.75		0.17	
3:5-Dinitroaniline	5.47	5.16	4.99	0.32	0.50
p-Nitroaniline	6.22	5.16		1.08	
2:4-Dibromoaniline	2.67	2.53	2.47	0.175	0.25
2:4:6-Tribromoaniline	1.73	1.53		0.28	
m-Bromoaniline	2.68	2.53		0.19	
3:5-Dibromoaniline	3.05	2.83	2.76	0.25	0.32
p-Bromoaniline	3.01	2.83		0.20	
2:4-Dinitromethylaniline	6.33	4.91	4.75	1.53	1.71
p-Nitromethylaniline	6.84	5.41		1.44	
2-Methyl-4-nitroaniline	6.42	5.36		1.10	

Column (a) in both cases gives the moments calculated from the monosubstituted benzenes and column (b) those calculated from the disubstituted benzenes.

Section V

The Relationship between the "Dioxan Increment" and the Mesomeric Moment

The best test of the hypothesis that the difference, $\Delta\mu$, between the apparent moments of an amine in dioxan and in benzene is related to the mesomeric moment of the amine involves comparison of the data, from this work and elsewhere, for compounds in which the minimum of complications are likely to arise. It has been pointed out that for compounds such as p-chlorotoluene, where there appears to be no appreciable change in the mesomeric effect of either substituent as a result of the presence of the other, the moments can be calculated fairly accurately by vector addition of the group moments. Therefore, it is reasonable to interpret the difference between the observed and calculated moments of other p-substituted compounds as interaction moments.

TABLE VI

	Ref.	μ_B	μ_D	$\mu_{calc.}$	$\mu_{int.}$	$\Delta\mu$
Aniline	(3)	1.53	1.77	1.53	0.00	0.24
p-Chloroaniline	(2)	3.01	3.39	2.85	0.18	0.38
p-Bromoaniline	(*)	3.01	3.36	2.83	0.20	0.35
p-Nitroaniline	(*)	6.22	6.82	5.16	1.08	0.60
p-Aminobenzonitrile	(33)	5.96	6.46	5.18	0.80	0.50
p-Xenylamine	(26)	1.74	2.02	1.53	0.29	0.28
β-Naphthylamine	(9)	1.77	2.10	1.53	0.33	0.33
Aminodurene	(3)	1.45	1.57	1.53	-0.12	0.12
Mesidine	(3)	1.45	1.57	1.53	-0.12	0.12
n-Butylamine	(3)	1.34	1.33	—	—	-0.01
2-Methyl-4-nitroaniline	(*)	6.42	7.00	5.36	1.10	0.58
Methylaniline	(3)	1.68	1.86	1.68	0.00	0.18
p-Nitromethylaniline	(*)	6.84	7.12	5.41	1.44	0.28
Methylmesidine	(3)	1.22	1.26	1.68	-0.46	0.04

* This work

The relevant figures for p-substituted anilines are collected in the first part of Table VI, where $\mu_{int.}$ indicates the additional moment above the value calculated from the moments of aniline and the appropriate mono-substituted benzene. The additional moment is assumed to act along the axis of the dipole of the latter. This interaction moment will actually include any increased mesomeric moments of

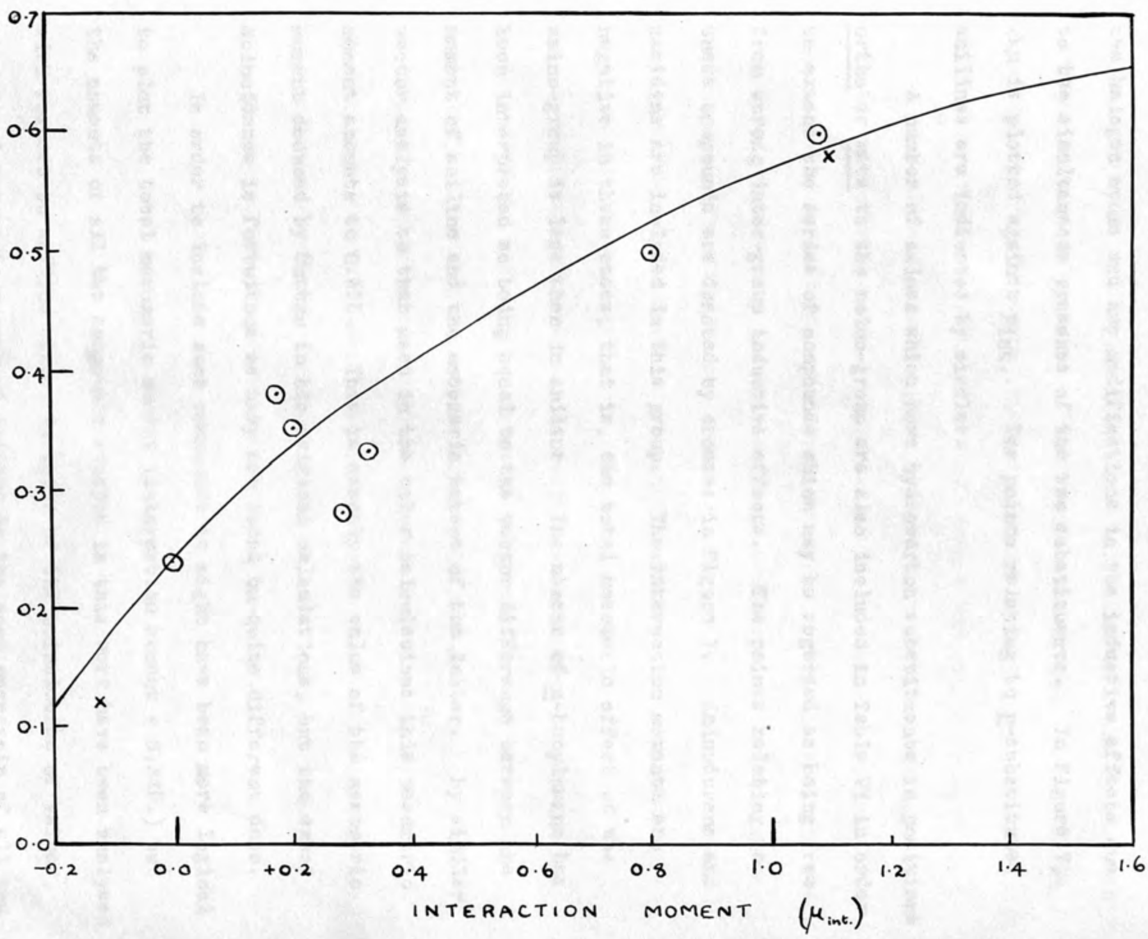

DIOXAN INCREMENT (Δμ)
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
-0·2
0·0
+0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
INTERACTION MOMENT ($\mu_{int.}$)

FIGURE 7

the amino-, nitro- or cyano- groups, any decreased mesomeric effects of the halogen atoms and any modifications in the inductive effects due to the simultaneous presence of the two substituents. In Figure 7, $\Delta\mu$ is plotted against $\mu_{int.}$. The points relating to p-substituted anilines are indicated by circles.

A number of amines which have hydrocarbon substituents in positions ortho or meta to the amino-group are also included in Table VI in order to extend the series of compounds which may be regarded as being free from strong inter-group inductive effects. The points relating to these compounds are denoted by crosses in Figure 7. Aminodurene and mesidine are included in this group. The interaction moments are negative in these cases, that is, the total mesomeric effect of the amino-group is less than in aniline. The moment of n-butylamine has been interpreted as being equal to the vector difference between the moment of aniline and the mesomeric moment of the latter. By similar vector analysis to that used in the other calculations this mesomeric moment amounts to 0.32D. This is exactly the value of the mesomeric moment deduced by Sutton in his original calculations, but the exact coincidence is fortuitous as they are based on quite different data.

In order to include such compounds it might have been more logical to plot the total mesomeric moment (interaction moment + 0.32D.) but the moments of all the compounds studied in this work have been analysed with respect to aniline since, in spite of the coincidence of values, the actual mesomeric moment of aniline is the most uncertain of all the quantities considered. Indeed, although the point for n-butylamine lies on the same curve as the other points shown on Figure 7, the true value of this is open to question as it indicates that the dipole axis in this compound is inclined at 58° to the axis of the C-N bond. This appears, on general grounds, to be too small an angle, whilst the alternative value of 122°, which would mean a "mesomeric moment" of 1.73D. in aniline, seems too great as the inclination of the dipole axis to the C-N bond would be expected to be less than the tetrahedral angle. This anomaly may arise from the tacit assumption that the sum of the H-N bond moments and the lone-pair moments remains the same in aniline as in the butylamines. Such an assumption is far less serious when comparing substituted anilines with aniline, as the changes are likely to be much smaller.

Even ignoring the butylamine point the variation of $\Delta\mu$ with $\mu_{int.}$ is very striking and a smooth curve can be drawn through the points. A similar relationship appears to exist between $\Delta\mu$ and $\mu_{int.}$ for the corresponding substituted methylanilines but here the available data are much more scanty. Also, the $\Delta\mu$ values are much smaller than for the aniline derivatives. This is to be expected as there is only one hydrogen atom available for bonding to the dioxan molecule.

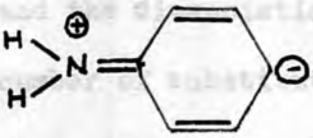
Section VI

Correlation with Dissociation Constant Data

An important consequence of the inductive and mesomeric effects in the aromatic ring is their influence on the acid or base strengths of the substituent groups. These are conveniently expressed in pK_a values ($pK_a = - \log K_a$). Thus phenol ($pK_a = 9.95$) is a much stronger acid than cyclohexanol ($pK_a = 18$). This may be explained through the circumstance that in the phenol ion both the inductive effect of the ~~positive~~ negative charge on the oxygen atom and the mesomeric effect into the ring, which arises from the presence of unshared electron pairs on the oxygen atom, tend to decrease the effective charge at the oxygen atom. Hence there is a tendency for the basic character of the phenol ion to be decreased. A similar mesomeric effect will occur in the phenol molecule. This will decrease the attraction of the oxygen atom for the proton of the O-H group. In cyclohexanol, on the other hand, there is no mesomeric effect and in its ion there is only the 'classical' inductive effect since it lacks the important contribution of non-classical effects which arise through polarisation of the π-electrons of the benzene ring. Hence, in the presence of the proton acceptors there will be much less tendency for release of the proton by cyclohexanol than by phenol.

The fact that the relative difference between the pK_a values of cyclohexane carboxylic acid (4.90) and benzoic acid (4.20) is much less than that referred to above indicates that both inductive and mesomeric effects are of importance. In the benzoate ion the inductive effect tends to decrease the charge at the oxygen atoms but the mesomeric effect which operates out of the ring tends to increase it. The result is that benzoic acid is only a slightly stronger acid than cyclohexane carboxylic acid.

As far as the amines are concerned, the substituted ammonium ions become the analogues of the undissociated acid molecules and the free amines the analogues of the acidic ions. No mesomeric effect is possible in the anilinium ion as there are no unshared pairs of electrons. On the other hand, there is a tendency for inductive effects produced by the symmetrically disposed $\overset{\longleftarrow\!\!\!+}{\text{N-H}}$ dipoles to decrease the negative charge at the nitrogen atom and so make proton release easier than in ammonia or an aliphatic amine. In free aniline mesomeric effects also come into play to decrease this effective charge. In the limit, if the aniline molecule is assumed to have the extreme configuration,



the "lone-pair" electrons would be used in forming a double bond to the carbon atom of the ring, so rendering them unavailable for the acceptance of a proton. It can be inferred that as the extent to which such forms contribute to the actual state of the aniline molecules increases the availability of these electrons for anilinium ion formation decreases. As a result, aniline is a much weaker base than n-butylamine. Comparison of such basic strengths are most easily made in terms of the

pK_a values of the corresponding substituted ammonium ions, as their measurement usually involves the determination of hydrogen ion concentration. For aqueous solutions, however, the actual basic dissociation constant (equilibrium constant of the reaction $RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH'$) is given by $pK_b = 14 - pK_a$. For aniline pK_a is 4.58 whilst for n-butylamine it is 10.61.

From these arguments, the introduction into the aniline molecule of substituent groups, which modify the inductive and mesomeric effects of the amino-group, would be expected to produce profound effects on the basic strength of the amine. This effect should be parallel to the changes in mesomeric effect which are revealed by dipole moment measurements and in turn they should show some relationship to the difference between the moments in dioxan and benzene. A rather rough correlation of this type has been observed by Hulett, Pegg and Sutton (34) with the association constants of the hydrogen bonded complexes of substituted phenol with trimethylamine, the change in dipole moment attending this formation and the dissociation constants of the phenols.

The pK_a values of a number of substituted anilines are listed in Table VII, together with the values of the "increased mesomeric moment" derived previously and the values of $\Delta \mu$, the difference between the moments of the amine in dioxan and in benzene.

The results are not strictly comparable as some of the compounds have been studied in water and the others in various ethyl alcohol-water mixtures. The general trend of the results shows a parallelism, the greatest divergences from which occur when there is a group (particularly a nitro-group) present in the position ortho to the amino-group, when the pK_a values are lower than would be expected from dipole moment values.

TABLE VII

	μ_{mt}	$\Delta\mu$	pK_a
Aniline	0.00	0.24	4.58
m-Bromoaniline	0.19	0.33	3.51
p-Bromoaniline	0.20	0.35	3.91
p-Chloroaniline	0.18	0.38	3.81
3:5-Dibromoaniline	0.32	0.44	2.45
2:4-Dibromoaniline	0.18	0.34	2.15
2:4:6-Tribromoaniline	0.28	0.27	
m-Nitroaniline	0.17	0.34	2.45
p-Nitroaniline	1.08	0.62	1.11
3:5-Dinitroaniline	0.50	0.44	
2:4-Dinitroaniline	1.35	0.63	-4.38
2:4:6-Trinitroaniline	1.44	0.45	-9.29

With halogen substituents the problem is complicated by the fact that the inductive effect of a halogen atom in any position tends to cause a withdrawal of electrons from the nitrogen atom, whereas the mesomeric effect of a halogen atom in a position ortho or para to the amino-group leads to a positive charge on the carbon atom to which the latter is bonded and this will tend to give a positive charge on the nitrogen atom. The evidence from both dipole moment and dissociation constant data for p-halogenoanilines indicates that the inductive effect prevails, since the dipole moments are higher than would be expected by vector addition, the $\Delta\mu$ values are higher than for aniline and they are weaker bases than aniline.

o-Halogenoanilines have not been studied in this work as the very large inductive effects render the results difficult to interpret. There is little doubt that in these compounds as well as in the 2:4:6 trihalogenoanilines the inductive effect of the o-halogen atoms becomes very great but owing to the juxtaposition of the Br and NH_2 dipoles it becomes somewhat obscured in the overall dipole moments of the molecules.

With nitro-groups as substituents in any position the inductive effect tends to decrease the electron density at the amino-nitrogen atom and when the substituent is ortho or para to the amino-group the mesomeric effect will act in the same sense. The view that both these factors are of importance is supported by the fact that the pK_a value of p-nitroaniline is much lower than that of m-nitroaniline. In 2:4-dinitro- and 2:4:6-trinitroaniline the combined effects become very strong indeed. The whole problem may be complicated here by the formation of internal hydrogen bonds which will tend to draw the amino-hydrogen atoms into or near to the plane of the ring and hence make the amines very weak bases indeed.

Section VII

Discussion of the Individual Results

p-Bromoaniline

This work has confirmed that the dipole moment of p-bromoaniline, like that of p-chloroaniline, is greater than the value calculated from vector addition of the moments of aniline and the halogenobenzene by an amount much in excess of that to be anticipated from the mutual inductive effects of the groups on each other. As the mesomeric effects of the two substituents in this compound act in direct opposition, it is rather surprising, at first sight, that the interaction moment is positive, that is, in the sense corresponding to an increased mesomeric effect of the amino-group. However, the interaction moment is a very complex function, including all modifications of the inductive and mesomeric effects which arise from the simultaneous presence of the two substituents.

The bromine atom has a very strong inductive effect that tends to cause a withdrawal of electron density from the ring. This condition favours an increased mesomeric moment in the sense in which it is propagated by the amino-group with, probably, a consequential decrease in the mesomeric effect in the sense favoured by the presence of the bromine atom. 2:4:6-Tribromoaniline is readily obtained by the bromination of p-bromoaniline. This supports the view that the resulting electron distribution in p-bromoaniline is of the form visualised by these considerations. Under suitable conditions the amino-group can readily pass further electron density to the ring. This could account for the fact that there is a sharp rise in the apparent moment when benzene is replaced by dioxan as solvent. There is no reason to suppose that, in the complex formed between the dioxan and amine molecules, the moment of the O.....H-N system is very different from that in the complex with aniline. Also, evidence was obtained that a considerable proportion of the aniline molecules in dioxan solution are in the form of the complex. It is unlikely that the higher value of $\Delta\mu$ for p-bromoaniline arises entirely from an increase in the proportion of the molecules entering into complexes. The most probable explanation, therefore, is that the apparent increase in moment is mainly a result of the fact that, owing to the inductive effect of the bromine atom the further passage of electron density to the ring occurs more readily from the equilibrium state of p-bromoaniline than from that of aniline itself.

m-Bromoaniline

In m-bromoaniline the mesomeric effects of the two substituents both tend to produce excess electron density at the carbon atoms in positions 2, 4 and 6. On this account, it might be expected that the two substituents would be unable to exercise their full mesomeric effects. As in the case of p-bromoaniline, however, the overriding factor may be the withdrawal of electron density from the ring by the bromine atom, which will tend to increase the mesomeric effect of the amino-group. Consequently, the overall effect might be expected to be slightly less than, but not very different from that in p-bromoaniline. Evidence from the values of the interaction moment, as calculated from the moment in benzene solution, and of $\Delta\mu$ shows that this is the case. It may not be strictly true in this case to assume here, as has been done in calculating the figures in Table V, that the interaction moment acts along the N-C bond axis, but even if the opposite extreme is adopted and it is taken as being equal to the scalar difference between the observed and calculated moments the same arguments hold.

3:5-Dibromoaniline

Similar arguments will hold for this compound. In the absence of all interaction effects the moment should be equal to that of p-bromoaniline. Even the classical inductive effects of one substituent on the other should be approximately equal, but these are only small. The slightly higher moment of 3:5-dibromoaniline, however, indicates that its interaction moment is slightly greater than that of p-bromoaniline. The inductive effects of the two bromine atoms in m-dibromobenzene are less than that of the bromine atom in bromobenzene but it must be inferred that the withdrawal of electron density from the ring produced by the two bromine atoms is greater than that caused by one atom only. Hence, it is to be anticipated that the interaction moment in 3:5-dibromoaniline, produced by the increased mesomeric effect of the amine group and the consequent adjustment of both mesomeric and inductive effects of the bromine atoms will be greater than in m-bromoaniline but not double that found in the latter. The observed value of $\mu_{int.}$ is actually increased by about 70% as compared with that of m-bromoaniline, whilst the increase in $\Delta\mu$ is about 56% of the difference from aniline to m-bromoaniline. These figures are of the order that would be expected from the qualitative argument given above.

2:4-Dibromoaniline and 2:4:6-Tribromoaniline

In the absence of all interaction effects the dipole moment of 2:4-dibromoaniline should be equal to that of m-bromoaniline, and the moment of 2:4:6-tribromoaniline should be the same as that of aniline. Some complications may be expected, however, from the close proximity of the amino-group and the ortho-bromine atoms, similar to that arising in o-bromobenzene.

The observed moment of 2:4-dibromoaniline is actually not very different from that of m-bromoaniline and, when the bromine group moments are assumed to be equal to the moment of m-dibromobenzene, the interaction moment calculated from it is slightly higher than for either m- or p-bromoaniline but less than that for 3:5-dibromoaniline. The use of this effective value of the bromine group moment seems to be justified by the value found by Few and Smith for the moment of 2:4:6-tribromoaniline which leads to a slightly higher interaction moment: in fact the increments of 0.05 and 0.03D. on successive additions of bromine atoms in the positions ortho to the amino-groups are reasonable, but are less than the increment of 0.13D. which occurs when a second bromine atom is introduced in the position meta to the amino-group in m-bromoaniline. This suggests that there may be some steric interference with the mesomeric effect, although this may be relatively slight.

The $\Delta\mu$ values for 2:4-dibromoaniline and 2:4:6-tribromoaniline are less than for p-bromoaniline in spite of the greater interaction moments. Thus, in Figure 7, where the points for these compounds are inserted on the $\Delta\mu - \mu_{int.}$ plots the results lie below the curve for the p-substituted anilines. It seems, therefore, that although the presence of the bromine atoms in positions ortho to the amino-group have only a small effect on the mesomeric moment of this group, they may tend to prevent its association with dioxan or to prevent the N-H bond in the association complex from coming into or near to the plane of the ring. In the case of the 2:4-dibromoaniline this steric effect will apply to coplanarity on one side only but in 2:4:6-tribromoaniline it should apply to both sides. This would explain the fact that $\Delta\mu$ is slightly below the expected value in the dibromo-compound but considerably below it in the tribromoaniline. Nevertheless, the fact that $\Delta\mu$ for 2:4:6-tribromoaniline is slightly greater than for aniline itself suggests that interference between the bromine atoms and the dioxan molecule is not complete.

An alternative explanation would be that there is a tendency to form intramolecular hydrogen bridges between the amine group and the bromine atoms similar to those that have been postulated by Anzilotti and Curran (27) to account for the values of the dipole moments of o-bromophenol. The formation of hydrogen bonds by bromine has never been proved, however, and in the present instance it would be expected to have a much greater effect upon the dipole moment in benzene than is observed. This alternative, therefore, is rather improbable.

Obstruction between the dioxan molecule in a complex and the *ortho*-methyl groups in mesidine and aminodurene may also account for the fact that the points on Figure 7 referring to these compounds, although coincident, lie below the best line for the points relating to other compounds where no such obstruction is to be anticipated.

p-*Nitroaniline*

In the case of the nitroanilines the nitro-group is *m*-directing whilst the amino-group is *op*-directing, whereas both groups in the bromoanilines are *op*-directing. Both the mesomeric and inductive effects of the nitro-group tend to cause a withdrawal of electron density from the ring. Hence, in *p*-nitroaniline the effects of the two groups can mutually enhance one another. In valence bond terms the result can be described as arising from contributions to the state of the molecules by structures of the type  The magnitude of the interaction effect is shown by the fact that the moment of *p*-nitroaniline exceeds the vector sum of the moments of the amino- and nitro-groups by no less than 1.06D. Nevertheless, even if the mesomeric moment in aniline itself is taken as being 1.73D. the total "mesomeric moment" amounts to 2.9D. As this includes not only the true electron displacement due to the mesomeric effect but also modifications in the moment resulting from the change in the state of hybridisation of the orbitals of the amino-group and from induction, the true mesomeric moment is less than this and, hence, it is too small to suggest that the mesomeric structure given above is the predominant structure contributing to the actual state of the molecule. This is in line with other evidence since, although a very weak base, p-nitroaniline has a definite basic dissociation constant: the structure given above would imply a complete coplanarity of the molecule and the complete disappearance of the basic character of the amino-group.

The apparent dipole moment of p-nitroaniline in dioxan solution is 0.60D. greater than in benzene solution, a result which would be anticipated from the magnitude of the interaction moment in the latter solvent. It is apparent that an increased electron density donation by the amino-group is readily accepted by the nitro-group in the para position, whereas in aniline the increase in mesomeric moment is opposed by electron densities already present at the positions ortho and para to the amino-group. In p-bromoaniline, the donation is facilitated by the inductive effect of the bromine atom but this does not specifically remove electron density from the atoms ortho to the amino-group.

m-Nitroaniline

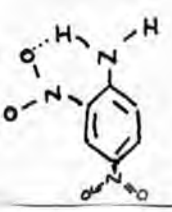
In this compound the mesomeric effects of the amino- and nitro-groups cannot act in conjugation, and, hence, it is only the inductive effect of the nitro-group which facilitates the mesomeric effect of the amino-group. The position is, therefore, similar to that of m- or p-bromoaniline. The amino- and nitro-groups are so oriented with respect to one another that, on the average, the moment induced in one group by the other can only be small. Almost the whole difference between the observed and calculated moments must arise through interaction between the mesomeric effect of the amino-group and the inductive effect of the nitro-group. It is not surprising, therefore, that both the interaction moment and the $\Delta\mu$ value are almost the same as they are for m-bromoaniline.

3:5-Dinitroaniline

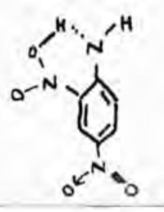
The measured moments of this compound show most clearly the importance of the relative positions of the groups in determining both the interaction moment and the $\Delta\mu$ value. In the absence of any mesomeric displacement which can tend to give conjugative structures throughout the molecule the moment of 3:5-dinitroaniline should be the same as that of p-nitroaniline but actually the values in benzene and dioxan solution are 0.75 and 0.89D., respectively, less than those for p-nitroaniline. The interaction moment, based on vector addition of the moments of aniline and m-dinitrobenzene, is, in fact, rather more than double that in m-nitroaniline. This may be due to slight experimental error or to the vectorial method used in calculating the interaction moments, but it seems to be significant that the difference between the $\Delta\mu$ values for 3:5-dinitroaniline and aniline is more than twice that between the equivalent values for m-nitroaniline and aniline. Actually, the points for both compounds lie reasonably near the mean curve of Figure 7.

2:4-Dinitroaniline and 2:4:6-Trinitroaniline

In these compounds the importance of the relative positions of the amino- and nitro-groups is again shown up rather dramatically since on



(Y)



(Z)

the simplest vector summation principle their moments should be equal to those of m-nitroaniline and aniline, respectively. The observed values for benzene solution actually exceed these values by 0.96 and 1.37D., respectively, and correspond to even greater interaction moments than those found for p-nitroaniline.

A possible complicating factor which arises here is an interaction between the amino- and nitro-groups similar to that occurring in o-nitrophenol. Internal hydrogen bonding or an internal salt formation (Y and Z) would be expected to lead to a greatly increased interaction moment in 2:4-dinitroaniline, but at the same time it would be expected to reduce the tendency of the amino-group to form a hydrogen bond with the dioxan molecule. However, the value of $\Delta\mu$ for 2:4-dinitroaniline is greater than for p-nitroaniline and it lies near the curve in Figure 7, so it seems that the association with dioxan is not appreciably interfered with. Any tendency to internal hydrogen bonding, therefore appears not to inhibit the association with dioxan.

Another possible interaction effect involves steric obstruction between the amino- and the 2-nitro-group, whereby one or both of these groups are prevented from coming into or near to the plane of the ring. This type of effect would cause a considerable decrease in the mesomeric effect of the group concerned and would tend to reduce its group moment towards the value shown in aliphatic compounds. The observed dipole moment of 2:4-dinitroaniline in benzene could be explained by a displacement of the nitro-group from possible coplanarity with the ring, but it seems very unlikely that this should occur without the amino-group also being at least partially inhibited from assuming the near-coplanar state. The dipole moment suggests that there is no such inhibition.

Smith (35) showed that inter-molecular hydrogen-bonding between an oxygen atom of nitrobenzene and the imino-hydrogen atom of diphenylamine does not occur to any significant extent in benzene solution, a result which tends to suggest that a strong intra-molecular hydrogen bond in 2:4-dinitroaniline is improbable. At the same time, however, it is unlikely that there is any great repulsion between the hydrogen atoms of the amine group and the oxygen atoms of the nitro-group so they may well act almost freely.

For 2:4:6-trinitroaniline, the moment in benzene solution may be a little high because there is a rather large atom polarisation due to the balanced dipoles in the molecule, but the value suggests a slightly greater interaction moment even than in 2:4-dinitroaniline. The $\Delta\mu$ value, however, is much smaller than for the latter compound, a result which is very similar to but even more pronounced than that observed with 2:4:6-tribromoaniline. The same explanation will also hold here, the formation of a complex with dioxan and particularly the approach of the N-H bonds, in such a complex, to the plane of the ring being sterically inhibited. In such cases, therefore, the parallelism between $\Delta\mu$ and the mesomeric moment of the amine group must break down.

The importance of the charge distributions in the respective groups in the steric inhibition of mesomeric effects is well illustrated by the measurements on 2:4:6-trinitro-1-chlorobenzene in dioxan solution. The fact that the inductive effects of the groups upon one another cannot be calculated with any certainty prevents an exact analysis of this problem but it seems highly probable that apart from inductive effects the effective moments of the nitro-groups in the positions <u>ortho</u> to the chlorine atom are appreciably smaller than that of the nitro-group in the <u>para</u> position. This would be expected if the chlorine atom tends to prevent coplanarity of the nitro-group with the ring in the same way as the bromine atoms do in 2:4:6-tribromonitrobenzene. It seems likely, therefore, that although the chlorine atom is physically smaller than an amino-group it can have a greater steric effect relative to a nitro-group.

2-Methyl-4-nitroaniline

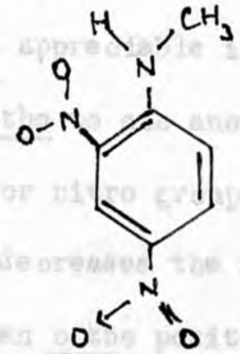
2-Methyl-4-nitroaniline only differs from p-nitroaniline in having a methyl group ortho to the amino-group. As the axis of the dipole in p-nitroaniline is only slightly inclined to the axis of the N-C bond, whilst the axis of the C-Me bond in 2-methyl-4-nitroaniline is inclined at 60^o to this axis it would be expected that, other complicating factors excluded, the moment of the 2-methyl compound would differ from that of p-nitroaniline by about 0.37cos60^o or 0.19D. The observed difference (0.20D.) suggests, therefore, that there is no appreciable inhibition of the mesomeric effect in this compound. On the other hand, $\Delta\mu$ is slightly less than it is for p-nitroaniline, an effect which could be explained by the hydrogen bonding to a dioxan molecule being inhibited on the side of the molecule adjacent to the methyl group.

Nitromethylanilines

The study of these compounds should assist in confirming conclusions drawn from measurements on the bromo- and nitroanilines, particularly in respect to the question of steric hindrance in the formation of complexes with dioxan. Combination of the values of the moments of methylaniline, 1.68D., and of N-methyl-p-toluidine, 1.41D., leads to $\cos\theta = 0.78$ and $\theta = 38\frac{1}{2}^{\circ}$ in methylaniline. This is reasonable in view of the angle of 48° for the inclination of the dipole in aniline and 34° in dimethylaniline, the value indicated from the moments of dimethylaniline and dimethyl-p-toluidine. This assignment implies that the mesomeric moment of methylaniline is appreciably greater than that of aniline and almost as great as that of dimethylaniline. The fact that the interaction moment of p-nitromethylaniline is much greater than that of p-nitroaniline and nearly as large as that of p-nitrodimethylaniline, 1.48D., suggests that this may be the case. This interaction moment may be interpreted in exactly the same way as that of p-nitroaniline.

The value of $\Delta\mu$ is considerably less than it is for p-nitroaniline. This is not surprising in view of the fact that the dioxan effect for methylaniline is much smaller than for aniline and it is probably to be associated with the smaller tendency on the part of the methylanilines to associate with dioxan rather than with a decrease in electron displacement accompanying the association.

The results for 2:4-dinitromethylaniline are particularly interesting in relation to possible steric effects in this compound. The interaction moment in benzene solution is slightly greater than that of p-nitromethylaniline but the difference between these interaction moments is less than that between the interaction moments of 2:4-dinitroaniline and p-nitroaniline. It is to be expected that the nitro-group and the methyl group will tend to obstruct one another and consequently near coplanarity will be possible only in the sense,



This is a condition for which, it was suggested earlier, association with dioxan should be sterically inhibited, the position being much the same as with 2:4:6-trinitroaniline. In accordance with this view, $\Delta \mu$ for 2:4-dinitromethylaniline is less than that for p-nitromethylaniline.

Conclusions

From the results of the measurements recorded here, taken in conjunction with previous data, the interaction moments of a number of substituted anilines and methylanilines have been calculated. It has been shown that the dipole moments of these compounds in benzene solution can be interpreted satisfactorily in terms of the mesomeric and inductive effects of the substituents concerned. In the absence of substituents in positions ortho to the amino-group the difference between the apparent moments of amines in dioxan and in benzene solutions (the "dioxan increment") increases progressively with increase in the interaction moment, and it is suggested that this may provide a means of estimating the value of the interaction moment in molecules for which the vector analysis of the moment value is difficult.

There is evidence that the presence of *ortho* bromine atoms produces a slight inhibition of the mesomeric effect of the amino group but there appears to be no appreciable interference between nitro and amino groups in positions *ortho* to one another. The presence of methyl groups, bromine atoms or nitro groups in both positions *ortho* to the amino group, however, decreases the dioxan increment. The presence of one nitro-group in an *ortho* position to the methylamino-group is sufficient to cause a similar decrease in this increment. These features are attributable to steric effects in the molecules.

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