# **134.** *The Mesomeric Effect of the Dimethylamino-group in Dimethylaniline, and the Nature of its Interaction with Halogen Groups.*

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THIS investigation was commenced in order to determine the electric dipole moment due to the " interaction " or " conjugation " of the dimethylamino-group with the benzene ring. As a qualitative test for the existence of such a moment, Ingold suggested (*Ann. Reports*, 1926, **23**, 149) that the sign of the moment of this group relative to the benzene ring should be determined. Later, a general, quantitative method of determining such moments was developed independently and applied by one of us (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668) to a number of groups : this is the method which is now used.* Its application requires a knowledge of the magnitudes and directions of the moments of corresponding aliphatic and aromatic compounds relative to some suitable common co-ordinates : the required moment is then the vector difference between the two. In order to determine the angle $\theta_2$ between the moment of dimethylaniline and the C–N bond which links the group to the benzene ring the moments of dimethylaniline and its *p*-methyl, chloro-, bromo-, iodo-, and nitro-derivatives were measured : that of the *p*-amino-derivative has also been measured.

Another method for determining $\theta_2$ has already been applied (Hertel and Dumont, *loc. cit.*), but it does not give an unambiguous answer; for instance, from the moments of dimethylaniline and of tetramethyl-*p*-phenylenediamine two possible angle values can be obtained by assuming that the groups rotate freely relative to one another and applying Williams's equation (*Z. physikal. Chem.*, 1928, *A*, **138**, 75) : by taking 1·58 and 1·23 as the respective moments (Fogelberg and Williams, *Physikal. Z.*, 1931, **32**, 27 ; Weissberger and Sängewald, *Z. physikal. Chem.*, 1929, *B*, **5**, 237), alternative values of approximately 33·5°

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* After the experimental work had been completed, Hertel and Dumont (*Z. physikal. Chem.*, 1935, *B*, **30**, 139) reported measurements of several *p*-substituted dimethylanilines, but they did not use them for the purpose mentioned.

and 146·5° are found. It was anticipated that this ambiguity could be resolved, and the value of $\theta_2$ checked, by the new data.

Those obtained and the results which they give are collected in Table I, which includes the data of other authors. The symbols used, *viz.*, $\mu_O$, $\mu_S$, and $\mu_T$, represent the original, the substituent, and the total resultant moment respectively * (Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 562).

TABLE I.

| Substituent group. | $\mu_S$. | $\mu_T$. | $\theta_2$. | Substituent group. | $\mu_S$. | $\mu_T$. | $\theta_2$. |
|---|---|---|---|---|---|---|---|
| H | — | 1·58 * | — | Br | 1·52 | 3·37 † | 0° |
|  |  | 1·58 † | — |  |  | 3·42 § |  |
|  |  | 1·55 § |  | I | 1·30 | 3·22 † | 0 |
| $CH_3$ | 0·4 | 1·29 † | 38° | CN | 3·97 | 5·90 § | 0 |
|  |  | 1·31 § |  | NO | 3·14 | 6·9 ‡ | 0 |
| Cl | 1·56 | 3·29 † | 0 | $NO_2$ | 3·95 | 6·87 † | 0 |
|  |  |  |  |  |  | 6·15 § |  |

* Fogelberg and Williams, *loc. cit.*
† Present work.
‡ Le Fèvre and Smith, J., 1932, 2239.
§ Hertel and Dumont, *loc. cit.*

Clearly, some of these results must be abnormal, and it may be presumed that the anomalies arise from some kind of interaction between the groups (Höjendahl, " Studies of Dipole Moments," Copenhagen, 1928, p. 113; Bennett, *Ann. Reports*, 1929, **26**, 132; Hampson and Sutton, *loc. cit.*).

Of the substituent groups, the methyl group is least likely to interact with the dimethylamino-group, and therefore it is reasonable to take 38° as the best available value for $\theta_2$. This agrees remarkably closely with the smaller of the two values from tetramethyl-*p*-phenylenediamine (33·5°), which fact indicates that any interaction between the dimethylamino-groups does not affect the rotating moments. As Dr. G. C. Hampson has pointed out to us, this might be expected, since such changes would affect the moments of the Ph–N bonds, which lie along the axis of rotation, rather than those of the $CH_3$–N bonds.

If now, in order to calculate the interaction moment, $\mu_e$, of the dimethylamino-group with the benzene ring, triethylamine be taken as the aliphatic standard for comparison, and it be assumed that the three C–N bonds are mutually inclined at the tetrahedral angle, it follows that $\mu_{\text{aliph.}}$ is 0·9 and $\theta_1$ is 109·5° while $\mu_{\text{arom.}}$ is 1·58 and $\theta_2$ is 38°; $\mu_e$ is then found to be 1·55. This moment has the positive sign required in the case of an *op*-directing group, and, although its magnitude is admittedly rough, the comparison with calculated $\mu_e$ values for the amino-, hydroxy-, and methoxy-groups is interesting. These are 1·12, 0·84, and 1·03 respectively.† Thus $\mu_e$ is greater in aniline than in phenol, and greater in anisole or dimethylaniline than in the unmethylated compounds; furthermore, the increase when two methyl groups are introduced, as in $N(CH_3)_2$, 0·43, is greater than that when only one is introduced as in $OCH_3$, 0·19. These facts are parallel to the changes in chemical properties of the groups (Robinson, *Rapp. Inst. Intern. Chim. Solvay*, 1931, p. 423; Ingold, *Rec. trav. chim.*, 1929, **48**, 797). The explanation of the existence of these moments for various groups as a result of permanent " electromeric " effects which occur in *all* molecules of the unsaturated compounds was given in 1931 by one of us (Sutton, *loc. cit.*). The origin and cause of the " electromeric " effects were at that time obscure, but since then they have been explained as a result of wave-mechanical " resonance " between different structures; when some of these are highly polar an electromeric moment is generated

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* Here and throughout, electric dipole moments are given in Debye units, *i.e.*, $10^{-18}$ e.s.u.

† These have been recalculated. The method for the hydroxyl group is that described previously (Sutton, *loc. cit.*), but some of the data are new: $\mu_{H_2O} = 1{\cdot}84$, $\mu_{CMe_3 \cdot OH} = 1{\cdot}66$, and $\mu_{PhOH} = 1{\cdot}61$. For the methoxyl group, $\mu_{Me_2O} = 1{\cdot}32$, $\theta_1 = 112°$ (Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473), $\mu_{PhOMe} = 1{\cdot}23$, and $\mu_{p\text{-}C_6H_4Me \cdot OCH_3} = 1{\cdot}20$ (whence $\theta_2 = 76°$) were taken. In treating the amino-group, the moment of N–H was calculated from $\mu_{NH_3} = 1{\cdot}47$, the valency angles being assumed to be 109·5°, and thence $\mu_{NH_2}$. The simplest solution to the problem of combining this with any value for $\mu_{CH_3N}$ to give the observed value of 1·23 for $CH_3 \cdot NH_2$ made $\theta = 90°$. Now, by taking $\mu_{PhNH_2} = 1{\cdot}53$ and $\mu_{p\text{-}C_6H_4Me \cdot NH_2} = 1{\cdot}27$ (whence $\theta_2 = 43° \; 29'$) the above value for $\mu_e$ is found. The moment values are taken from the table compiled by Sidgwick and collaborators (*Trans. Faraday Soc.*, 1934, **30**, appendix).

(Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789; Kumler and Porter, *J. Amer. Chem. Soc.*, 1934, **56**, 2549; Ingold, *Chem. Reviews*, 1934, **15**, 225). Robinson and Ingold have emphasised the view that the true determinant of the mode and ease of reaction of an organic molecule is the type and degree of resonance which occurs in a transient excited state of the molecule caused by approach of a molecule of the reagent. This they define as the " electromeric " effect proper, and they postulate that the " permanent electromeric effect," or mesomeric effect as Ingold has termed it, is relevant only in so far as it is a measure of the possible true " electromeric " effect.

Since, in the benzene derivatives, the mesomeric effect moments are only of the order of one-tenth of those of the highly polar structures (Sutton, *loc. cit.*), it is evident that the latter are of much higher energy content than the simple or classical structures, *i.e.*, they are excited structures, but that when the energy content of the molecule as a whole is increased by some activation process it is probable that these highly polar structures will become relatively more important. If, now, the mesomeric effect is greater in proportion for one compound than for another, it means that the energy levels of the excited polar structures lie closer to those of the classical structures in the former compound than they do in the latter, and therefore that they become relatively more important in the former than in the latter compound for a given amount of activating energy. Since the moments of the corresponding polar structures would all be approximately equal, it follows that it is likely that the mesomeric and electromeric effects are monotonically related. Whatever the reaction mechanism, the fact is that there is a qualitative relation between the *op*- or the *m*-directing powers of a group and the positive or negative magnitude of the mesomeric effect between it and the benzene ring.

It remains to discuss the interactions already remarked upon (p. 600). It has long been recognised that when a *m*-directing group is substituted para to an *op*-directing one, an anomaly due to interaction of some kind may appear, and those noted above with the nitro-, nitroso-, and cyano-groups are therefore only further examples of this.

The interactions with the halogens, which are themselves *op*-directing, are however of a type only recently discovered by Bennett and Glasstone (*Proc. Roy. Soc.*, 1934, *A*, **145**, 71; *Trans. Faraday Soc.*, 1934, **30**, 853), who pointed out that the data given by Bergmann and Tschudnowsky for the substituted anisoles clearly showed their existence. Sutton and Hampson (*Trans. Faraday Soc.*, 1935, **31**, 945) found interactions in diphenyl ethers also, and mentioned that the data of Bergmann and Tschudnowsky for the anilines (*Z. physikal. Chem.*, 1932, *B*, **17**, 100) provided further examples, whereas those for the phenols (Donle and Gehrckens, *ibid.*, **18**, 316) do not; this suggests that only the most powerful *op*-directing groups can produce them with the halogens. No marked interactions of either kind occur in the *p*-substituted toluenes.

In Table II, data relevant to interactions of both kinds are collected, and interaction moments ($\mu_{\text{int.}}$) are calculated in the following way. The moment of the compound is calculated on the assumption that no interaction occurs, the direction $\theta_2$ of the " main " group moment being taken as that given by the moment of the *p*-methyl derivative: the interaction moment is then calculated as that moment, parallel to the axis passing through the two substituent-bearing carbon atoms of the benzene ring, which changes the calculated to the observed value. For example, the moment calculated for *p*-bromodimethylaniline, from the moments of dimethylaniline and bromobenzene ($\theta_2$ being taken as 38°) is 2·95; the moment along the Br–C . . . C–N axis necessary to make this equal to the observed value, 3·37, is one of 0·45 with its negative end toward the bromine atom, *i.e.*, positive relative to the dimethylamino-group.

It will be noticed (i) that for a given substituent group the interaction moment decreases in the order $-NMe_2 > (-NH_2, -OPh, -OCH_3) > -OH$, *i.e.*, roughly in the order of decrease of *op*-directing power and of mesomeric moment of the groups; (ii) that the interaction moment is always positive relative to the main group for any of the substituent groups used; (iii) that, as pointed out by Bennett and Glasstone, for any one main group the interaction moment increases in the following order for substituent groups: $F < Cl < Br < I < NO_2$.

It may easily be shown that the large interactions are not due merely to mutual electrostatic polarisations of the groups by one another. Either of these polarisations may be

TABLE II.*

| | *Toluenes.* | | | *Phenols.* | | | *Anilines.* | | |
|---|---|---|---|---|---|---|---|---|---|
| *p*-Substituent. | $\mu_{\text{calc.}}$ | $\mu_{\text{obs.}}$ | $\mu_{\text{int.}}$ | $\mu_{\text{calc.}}$ | $\mu_{\text{obs.}}$ | $\mu_{\text{int.}}$ | $\mu_{\text{calc.}}$ | $\mu_{\text{obs.}}$ | $\mu_{\text{int.}}$ |
| F ................ | — | — | — | — | — | — | 2·74 | 2·75 | 0·01 |
| Cl ................ | 1·96 | 1·95 | −0·01 | 2·30 | 2·27 | −0·03 | 2·87 | 2·93 | 0·06 |
| Br ................ | 1·92 | 1·96 | +0·04 | 2·27 | 2·18 | −0·09 | 2·82 | 2·87 | 0·05 |
| I ................ | 1·70 | 1·71 | 0·01 | — | — | — | 2·63 | 2·82 | 0·21 |
| NO ................ | — | — | — | (3·60) | 4·72 | +(1·12) | — | — | — |
| $NO_2$ ................ | 4·35 | 4·42 | 0·07 | 4·34 | 5·04 | 0·71 | 5·17 | 6·2 | 0·95 |
| CN ................ | 4·30 | 4·37 | 0·07 | — | — | — | — | — | — |
| | *Anisoles.* | | | *Diphenyl ethers.* | | | *Dimethylanilines.* | | |
| F ................ | 2·09 | 2·09 | 0·00 | — | — | — | — | — | — |
| Cl ................ | 2·20 | 2·24 | 0·04 | — | — | — | 2·97 | 3·29 | 0·34 |
| Br ................ | 2·17 | 2·30 | 0·15 | — | — | 0·17—0·19† | 2·93 | 3·37 | 0·46 |
| I ................ | 1·99 | 2·12 | 0·16 | — | — | — | 2·57 | 3·22 | 0·69 |
| NO ................ | — | — | — | — | — | — | (4·49) | 6·90 | (2·41) |
| $NO_2$ ................ | 4·41 | 4·76 | 0·37 | — | — | 0·70—0·76† | 5·04 | 6·87 | 1·86 |
| CN ................ | — | — | — | — | — | — | 5·20 | 5·90 | 0·71 |

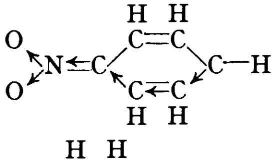
* The moment values used in performing these calculations were derived from the " Table of Dipole Moments " of Sidgwick and collaborators (*loc. cit.*) and are : for phenol, 1·61 ; *p*-cresol, 1·64 ; toluene, 0·40 ; aniline, 1·53 ; *p*-toluidine, 1·27 ; anisole, 1·23 ; *p*-tolyl methyl ether, 1·20 ; dimethylaniline, 1·58 ; dimethyl-*p*-toluidine, 1·29 ; fluorobenzene, 1·42 ; chlorobenzene, 1·56 ; bromobenzene, 1·52 ; iodobenzene, 1·30 ; benzonitrile, 3·97 ; nitrosobenzene, 3·14 ; nitrobenzene, 3·95.

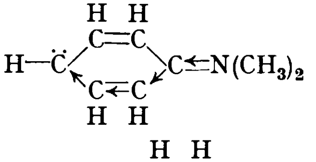
† These are calculated by a different method and are taken from a paper by Sutton and Hampson (*loc. cit.*).

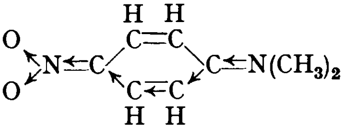
calculated separately with sufficient accuracy by a modification * of the method of Smallwood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, **52**, 1919), and the combined effect thus found. The moment induced in a group of refractivity 6—9 c.c. (*e.g.*, $-NO_2$, $-Br$) by one of 1·5 in the *p*-position, is of the order of 0·05—0·08 ; by one of 4, 0·13—0·21. In *p*-nitrodimethylaniline, where the two polarisations combine, an interaction moment of 0·35 at the most would be expected ($_{E}P_{NMe_2}$ = 14·5 c.c.), not one of 1·86. In *p*-chlorodimethylaniline the combined moments should be 0·15, instead of 0·34 as observed, and again in *p*-iododimethylaniline ($_{E}P_{I}$ = 14 c.c.) the moment anticipated would be 0·20, not 0·69. That this method of calculation gives results of the right order in cases where probably no other effect occurs, is shown by the fact that the interaction calculated for *p*-nitrotoluene, 0·15, agrees quite well with the observed value, 0·09.

The considerable residual abnormalities of moment are therefore to be attributed to mutual alteration of mesomeric effect.

In those compounds which have an *op*-directing group in the para-position to a *m*-directing group, the two groups are complementary to one another, since they both require the same type of electron redistribution in the excited forms which are responsible for their individual mesomeric effects, thus :







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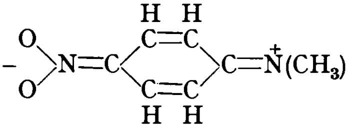

There is, therefore, a mutual stabilisation of this common excited form, and consequently an augmentation of its relative importance, which is made evident by the large positive

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* The modification consists of making an allowance for the dielectric effect of the benzene ring which is interposed between the two groups. The factor $(\epsilon + 2)/3$, given by the Clausius and Mosotti model and employed, *e.g.*, by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171), is introduced ; $\epsilon$, the dielectric constant of the benzene ring, is taken to be 3.

interaction moment. This has, in essence, long been realised. It will be noticed that the interaction with the cyano-group is much less than that with the nitro-group, but that with the nitroso-group is almost as great; this order corresponds qualitatively to the relative *m*-directing powers of these groups (Robinson, *loc. cit.*; Ingold, *loc. cit.*; Hammick, New, and Sutton, J., 1932, 742).

In the case of the *p*-halogeno-amines and -ethers, both groups are *op*-directing, and consequently their mesomeric effects are not parallel but anti-parallel; not complementary but opposed. However, it may readily be seen that if one group is more powerfully directing than the other, the mesomeric effect of the weaker group may be diminished by that of the other, and then the direction of the interaction moment will be opposite to that of the normal mesomeric moment of the weaker group. In particular, if the dimethylamino-group reduces the mesomeric effect of the halogens, there will be generated an interaction of the same sign as that found with the *m*-directing groups, for a decrease of a positive electromeric effect (relative to the halogen, but negative relative to the dimethylamino-group) is equivalent to an increase of a negative one.

It has been pointed out to us by Dr. G. C. Hampson that increase or decrease of the relative importance of the excited, polar structures may be produced, not only by the similar or dissimilar requirements of valency arrangement therein by the two groups, but also by the fields of the groups, and that the two causes cannot easily be disentangled. What we may distinguish as the " valency " effects and the " polar " effects sometimes will act together and sometimes will not. Thus, in *p*-nitrodimethylaniline both effects favour an increased mesomeric effect: in *p*-iodonitrobenzene the " valency " effects augment one another, but whereas the field of the nitro-group augments the mesomeric effect of the iodo-group, that of the carbon–iodine dipole diminishes the mesomeric effect of the nitro-group somewhat; in *p*-iododimethylaniline the " valency " effects oppose, but the carbon–iodine dipole augments the mesomeric effect of the dimethylamino-group, while the moment of the latter group diminishes the mesomeric effect of the former. To discuss the question generally would be beyond the scope of this paper, but it is appropriate to consider the relative importance of the two effects in the particular cases under discussion. Dr. Hampson has suggested that the polar interaction in a compound AB would be the algebraic difference $k(\mu_A \mu_{e_B} - \mu_B \mu_{e_A})$, $\mu$ being the moment of a group, $\mu_e$ its mesomeric moment, and $k$ being a constant. Now, by inserting $\mu$ and $\mu_e$ values [the latter from a paper by one of us (Sutton, *loc. cit.*) or the present paper] and equating to the observed interaction moments, a value of $k$ may be calculated which should include both the " polar " and the " valency " effects; $k$ for the former effect should be universal, so large observed variations would indicate considerable " valency " effects. The results obtained for the dimethylanilines are given in Table III. The first set of $k$ values were calculated without making allowance for the fact that the moment of the dimethylamino-group makes an angle of 38° with the Ph–N axis; the second set show the effect of making some allowance for this by taking the effective moment of the dimethylamino-group to be half its gross value. The differences are accentuated rather than diminished thereby.

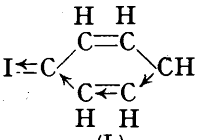
TABLE III.

| | *k.* | | | *k.* | |
|---|---|---|---|---|---|
| *p*-Chlorodimethylaniline ... | 0·1015 | 0·118 | *p*-Nitrodimethylaniline ... | 0·248 | 0·273 |
| *p*-Bromo " ... | 0·133 | 0·159 | *p*-Nitroso " ... | (0·459) | (0·502) |
| *p*-Iodo " ... | 0·204 | 0·258 | *p*-Cyano " ... | 0·106 | 0·1115 |

The $\mu_e$ values used are admittedly rough, and it is impossible to say what value $k$ should have; nevertheless, it seems a reasonable conclusion that in those cases where $k$ is much greater than 0·1 there is probably a large "valency" effect in addition to any " polar " effect.

The conclusions that the iodo-compounds show such marked interactions and that these are due largely to valency effects give support to a hypothesis advanced by Robinson (J., 1933, 1114) that the ease of suppression of the mesomeric effect of a group depends upon its electrostatic deformation polarisability. Ingold (*loc. cit.*) has emphasised the converse, the importance of deformation polarisability in determining the mesomeric effect of a group itself. It would not be expected that polarisability would be the sole determinant of mesomeric effect, for the rearrangement of bonds in the excited structures is not merely an electrostatic process; this is shown, *e.g.*, by the fact that, although the hydroxy- and the amino-group are less deformable than bromine, they produce greater mesomeric effects than it does. Therefore, we may consider that the mesomeric effect of a group depends upon two factors (in addition to the " polar " or " inductive " factor due to the moment of the group): the deformation polarisability, $\alpha$, and what may be called a " bond type factor," $\chi$, so that $\mu_e = \alpha\chi$. The process by which one group alters the mesomeric effect of another, through the " valency " effect, is by altering $\chi$. Thus, if the *p*-substituent reduces $\chi$ for each of the halogens by the same amount, $x$, $\mu_e$ becomes $\alpha(\chi - x)$, and the abnormality, or interaction moment, is $- \alpha x$. Even if $x$ is not constant, but decreases considerably from fluorine to iodine, $\alpha$ increases so rapidly in this order that it would still be possible for the interaction moment to increase in this, the observed, order.

It has been suggested by Klug (*J. Chem. Physics*, 1935, **3**, 747) that in *p*-di-iodobenzene and *trans*-di-iodoethylene the iodine participates in excited structures of the type (I), wherein it has the same electronic structure as it has in the iodochlorides and similar compounds, *i.e.*, a decet in the fifth main quantum group. It is obviously possible that structures of this type might become important in compounds having a strong *op*-directing group para to the iodine atom, but even in *p*-iododimethylaniline, since the observed abnormality, 0·69, does not *exceed* the supposed mesomeric effect of the iodo-group itself, 0·86, we can only say that it is not essential to postulate this process, but that, nevertheless it may occur. The almost complete suppression of the mesomeric effect of the iodo-group should make the chemical properties of this compound of considerable interest.


(I.)

EXPERIMENTAL.

*Determination of Electric Dipole Moments.*—All measurements were made in benzene solution at 25·0° The dielectric constants were measured by the heterodyne apparatus previously described (Sutton, *loc. cit.*; cf. Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147). For some measurements the dilution condenser described by Sutton was used; for others, a single-solution condenser, essentially similar to the one described by Jenkins and Sutton (J., 1935, 609), but with a larger capacity, was used. Refractivities and densities were measured as before. The benzene density used in the calculations for any particular run was the value to which the density-$f_2$ curve extrapolated, since small variations were noticed.

*Preparation and Purification of Materials.*—*Benzene.* B.D.H. " A.R." Benzene was further purified by three fractional freezings and distillation from phosphoric oxide. Uniformity of samples was checked by f.p. determinations.

*Dimethylaniline.* A good commercial specimen (m. p. 1·85°) was refluxed for one hour with enough acetic anhydride to acetylate up to 10% by weight of monomethylaniline. The mixture was just neutralised with fairly dilute sodium carbonate solution, and steam-distilled. The distillate was extracted with ether, the extract dried and evaporated, and the product fractionated. The fraction, b. p. 191·5—194°, was dried over solid potassium hydroxide and again fractionated. The fraction, b. p. 193·0—193·4° (uncorr.; Anschütz)/753 mm., f. p. 2·35°, was retained and redistilled just before measurement; Perkin (J., 1896, **69**, 1207) gives b. p. 193° (corr.)/760 mm.; Beilstein gives f. p. 2·5°.

*Dimethyl-*p*-toluidine.* A commercial specimen was purified according to Hodgson and Kershaw (J., 1930, 277). The fraction, b. p. 207° (uncorr.) (cf. 207°, Hodgson and Kershaw, *loc. cit.*), obtained on fractionating the dried, ethereal extract of the steam-distillate, was used.

p-*Aminodimethylaniline.* *p*-Nitrosodimethylaniline, prepared from dimethylaniline (" Organic Syntheses," **2**, 17), was reduced by tin and hydrochloric acid (Wurster, *Ber.*, 1879, **12**, 523). The product was purified repeatedly by Wurster's method but retained a slight pink coloration; m. p. 38·5—39° (Wurster, *loc. cit.*, gives 41°).

p-*Chlorodimethylaniline.* A Sandmeyer reaction was performed with diazotised *p*-aminodimethylaniline (by Mr. J. Jackson). The product was recrystallised twice from ligroin (b. p. 40—60°) and once from ethyl alcohol; m. p. 33·5° (35·5°, Beilstein).

p-*Bromodimethylaniline.* Dimethylaniline was brominated directly, by Mr. J. Jackson, as directed by Weber (*Ber.*, 1875, **8**, 715; 1877, **10**, 763). The crude product, precipitated by alkali, was washed, and recrystallised four times from ethyl alcohol; m. p. 54·7° (55°, Weber, *loc. cit.*).

*p*-Iododimethylaniline was prepared by direct iodination of dimethylaniline (Weber, *ibid.*, p. 765; Baeyer, *ibid.*, 1905, **38**, 2762) in methyl-alcoholic solution at room temperature in the presence of mercuric oxide, the reaction being complete in a few minutes. The solution was greatly diluted with water and extracted with ether. The extract was concentrated somewhat and shaken several times with thiosulphate solution. This removed the violet substance which had already formed (Weber, *loc. cit.*) and reduced the tendency for its further formation, possibly by removing a catalyst. The extract was further concentrated, and the product thrice recrystallised from ligroin (b. p. 60—80°) (Norit), and then from ethyl alcohol. The m. p., 79—80·5° (corr.), was not altered by the final recrystallisation (Weber, *loc. cit.*, 79° ; Baeyer, *loc. cit.*, 82°).

p-*Nitrodimethylaniline*. Two methods of preparation were used : (1) The reaction between trimethylamine and *p*-chloronitrobenzene (m. p. 83·5° ; cf., 83°, Ssokolow, *Z. Chem.*, 1865, 602), as described by Leymann (*Ber.*, 1882, **15**, 1234) ; the product was recrystallised twice from ethyl alcohol; m. p. 164° (corr.). (2) To *p*-nitrosodimethylaniline (9 g.) in water (1 l.) was slowly added a solution of potassium permanganate (9 g.) in water (1·5 l.), and the manganese dioxide formed was removed by sulphur dioxide. The crude product was recrystallised successively from ethyl alcohol, ligroin–benzene, and ethyl alcohol; m. p. 164° (lit., 162—169° ; many values near 164°). The purified product from the latter preparation was darker than that from the former, but they gave a mixed m. p. of 164°.

*Polarisation Results*.—The dielectric constant of benzene at 25·0° was taken as 2·2727 (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664; Sugden, J., 1933, 768, gives 2·272) and the refractive index as 2·2571 (obs.). The symbols have the same meaning as in previous papers from this laboratory.

The densities were not corrected for buoyancy, this having a negligible effect on the polarisations. The values marked * are interpolated or smoothed values.

| $f_2$. | $d_{4°}^{25°}$. | $\epsilon$. | $n^2$. | $P_2$. | $_{\mathrm{E}}P_2$. |
|---|---|---|---|---|---|
| | | *Dimethylaniline.* | | | |
| 0·04004 | 0·8781 | 2·4246 | 2·2668 | 92·6 | 41·2 |
| 0·02412 | 0·8764 | 2·3657 | 2·2632 | 93·9 | 41·3 |
| 0·02022 | 0·8759 | 2·3493 | 2·2618 | 93·1 | 41·1 |
| 0·01585 | 0·8754$_5$ | 2·3328 | 2·2612 | 93·2 | 41·4 |
| 0·00000 | 0·8737* | — | — | — | — |

$^{\infty}P_2 = 93{\cdot}6 \pm 0{\cdot}5$ c.c.; $^{\infty}_{\mathrm{E}}P_2 = 41{\cdot}6$ c.c.;
$\mu = 1{\cdot}58$.

p-*Aminodimethylaniline.*

| | | | | | |
|---|---|---|---|---|---|
| 0·02383 | 0·8792 | 2·3486 | 2·2688 | 85·9 | 46·4 |
| 0·01877 | 0·8780$_5$ | 2·3322 | 2·2662 | 85·7 | 46·3 |
| 0·01266 | 0·8766$_5$ | 2·3134 | 2·2631 | 86·5 | 46·1 |
| 0·00860 | 0·8757$_5$ | 2·3012 | — | 88·0 | — |
| 0·01261 | 0·8766$_5$ | 2·3142 | 2·2635 | 87·7 | 46·6 |
| 0·00910 | 0·8758 | 2·3022 | 2·2616 | 87·2 | 46·5 |
| 0·00616 | 0·8751$_5$ | 2·2928 | — | 87·4 | — |
| 0·00000 | 0·8738* | — | — | — | — |

$^{\infty}P_2 = 88 \pm 1{\cdot}0$ c.c.; $^{\infty}_{\mathrm{E}}P_2 = 46{\cdot}4$ c.c.;
$\mu = 1{\cdot}42$.

p-*Bromodimethylaniline.*

| | | | | | |
|---|---|---|---|---|---|
| 0·00780 | 0·8799 | 2·3973 | 2·2609 | 271·9 | 49·8 |
| 0·00577 | 0·8781 | 2·3659 | 2·2602 | 276·3 | 51·0 |
| 0·00390 | 0·8767 | 2·3363 | 2·2587 | 279·8 | 48·7 |
| 0·00261 | 0·8755$_5$ | 2·3160 | — | 285·2 | — |
| 0·00000 | 0·8734* | — | — | — | — |

$^{\infty}P_2 = 288{\cdot}5 \pm 3{\cdot}0$ c.c.; $^{\infty}_{\mathrm{E}}P_2 = 49{\cdot}8$ c.c.;
$\mu = 3{\cdot}39$.

| | | | | | |
|---|---|---|---|---|---|
| 0·00975 | 0·8816 | 2·4280 | 2·2622 | 269·6 | 49·9 |
| 0·00713 | 0·8794 | 2·3872 | 2·2605 | 273·4 | 49·3 |
| 0·00483 | 0·8775 | 2·3509 | 2·2595 | 276·9 | 50·2 |

$^{\infty}P_2 = 284{\cdot}1 \pm 1{\cdot}0$ c.c.; $^{\infty}_{\mathrm{E}}P_2 = 49{\cdot}8$ c.c.;
$\mu = 3{\cdot}36$.
$\mu$ (mean) $= 3{\cdot}375$.

| $_2$. | $d_{4°}^{25°}$. | $\epsilon$. | $n^2$. | $P_2$. | $_{\mathrm{E}}P_2$. |
|---|---|---|---|---|---|
| | | *Dimethyl*-p-*toluidine.* | | | |
| 0·04424 | 0·8778 | 2·3816 | 2·2680 | 79·4$_5$ | 46·6 |
| 0·01989 | 0·8756 | 2·3234 | 2·2624 | 80·7 | 46·8 |
| 0·01847 | 0·8754* | 2·3190 | 2·2626 | 80·1 | 47·4 |
| 0·00936 | 0·8747 | 2·2970 | 2·2599 | 81·2$_5$ | 47·2 |
| 0·00000 | 0·8738* | — | — | — | — |

$^{\infty}P_2 = 81{\cdot}6$ c.c.; $^{\infty}_{\mathrm{E}}P_2 = 47{\cdot}0$ c.c.; $\mu = 1{\cdot}29$.

p-*Chlorodimethylaniline.*

| | | | | | |
|---|---|---|---|---|---|
| 0·02186 | 0·8819 | 2·6121 | 2·2650 | 254·7 | 46·1 |
| 0·01676 | 0·8799 | 2·5349 | 2·2633 | 259·5 | 46·2 |
| 0·01125 | 0·8777 | 2·4492 | 2·2615 | 263·8 | 46·6 |
| 0·00756 | 0·8762$_5$ | 2·3955 | 2·2594 | 274·2 | 45·3 |

$^{\infty}P_2 = 274 \pm 1$ c.c.; $^{\infty}_{\mathrm{E}}P_2 = 47$ c.c.; $\mu = 3{\cdot}30$.

| | | | | | |
|---|---|---|---|---|---|
| 0·01203$_5$ | 0·8779 | 2·4595 | 2·2616 | 261·3 | 46·6 |
| 0·00909 | 0·8766 | 2·4144 | 2·2605 | 264·7 | 47·2 |
| 0·00610 | 0·8756$_5$ | 2·3678 | 2·2594 | 266·0 | 46·7 |
| 0·00000 | 0·8733* | — | — | — | — |

$^{\infty}P_2 = 272 \pm 1$ c.c.; $^{\infty}_{\mathrm{E}}P_2 = 47$ c.c.; $\mu = 3{\cdot}29$.
$\mu$ (mean) $= 3{\cdot}29_5$.

p-*Iododimethylaniline.*

| | | | | | |
|---|---|---|---|---|---|
| 0·01139 | 0·8877 | 2·4480 | 2·2654 | 264·8 | 56·9 |
| 0·00712 | 0·8825 | 2·3825 | 2·2626 | 267·3 | 57·4 |
| 0·00483 | 0·8793 | 2·3480 | 2·2607 | 269·9 | 56·3 |
| 0·00293 | 0·8772 | 2·3178 | 2·2594 | 269·6 | 59·0 |
| 0·00000 | 0·8735* | — | — | — | — |

$^{\infty}P_2 = 272 \pm 2$ c.c.; $^{\infty}_{\mathrm{E}}P_2 = 57 \pm 0{\cdot}5$ c.c.;
$\mu = 3{\cdot}22 \pm 0{\cdot}02$.

p-*Nitrodimethylaniline.*

| | | | | | |
|---|---|---|---|---|---|
| 0·00793 | 0·8777$_5$ | 2·7910 | 2·2657 | 900·6 | 56·8 |
| 0·00652 | 0·8770$_5$ | 2·7023 | — | 922·9 | — |
| 0·00589 | 0·8768 | 2·6635 | 2·2633 | 935·9 | 56·1 |
| 0·00396 | 0·8757 | 2·5380 | 2·2612 | 970·4 | 56·6 |
| 0·00324 | 0·8754 | 2·4878 | — | 970·2 | — |
| 0·00189 | 0·8744 | 2·3977 | 2·2590 | 983·9 | 56·0 |
| 0·00000 | 0·87375* | — | — | — | — |

$^{\infty}P_2 = 1{,}035 \pm 5$ c.c.; $^{\infty}_{\mathrm{E}}P_2 = 56{\cdot}25$ c.c.;
$\mu = 6{\cdot}87$.

## SUMMARY.

The electric dipole moments of dimethylaniline and its *p*-methyl-, *p*-chloro-, *p*-bromo-, *p*-iodo-, *p*-nitro-, and *p*-amino-derivatives have been measured in benzene solution at 25° : they are 1·58, 1·29, 3·29, 3·37, 3·24, 6·87, and 1·42 respectively.

The mesomeric effect of the dimethylamino-group and the benzene ring has been calculated to be 1·55.

The interaction moments between the dimethylamino-group and the substituent groups have been calculated on the assumption that that with the methyl group is zero : they are Cl 0·34, Br 0·46, I 0·69, and $NO_2$ 1·86.

It has been shown that the dimethylamino-group reduces the mesomeric effect of the halogens, suppressing it almost completely in the iodo-derivative.

The nature and significance of mesomeric effects have been discussed.

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