764. Molecular Polarisation and Molecular Interaction. Part VIII.* The Apparent Dipole Moments of Some Derivatives of N-Methylaniline in Benzene and Dioxan Solutions.

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The dipole moments of *p*-bromo-, 2,4-dibromo-, 2,4,6-tribromo-, *p*-nitro-, and 2,4-dinitro-*N*-methylaniline have been determined in benzene and in dioxan. The dipole moments suggest that the mesomeric effect of the methylamino-group is repressed only slightly by one *o*-methyl group and not at all by one *o*-bromine atom. It is sterically hindered strongly, however, by two *o*-methyl groups but is only partially inhibited by two *o*-bromine atoms. These observations support the suggestion that the forces between a hydrogen atom or methyl group and a bromine atom may be less repulsive than those between a hydrogen atom or methyl group and another methyl group. When no steric effects arise the additional moments in dioxan increase with increasing interaction moment. For 2,4-dibromo-, and 2,4,6-tribromo-methylaniline, however, they are lower than for methylaniline itself, this reflecting the steric opposition to complex formation or to the mesomerism of the dioxan complex.

THE dipole moments of mesidine and aminodurene in benzene are equal[1] (1·45 D) and slightly lower than the moment of aniline (1·53 D), suggesting that *o*-methyl groups may cause a slight steric repression of the mesomeric effect of the amino-group. On the other hand the moment of 2,4,6-tribromoaniline[2] (1·73 D) is appreciably greater than that of aniline, indicating that there is no repression of mesomerism in this compound. The dipole moments of dimethylmesidine[3] (1·03 D) and 2,4,6-tribromo-*NN*-dimethylaniline[2] (1·02 D), however, are nearly equal and much lower than that of*NN*-dimethylaniline (1·58 D), indicating that there is almost complete repression of the mesomerism in these compounds. It appears, therefore, that *ortho*-substituents prevent the plane of the

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* Part VII, *J.*, 1957, 4527.

[1] Smith, *J.*, 1953, 109.

[2] Few and Smith, *J.*, 1949, 2663.

[3] Ingham and Hampson, *J.*, 1939, 981.

dimethylamino-group from coming near to the plane of the aromatic ring, but have no such steric effect, or only a slight one, upon the amino-group. Similar evidence is provided by the ultraviolet absorption spectra and molecular refractions of these compounds.[4]

Further, the apparent dipole moments of primary aromatic amines are appreciably greater in dioxan than in benzene solution. For nuclear-substituted anilines the difference between the observed moment in benzene solution and the value calculated by vector summation of the moments of the substituent groups has been intepreted as an interaction moment μ_{int}, and the difference between the apparent moments in dioxan and benzene solutions as an additional component $\Delta\mu_{\text{vect}}$ arising from electron displacements accompanying hydrogen bonding between an amino-hydrogen atom and an oxygen atom of a dioxan molecule.[5] For *para*-monosubstituted and other symmetrically substituted anilines both μ_{int} and $\Delta\mu_{\text{vect}}$ were assumed to act along the axis of the N–C bond, whilst for *meta*-monosubstituted and 2,4-disubstituted anilines they were assumed to act along an axis parallel to the line joining $C_{(1)}$ and $C_{(3)}$. For *meta*- and *para*-monosubstituted and 2,4- and 3,5-disubstituted anilines the values of μ_{int} and $\Delta\mu_{\text{vect}}$ derived on this basis are related, within experimental error, by the empirical expression $\Delta\mu_{\text{vect}} = 0{\cdot}33 + 0{\cdot}255\ \mu_{\text{int}}$. For 2,4,6-trisubstituted anilines, however, $\Delta\mu_{\text{vect}}$ is lower than would be expected from this relationship, an effect which is attributable to steric inhibition of the mesomeric effect in the complex with dioxan.[6]

It would therefore be expected that the mesomeric effect of the methylamino-group should be, at most, only slightly restricted by the presence of one *ortho*-substituent, since it can attain near coplanarity with the ring when the methyl group is towards the side of the molecule remote from the substituent. On the other hand there might be some steric effect in the dioxan complex. It would be expected, however, that the mesomerism might be inhibited strongly by the presence of two *ortho*-substituents. Evidence in this direction was provided by the observation [1] that the dipole moment of methylmesidine in benzene (1·22 D) is much lower than that of *N*-methylaniline (1·68 D), whilst its moment in dioxan is only slightly higher than that in benzene.

The dipole moments of other derivatives of methylamine have now been measured in benzene and dioxan. The results are summarised in Table 1, which also includes data for methylmesidine and for benzene solutions of *N*-methyl-*o*-toluidine and *N*-methyl-2,4- and -2,6-xylidine.

TABLE 1. *Dipole moments* (D).

	μ_{benz}	μ_{diox}	μ_{calc}	μ_{int}	$\Delta\mu_{\text{vect}}$
N-Methylaniline	1·68	1·86	—	—	0·23
N-Methyl-*o*-toluidine	1·76 [7]	—	1·85	−0·08	—
N-Methyl-2,4-xylidine	1·54 [7]	—	1·58	−0·08	—
N-Methyl-2,6-xylidine	1·28 [7]	—	1·98	−0·97	—
N-Methylmesidine	1·22 [1]	1·26 [1]	1·68	−0·72	0·08
p-Bromo-*N*-methylaniline	3·31	3·56	3·04	0·29	0·26
2,4-Dibromo-*N*-methylaniline	2·88	3·10	2·62	0·28	0·23
2,4,6-Tribromo-*N*-methylaniline	1·68	1·81	1·68	0·00	0·17
N-Methyl-*p*-nitroaniline	6·82	7·12	5·41	1·43	0·30
N-Methyl-2,4-dinitroaniline	6·36	6·58	4·74	1·70	0·23

To interpret the dipole moments in terms of μ_{int} and $\Delta\mu_{\text{vect}}$, some assumption must be made regarding the axis of the dipole in the *N*-methylaniline molecule. If the mesomeric effect in *N*-methyl-*p*-toluidine is the same as in *N*-methylaniline, it follows from the dipole moments of these molecules in benzene solution (1·41 [7] and 1·68 D,[1] respectively) and the dipole moment of toluene (0·37 D) that the axis of the dipole is inclined at 38½° to the bond linking the nitrogen atom to the ring, the positive end being away from the ring. Similar

[4] Wepster, *Rec. Trav. chim.*, 1957, **76**, 357.
[5] Smith and Walshaw, *J.*, 1957, 3217.
[6] Smith and Walshaw, *J.*, 1957, 4527.

calculation from the moment of *N*-methyl-*m*-toluidine[7] (1·58 D) leads to an angle of 42°. In the latter case the calculation involves the assumption that if there are any preferred conformations of the methylamino-group, those in which the *N*-methyl group is on the same side of the molecule as the *C*-methyl group have equal probability with the conformations in which the amino-hydrogen atom is on that side of the molecule. Analogous calculations indicate that in aniline and dimethylaniline the dipoles are inclined at 48½° and 34°, respectively, to the bond joining the nitrogen atom to the ring, so an inclination of 40° to this bond in methylaniline seems to be a reasonable assumption.

On this basis " theoretical " moments of the compounds have been calculated from the contributory group moments, which have been taken as 1·56 and 4·01 D, respectively, for a single bromine atom and nitro-group, and as 1·47 and 3·83 D, respectively, for the two bromine atoms and two nitro-groups in the 2,4-disubstituted methylanilines. The results are shown in the third column of Table 1, the fourth and fifth columns of which indicate the values of μ_{int} and $\Delta\mu_{\text{vect}}$, which were deduced from the observed and calculated moments by the same method as was used for the derivatives of aniline.[6]

The moments of *N*-methylmesidine and *N*-methyl-2,4-xylidine indicate that two *o*-methyl groups produce a very considerable steric depression of the mesomerism of the methylamino-group. One *o*-methyl group, however, has a much smaller effect, comparable with that suggested by the moments of *o*-toluidine and mesidine. The ultraviolet absorption spectra of both aniline and *N*-methylaniline derivatives suggest that *o*-methyl groups produce no depression of the mesomerism.[4,8] It is possible, therefore, that the decrease in the dipole moments of these compounds as compared with the calculated values may be due to in-plane deflexion of the methyl groups, but such deflexion would have to amount to about 17° to account for the results. It seems more likely, therefore, that the discrepancy is concerned with the fact that the dipole moment depends only on the ground state of the molecule, but the ultraviolet spectrum depends also on the excited state.

The interaction moments of *p*-bromo- and *p*-nitro-*N*-methylaniline are greater than those of the corresponding aniline derivatives (0·20 and 1·08 D, respectively[5]), but less than those of the *NN*-dimethylaniline derivatives (0·37 and 1·48 D, respectively[9]). As in the aniline series the interaction moment for the 2,4-dinitro-compound is greater than that of the *p*-nitro-derivative, so the tendency for intramolecular hydrogen-bond formation seems to encourage, rather than otherwise, the near-coplanarity of the methylamino-group with the plane of the ring. There appears to be little, if any, steric inhibition of mesomerism in 2,4-dibromo-*N*-methylaniline, since for this compound μ_{int} is, within experimental error, the same as for *p*-bromo-*N*-methylaniline.

In benzene solution the dipole moment of 2,4,6-tribromo-*N*-methylaniline is equal to that of methylaniline and much higher than that of methylmesidine. This contrasts with the relative values for the corresponding derivatives of dimethylaniline. The evidence suggests, therefore, that the mesomerism is suppressed strongly in methylmesidine, but is only partly repressed in 2,4,6-tribromo-*N*-methylaniline. This inference becomes reasonable if it is assumed that the molecule cannot assume a conformation with the methyl group near to the bromine atom, but can take up a conformation with the amino-hydrogen atom near to the plane of the benzene ring and in proximity to the bromine atom (Figure, *A*). In such a conformation the orientation of the lone-pair orbital of the nitrogen atom relative to the plane of the ring will not permit so great an orbital overlap with the π-orbitals of the ring as does the most favourable conformation of *N*-methylaniline itself (Figure, *B*), but should furnish an appreciable overlap without bringing the methyl group near to a bromine atom. Hence a diminished, but still substantial mesomeric effect would be expected. Such a conformation would not be possible for 2,4,6-tribromo-*NN*-dimethylaniline, so the dimethylamino-group must be arranged with the

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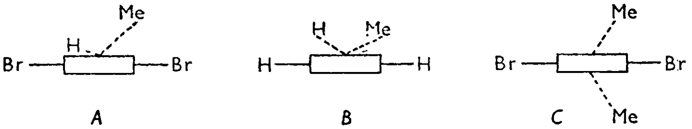
[7] Fischer, *Acta Chem. Scand.*, 1950, **4**, 1197.

[8] Burgers, Hoefnagel, Verkade, Visser, and Wepster, *Rec. Trav. chim.*, 1958, **77**, 491.

[9] Smith, " Steric Effects in Conjugated Systems," Butterworths, London, 1958, p. 141.

two methyl groups on opposite sides of the plane of the ring and roughly equidistant from it (Figure, *C*), a conformation which precludes appreciable mesomerism between the group and the ring.

It appears that the methylmesidine molecule cannot take up a conformation corresponding with that proposed for 2,4,6-tribromo-*N*-methylaniline. This supports the suggestion made previously that the forces between a hydrogen atom or methyl group and a bromine atom may not be so repulsive as those between a hydrogen atom or methyl group and another methyl group.



The values of $\Delta\mu_{\text{vect}}$ are all much smaller than for the corresponding aniline derivatives. This may arise either because of a smaller extent of formation of a hydrogen-bonded complex, or because such bonding is attended by a smaller electron displacement. The values parallel the results for aniline derivatives, however, in indicating that when no steric effects arise $\Delta\mu_{\text{vect}}$ increases with increasing μ_{int}. The fact that the values for 2,4-dibromo- and 2,4,6-tribromo-*N*-methylaniline are smaller even than the value for *N*-methylaniline itself reflects the steric opposition to complex formation or to the mesomerism of the dioxan complex. Similar effects were observed with 2,4,6-trisubstituted anilines.[6]

EXPERIMENTAL

Materials.—*p*-Bromo-*N*-methylaniline was prepared by treating *p*-bromoaniline toluene-*p*-sulphonate with dimethyl sulphate. After repeated recrystallisation from aqueous alcohol, the product was hydrolysed with 70% sulphuric acid and the mine separaated by steam distillation. After being dried (CaO) it was distilled *in vacuo*: it had b. p. 135°/12 mm. (lit.[10] 137—138°/14 mm.).

2,4-Dibromomethylaniline was prepared by brominating *N*-methylaniline by Fries's method [10] and recrystallised from alcohol: it had m. p. 48·6° (lit.[10] 48°).

2,4,6-Tribromo-*N*-methylaniline was also made by Fries's method, but it was found necessary to keep the reaction mixture for about three weeks at room temperature to complete the reaction. After being recrystallised from alcohol: it had m. p. 39·5° (lit.[10] 39°).

Commericial, pure *N*-methyl-*p*-nitroaniline was recrystallised repeatedly from aqueous alcohol: it had m. p. 152·2° (lit.[11, 12] 151—152°). *N*-Methyl-2,4-dinitroaniline was prepared by Glazer, Hughes, Ingold, James, Jones, and Roberts's method [13] and recrystallised from aqueous acetone: it had m. p. 178·7° (lit.[13] 177—178°).

Benzene and dioxan were purified and dried as described previously.[14]

Methods and Results.—The dielectric constants, specific volumes, and refractive indices of the solutions were determined at 25° by the methods used previously.[6] The results are recorded in Table 2, where $\Delta\varepsilon$, Δv, and Δn indicate the differences between the dielectric constants, specific volumes, and refractive indices, respectively, of the solutions and those of the pure solvents. The calculations from these results are summarised in Table 3, where α, β, and γ indicate the limiting values of $d\varepsilon/dw$, dv/dw, and dn^2/dw, respectively, at zero concentration, and the other symbols have their usual significance. The accurate determination of $[R_D]$ for *N*-methyl-*p*-nitro- and 2,4-dinitro-aniline was precluded by the sparing solubility of these compounds in benzene: the values shown in brackets in Table 3 were obtained by adding the difference between the $[R_D]$ values of methylaniline and aniline to the $[R_D]$ values of *p*-nitro- and 2,4-dinitro-aniline, respectively. Otherwise $P_{2\infty}$ and $[R_D]_2$ were also calculated by the procedures used previously.[14] The values of the dipole moments shown and used in the

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[10] Fries, *Annalen*, 1906, **346**, 174.

[11] Blanksma, *Rec. Trav. chim.*, 1902, **21**, 270.

[12] Meldola and Salmon, *J.*, 1888, **53**, 775.

[13] Glazer, Hughes, Ingold, James, Jones, and Roberts, *J.*, 1950, 2674.

[14] Few and Smith, *J.*, 1949, 753.

TABLE 2. *Polarisation data.*

10^6w	$10^4\Delta\varepsilon$	$-10^5\Delta v$	$10^4\Delta n$
p-*Bromo*-N-*methylaniline in benzene*			
11,717	779	563	9
28,019	1882	1347	21
44,473	3000	2137	33
60,471	4135	2907	45
87,383	6037	4201	65
p-*Bromo*-N-*methylaniline in dioxan*			
10,717	930	325	11
19,992	1776	605	25
35,156	3118	1066	47
59,635	5357	1805	80
2,4-*Dibromo*-N-*methylaniline in benzene*			
9194	341	575	7
19,838	737	1246	15
31,662	1185	1968	24
42,066	1585	2606	32
61,417	2353	3814	47
2,4-*Dibromo*-N-*methylaniline in dioxan*			
11,026	529	487	15
22,906	1104	1017	30
32,507	1577	1437	43
42,479	2073	1878	56
53,728	2632	2371	70
2,4,6-*Tribromo*-N-*methylaniline in benzene*			
14,239	155	985	10
25,228	275	1742	17
34,904	381	2401	24
48,062	527	3321	32
54,921	608	3789	39

10^6w	$10^4\Delta\varepsilon$	$-10^5\Delta v$	$10^4\Delta n$
2,4,6-*Tribromo*-N-*methylaniline in dioxan*			
12,885	187	664	15
21,475	311	1107	25
29,327	425	1507	34
37,791	548	1944	44
46,525	674	2391	54
57,725	836	2965	67
N-*Methyl*-p-*nitroaniline in benzene*			
517	173	17	—
942	317	32	—
1521	511	57	—
2035	680	72	—
2675	893	98	—
3384	1133	121	—
N-*Methyl*-p-*nitroaniline in dioxan*			
1786	742	32	5
3359	1406	65	9
5372	2251	99	13
6842	2867	129	18
9486	3970	180	23
12,675	5304	233	31
N-*Methyl*-2,4-*dinitroaniline in benzene*			
353	75	15	—
615	133	27	—
1174	256	51	—
1614	363	73	—
2060	463	91	—
N-*Methyl*-2,4-*dinitroaniline in dioxan*			
683	181	21	1
1809	498	52	3
2472	655	73	4
3094	861	93	6
4029	1114	123	8

TABLE 3.

N-Methylaniline derivative	Solvent	100α	$-10^3\beta$	$10^3\gamma$	$P_{2\infty}$ (c.c.)	$[R_D]$ (c.c.)	μ (D)
p-Bromo-	Benzene	662	481	223	268·3	44·1	3·31
	Dioxan	871	303	382	303·3	44·4	3·56
2,4-Dibromo-	Benzene	363	621	228	222·5	52·2	2·86
	Dioxan	480	442	371	250·3	53·4	3·10
2,4,6-Tribromo-	Benzene	109	690	206	117·1	59·3	1·68
	Dioxan	145	514	331	127·5	60·5	1·81
p-Nitro-	Benzene	3350	358	—	933·8	[42·4]	6·82
	Dioxan	4185	187	690	1085·7	49·3	7·12
2,4-Dinitro-	Benzene	2250	442	—	865·0	[49·0]	6·36
	Dioxan	2765	300	560	932·6	52·3	6·58

discussion were calculated on the assumption that ${}_{\mu}P = {}_{\mathrm{T}}P - [R_D]$. The assumption that the distortion polarisation is represented by 1·05 $[R_D]$ leads to values 0·01—0·02 D lower.

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