16. *Steric Repression of the Mesomeric Effect in Derivatives of* NN-*Di-methylaniline. The Mesomeric Moments of Amino-, Methylamino-, and Dimethylamino-groups.*

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In benzene solution the dipole moments of α-naphthylamine, *NN*-di-methyl-*o*-toluidine, and *NN*-dimethyl-α-naphthylamine are 1·50, 0·95, and 1·06 D, respectively, indicating that in the last two compounds steric repression of the mesomeric effect of the dimethylamino-group must be very strong. The value for *NN*-dimethyl-*o*-toluidine supports the view that in *NN*-dimethylmesidine the axis of the dipole is directed with its negative end away from the aromatic ring.

Evidence regarding the magnitudes of the mesomeric moments in aniline, *N*-methylaniline, and *NN*-dimethylaniline is reviewed and shown to indicate that the vector differences between the moments of these molecules and the " primary dipoles " of the amino-groups are 1·42, 1·66, and 1·69 D, respect-ively, whilst their components arising solely from the mesomeric effect are about 1·67, 1·93, and 2·06 D, respectively.

As is shown in Table 1, the dipole moments of *NN*-dimethylmesidine and 2,4,6-tribromo-*NN*-dimethylaniline are almost equal and much lower than the dipole moment of *NN*-di-methylaniline, suggesting that the mesomeric effect of the dimethylamino-group may be repressed completely by the steric effects arising in these compounds. On the other hand, the relative values of the dipole moments of *N*-methylaniline, *N*-methylmesidine, 2,4,6-tribromo-*N*-methylaniline, and 2,4-dibromo-*N*-methylaniline suggest that steric inhibition of the mesomeric effect of the methylamino-group is strong in the presence of two *o*-methyl groups, but only slight in the presence of two *o*-bromine atoms and non-existent with only one *o*-bromine atom. These observations were interpreted [1] as indicating that the molecules cannot take up conformations with the *N*-methyl groups near an *o*-methyl or an *o*-bromine atom, or with the amino-hydrogen atom near to an *o*-methyl group. On the other hand, the methylamino-group seems to be able to assume a conformation with the amino-hydrogen atom near an *o*-bromine atom, so that in 2,4,6-tribromo-*N*-methylaniline a conformation is possible which does not permit so great a π-orbital overlap as does the

TABLE 1. *Observed and calculated values of the dipole moments of amines.*

	Unsubstituted		*N*-Methyl		*NN*-Dimethyl	
	Obs. (D)	Calc. (D)	Obs. (D)	Calc. (D)	Obs. (D)	Calc. (D)
Aniline	1·53 [a]	—	1·68 [a]	—	1·61 [a,b]	—
Mesidine	1·45 [c]	1·53	1·22 [c]	1·68	1·03 [d]	1·61
2,4-Xylidine	1·40 [e]	1·45 *	1·54 [e]	1·57 *	0·71 [e]	1·49 *
o-Toluidine	1·59	1·69 *	1·76 [e]	1·86 *	0·96	1·79 *
2,4,6-Tribromoaniline ...	1·73 [f]	>1·53	1·68 [f]	>1·68	1·02	>1·61
2,4-Dibromoaniline	2·65 [g]	>2·45 *	2·88 [g]	>2·62 *	—	—
α-Naphthylamine	1·50	—	—	—	1·06	∼1·58

* Calc. on the basis of free rotation about the N–C bond.
[a] Few and Smith, *J.*, 1949, 753. [b] Everard, Kumar, and Sutton, *J.*, 1951, 2807. [c] Smith, *J.*, 1953, 109. [d] Ingham and Hampson, *J.*, 1939, 981. [e] Fischer, *Acta Chem. Scand.*, 1950, **4**, 1197. [f] Few and Smith, *J.*, 1949, 2663. [g] Smith and Walshaw, *J.*, 1957, 4527.

most favourable conformation of *N*-methylaniline itself, but which nevertheless furnishes appreciable overlap without bringing the *N*-methyl group very near a bromine atom. In *N*-methylmesidine and the trisubstituted *NN*-dimethylanilines the analogous conform-ations seem to be impossible; so in the latter type of compound the methyl groups must be disposed on opposite sides of the plane of the aromatic ring, thereby making the overlap

[1] Smith and Walshaw, *J.*, 1959, 3784.

of the lone-pair orbital with the π-orbital system of the ring very small. As an amino-hydrogen atom must be effectively smaller than a N-methyl group the repression of the mesomerism, though very strong, may not be quite so complete in N-methylmesidine as in NN-dimethylmesidine.

If these views are correct it would be expected that the mesomeric effect of the dimethylamino-group would also be strongly sterically inhibited by one obstructive *ortho*-group, such as a methyl group, since at one of the positions of nearest approach of the *o*-methyl and N-methyl groups the second N-methyl group would be very close to the *o*-hydrogen atom (A, Fig. 1), whilst at the other position the two N-methyl groups would

FIG. 1.

(A)   (B)   (C)
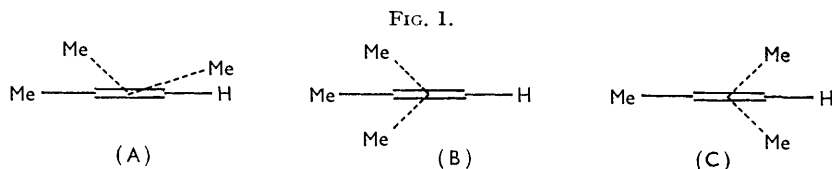
be at opposite sides of the plane of the ring (B). In fact, the conformation (C), with both N-methyl groups remote from the *o*-methyl group, would be expected to be preferred. In this connexion Wepster [2] has observed that the ultraviolet absorption spectra and relative basic strengths of the amines indicate that the steric inhibition of mesomerism in NN-dimethyl-*o*-toluidine is equal to that in N-methylmesidine, but less than that in NN-dimethylaminodurene. These measurements, however, depend also on the excited states and on the conformations assumed by the $NMeH_2^+$ or NMe_2H^+ groups in the ions, respectively, and it is interesting that his molecular-refraction values appear to show less differences between the steric effects in these compounds.

In view of these facts the dipole moments of NN-dimethyl-*o*-toluidine and NN-dimethyl-α-naphthylamine have now been determined from measurements on benzene solutions, the values obtained being 0·95 and 1·06 D, respectively. Owing to wide divergencies in the literature, the moment of α-naphthylamine has also been redetermined and found to be 1·50 D. As the dipole moment of aniline is 1·53 D, the dipole moment of NN-dimethyl-α-naphthylamine would, in the absence of steric effects, be expected to be only slightly less than that of NN-dimethylaniline. The observed value, however, is close to, but slightly higher than, the moment of NN-dimethylmesidine, so the evidence suggests that there is very strong, but possibly not quite complete, repression of mesomerism. This is compatible with the chemical evidence afforded by the fact that NN-dimethyl-4-nitroso-α-naphthylamine, unlike NN-dimethyl-*p*-nitrosoaniline, is unstable.[3]

Steric inhibition of mesomerism must also be strong in NN-dimethyl-*o*-toluidine. The dipole moments of toluene (0·37 D), NN-dimethylaniline (1·61 D), and NN-dimethyl-*p*-toluidine [4] (1·29 D), calculated by Marsden and Sutton's method,[4] indicate that in NN-dimethylaniline the angle of inclination of the dipole axis to the 1–4 axis of the ring (θ) is 30°. Similarly, calculation from the moments of NN-dimethylaniline and $NNN'N'$-tetramethyl-*p*-phenylenediamine [5] (1·12 D), by use of Williams's equation,[6] indicates [7] that the component of the moment of the former at right angles to the 1–4 axis is 0·79 D, and this leads to $\theta = 29\cdot5°$ or 150·5°, of which the former is obviously the value to be accepted. In view of the critical dependence of the derived value of θ upon the exact values of the dipole moments used in the calculations, the agreement between the two methods is remarkably good. If we assume that for NN-dimethylaniline $\theta = 29\cdot5°$, the

² Wepster, *Rec. Trav. chim.*, 1957, **76**, 357.
³ Gokhlé and Mason, *J.*, 1930, 1757.
⁴ Marsden and Sutton, *J.*, 1936, 599.
⁵ Everard, Kumar, and Sutton, *J.*, 1951, 2807.
⁶ Williams, *Z. phys. Chem.*, 1928, **130**, *A*, 75.
⁷ Everard and Sutton, *J.*, 1951, 2818.

resultant moment of *NN*-dimethyl-*o*-toluidine should be about 1·79 D for free rotation of the dimethylamino-group about the N–C bond or for the conformation in which this group lies as nearly coplanar as possible with the ring. The very much lower observed value indicates strong steric inhibition of mesomerism.

On the assumption that the component of the moment at right angles to the 1–4 axis is the same (0·79 D) in both *NN*-dimethylaniline and *NN*-dimethylmesidine, Everard and Sutton [8] deduced that the component of the dipole moment of the latter compound along the 1–4 axis is ±0·66 D. The dipole moment of *NN*-dimethyl-2,6-xylidine [9] (0·94 D) being less than that of *NN*-dimethylmesidine, the negative value is indicated, showing that for the latter compound θ = 139°. If mesomerism were restricted to the same extent in *NN*-dimethyl-*o*-toluidine as in *NN*-dimethylmesidine, the calculated moments for the conformations B and C (Fig. 1) of the former compound would be 1·21 and 0·67 D,

FIG. 2.
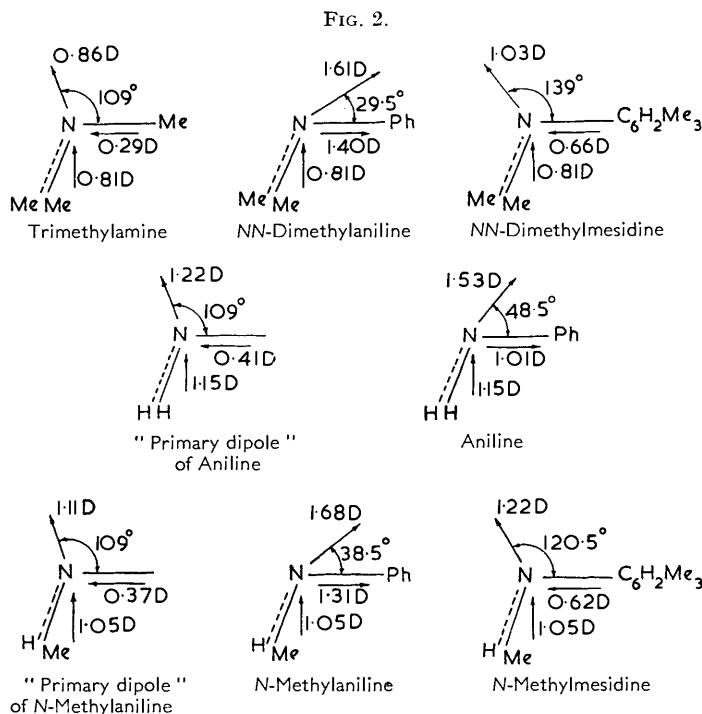
respectively, and that for free rotation about the N–C bond 0·98 D. The observed dipole moment is therefore much nearer the value expected if mesomerism were as restricted as in *NN*-dimethylmesidine than it is to that for no restriction. It is, in fact, compatible with a very strong, but not necessarily complete, restriction of mesomerism, accompanied by a slight preference for the conformation with the methyl groups remote. The experimental value also supports Everard and Sutton's assignment of the sense of the component of the moment of *NN*-dimethylmesidine along the 1–4 axis: if this were +0·66 D, the dipole moment of *NN*-dimethyl-*o*-toluidine should be at least 0·97 D for conformation C and 1·40 D for conformation B.

The present measurements, which indicate that one *ortho*-substituent suppresses the mesomeric effect of the dimethylamino-group strongly, also support the view that in *NN*-dimethylmesidine this effect may be repressed completely. This lends additional weight, therefore, to Everard and Sutton's calculation of the true mesomeric moment in

[8] Everard and Sutton, *J.*, 1951, 2821.
[9] Fischer, *Acta Chem. Scand.*, 1950, **4**, 1197.

NN-dimethylaniline. The value of this may be deduced rather more simply in the following way. In benzene solution the dipole moment of trimethylamine [10] is 0·86 D, and, since the C–N–C angles are near the tetrahedral value,[11] the components of this moment along and at right angles to one of the N–C bonds, as shown in Fig. 2, are therefore −0·29 and +0·81 D, respectively. The latter is almost equal to the component at right angles to the 1–4 axis in *NN*-dimethylaniline, so the change in moment on passing from trimethylamine to dimethylaniline can be represented by a component of 1·40 + 0·29 = 1·69 D along the 1–4 axis. This will include contributions arising from induction and from the change in type of the carbon orbitals used in the N–C and C–H bonds, as well as from the mesomeric effect. However, if the mesomeric effect is assumed to be repressed completely in *NN*-dimethylmesidine, the difference between the component of its moment along the 1–4 axis (−0·66 D) and that of trimethylamine along an N–C bond (−0·29 D) can be taken as a measure of the first two effects. As a result the true mesomeric moment of *NN*-dimethylaniline appears to be 1·69 + 0·37 = 2·06 D. This confirms the value suggested by Everard and Sutton (2·04 D), but is less than that derived by Ingold [12] on the extreme assumption that the aromatic dimethylamino-group becomes co-planar with the ring.

The corresponding calculation of the mesomeric moment of aniline is not quite so straightforward. In benzene solution the dipole moment of ammonia [10] is 1·45 D, whilst the H–N–H valency angle [11] is about 107°. Hence the components of the moment along and at right angles to one of the N–H bonds are −0·54 and 1·34 D, respectively. If the effective moments of the N–H bonds and their dispositions remained the same in aniline ($\mu = 1·53$ D) as in ammonia, the angle θ for aniline would be $\sin^{-1}$ (1·34/1·53) (= 61°). When this is taken in conjunction with the dipole moment of toluene (0·37 D), the calculated moments of *p*-toluidine, *m*-toluidine, and *p*-phenylenediamine are 1·39, 1·48, and 1·89 D, respectively, whereas the observed values are 1·32, 1·45, and 1·60 D, respectively.[6,13] On the other hand, combination of these experimental moments with those of aniline and toluene leads to angles θ of 49°, 48·5°, and 48°, respectively, with a component to the moment of aniline at right angles to the 1–4 axis of 1·15, 1·15, and 1·14 D, respectively. With some confidence, therefore, θ can be taken as about 48·5°, and the components along and at right angles to the 1–4 axis as 1·01 and 1·15 D, respectively (see Fig. 2). It is apparent, therefore, that the component at right angles to the N–C bond in aniline is reduced, as compared with that at right angles to the N–H bond in ammonia. Nevertheless, if the primary moment is assumed to be directed at the tetrahedral angle to this bond, its value must be about 1·22 D, and its component along the 1–4 axis −0·41 D. The sum of the mesomeric and the inductive moment, and the effects arising from the change in state of hybridisation of the carbon orbitals, is therefore 1·01 + 0·41 = 1·42 D. This is appreciably greater than the value (1·02 D) suggested by Everard and Sutton. The separate contributions from the various effects are difficult to assess, but if, by analogy with the figures for *NN*-dimethylaniline, the sum of the contributions from the inductive effect and from the change in carbon bonding orbitals are taken as −0·25 D, the true mesomeric moment of aniline becomes 1·67 D.

Similarly, from the dipole moments of *N*-methylaniline (1·68 D), *N*-methyl-*p*-toluidine [9] (1·41 D), and toluene it may be deduced that in *N*-methylaniline θ is 38·5°, the components of the moment along and at right angles to the 1–4 axis being 1·31 and 1·05 D, respectively. As the largest contribution to the primary moment must come from the lone-pair orbital, this primary moment may still be taken as being at about the tetrahedral angle to the 1–4 axis, in which case its value must be 1·11 D and its component along the 1–4 axis

[10] Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374.

[11] Sutton, " Tables of Interatomic Distances and Configurations in Molecules and Ions," Chem. Soc. Spec. Publ. No. 11, 1958.

[12] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 102.

[13] Smith and Walshaw, *J.*, 1957, 4527.

—0·37 D. Hence the sum of the effects due to mesomerism, induction, and change of orbital character comes to $1·31 + 0·37 = 1·68$ D. Further, there is evidence that mesomerism is strongly inhibited in N-methylmesidine [14] (μ 1·22 D). If the component to the moment at right angles to the 1–4 axis in this compound is the same as in N-methylaniline, the component along this bond must be $\pm 0·62$ D. No guidance as to which of these values should be taken can be obtained from the moment of N-methyl-2,6-xylidine, which has been reported [9] as 1·28 D, whereas the calculated values are 1·44 and 1·08 D, respectively. In view of the undoubtedly strong inhibition of mesomerism in N-methylmesidine, however, it seems reasonable to take the component along the 1–4 axis as —0·62 D. It follows, therefore, that the sum of the components arising from induction and change in state of orbital hybridisation must be at least —0·25 D and the true mesomeric moment at least 1·93 D.

EXPERIMENTAL

Materials.—Thiophen-free benzene was purified by repeated crystallisation, followed by drying over sodium.

α-Naphthylamine was distilled twice *in vacuo*, and then crystallised from light petroleum (b. p. 60—80°): it had m. p. 50·0°.

NN-Dimethyl-α-naphthylamine was prepared from α-naphthylamine and dimethyl sulphate by Gokhle and Mason's method [3] and distilled *in vacuo*. It had b. p. 120°/10 mm., n_D^{25} 1·6202, d_4^{25} 1·0377, whence $[R_D] = 58·0$ c.c. (Perkin [15] gave d_{25}^{25} 1·0391, d_4^{25} 1·0361).

Commercial " pure " NN-dimethyl-o-toluidine was distilled, the middle fraction (b. p. 184—185°/758 mm.) being used. It had n_D^{25} 1·5240, d_{25}^{25} 0·9238, whence $[R_D] = 44·8$ c.c. (Ley and Pfeiffer [16] gave b. p. 184·6—185·4/762 mm., n_D^{20} 1·52548, d_4^{25} 0·9287).

Methods and Results.—The solutions were prepared under anhydrous conditions and the dielectric constants (relative to benzene $= 2·2741$), specific volumes, and refractive indices determined at 25·0° by the method previously described.[17]

TABLE 2.

	α-Naphthylamine				NN-Dimethyl-α-naphthylamine		
100w	ε	v	n_D	100w	ε	v	n_D
0·0000	2·2741	1·14460	1·4980	0·0000	2·2741	1·14460	1·4980
1·1550	2·2991	1·14145	1·4997	1·3476	2·2875	1·14208	1·4993
1·8302	2·3138	1·13965	1·5007	2·1849	2·2960	1·14050	1·5002
3·1029	2·3420	1·13611	1·5028	3·1932	2·3061	1·13863	1·5012
4·1113	2·3146	1·13336	1·5042	4·8121	2·3220	1·13556	1·5032
				6·4270	2·3376	1·13262	1·5051
				7·2675	2·3457	1·13108	1·5058

$\alpha = 2·15$, $\beta = -0·2735$, $\gamma = 0·453$.
$P_{2\infty} = 95·0$ c.c., $[R_D] = 48·9$ c.c.
$\mu = 1·50$ D (lit.,[18] 1·44 — 1·53 D).

$\alpha = 1·014$, $\beta = -0·1868$, $\gamma = 0·319$.
$P_{2\infty} = 81·5$ c.c., $[R_D] = 58·5$ c.c.
$\mu = 1·06$ D.

NN-Dimethyl-o-toluidine

100w	ε	v	n_D	100w	ε	v	n_D
0·0000	0·2741	1·14460	1·4980	4·5905	2·3087	1·14204	1·4989
1·2794	2·2837	1·14389	1·4982	6·3047	2·3213	1·14104	1·4992
2·9190	2·2960	1·14299	1·4985	8·3296	2·3367	1·13982	1·4996
4·2274	2·3057	1·14222	1·4988				

$\alpha = 0·75$, $\beta = -0·0564$, $\gamma = 0·056$.
$P_{2\infty} = 62·9$ c.c., $[R_D] = 44·6$ c.c., $\mu = 0·95$ D (Fischer [9] found $\mu = 0·88$ D).

The results are recorded in Table 2, 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 dipole moments derived from these data, and the values for other substances referred to in the discussion, are all calculated on the assumption that $_\mu P = {}_T P - [R_D]$.

[14] Smith, *J.*, 1953, 109.
[15] Perkin, *J.*, 1895, **69**, 1213.
[16] Ley and Pfeiffer, *Ber.*, 1921, **54**, 363.
[17] Few and Smith, *J.*, 1949, 753.
[18] Wesson, " Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.

The moment now found for α-naphthylamine differs from that of Cowley and Partington [19] principally on account of the different $[R_D]$ value used.   The experimental figure (48·9 c.c.) is in agreement with the value calculated by adding the difference between the molar refractions of naphthalene (44·4 c.c.) and benzene (26·2 c.c.) to that of aniline (30·7 c.c.).   On the other hand, the experimental values of $[R_D]$ for *NN*-dimethyl-α-naphthylamine and *NN*-dimethyl-*o*-toluidine, whether deduced from the measurements on the solutions or from the properties of the pure liquids, are appreciably less than the values calculated in a similar way from the molar refraction of *NN*-dimethylaniline.   This furnishes additional evidence for strong steric inhibition of mesomerism in their molecules.

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[19] Cowley and Partington, *J.*, 1938, 1598.