A Dipole Moment Study of the *ortho*-Effect in Di- and Tri-substituted *NN*-Dimethylanilines

By **Geoffrey Hallas**, Department of Colour Chemistry, The University, Leeds LS2 9JT
John D. Hepworth and **Peter Jones**, Division of Chemistry, Preston Polytechnic, Preston PR1 2TQ
Douglas A. Ibbitson and **Alan M. Jones**, Division of Chemistry and Materials Science, Derby College of Art and Technology, Kedleston Road, Derby DE3 1GB

Apparent dipole moments in benzene of 2-methyl-, 2,3-, 2,4-, 2,5-, 2,6-, and 3,5-dimethyl-, 4-bromo-2,6-dimethyl, 2,6-dimethyl-4-nitro-, 2,4,6-trimethyl-, and 2,4,6-tribromo-*NN*-dimethylaniline have been determined. Values for the magnitude and direction of the *NN*-dimethylaniline moment necessary to explain the dipole moments of six of these compounds are discussed in terms of the rotation of the dimethylamino-group from its position of maximum conjugation with the ring and the consequent change in vector moment in the direction of the major axis of the ring. The effect of *p*-substitution in restoring some conjugation between the dimethylamino-group and the ring is also noted.

IN the course of a study of the *ortho*-effect in some 2-trifluoromethyl-*NN*-dimethylanilines, attention was once again drawn to the difficulties in explaining the dipole moments of hindered methyl-substituted *NN*-dimethylanilines.[1,2a] A repeat determination of the moment of 2,4,6,*NN*-pentamethylaniline in benzene gave a value of 0.64 D rather than the previously accepted [3] value of 1.03 D. In view of this difference, it was decided to determine and, by using the former value, to attempt to rationalise the explanation of the dipole moments of 2-methyl-, 2,3-, 2,4-, 2,5-, 2,6-, and 3,5-dimethyl-, 2,6-dimethyl-4-bromo-, 2,6-dimethyl-4-nitro-, 2,4,6-trimethyl-, and 2,4,6-tribromo-*NN*-dimethylaniline.

EXPERIMENTAL

The apparent dipole moments were calculated as described previously [4] from experimental measurements at 25.0 °C of dielectric constant, specific volume, and refractive index to the sodium D-line [listed in Supplementary Publication No. SUP 21953 (11 pp.) †] of a series of dilute solutions of graded concentration of each solute in benzene. The slopes (α, β, and ν, respectively) of the linear graphs of dielectric constant, specific volume, and refractive index squared against weight fraction, together with polarisation data, in which the symbols have their usual significance, and the computed dipole moments (μ) are given in the Table.

Materials.—Benzene was purified as previously.[5] The solutes, which gave satisfactory microanalytical data and n.m.r. spectra, were distilled under reduced pressure immediately before use and were shown to be pure by g.l.c. 2,6-Dimethylaniline reacted with 2,4,4,6-tetrabromocyclohexa-2,5-dienone [6] to yield the 4-bromo-derivative, m.p. 49° [from light petroleum (b.p. 60—80 °C)].[7] Tertiary amines were prepared from the primary amines by reaction

Polarisation data and dipole moments (μ) at 25.0 °C for solutions in benzene

Derivative of *NN*-dimethylaniline	B.p. (°C) [mmHg] (m.p.)	α	β	ν	$P_{2\infty}$/cm^3	$_EP_2$/cm^3	μ/D
2-Methyl-	45 [1.0]	0.723 (0.044) [d]	−0.062 (0.001)	0.069 (0.002)	62.02	44.68	0.92 (0.88 [a]) (0.03)
2,3-Dimethyl-	63—64 [1.0]	0.443 (0.026)	−0.055 (0.003)	0.071 (0.004)	60.91	49.67	0.74 (0.02)
2,4-Dimethyl-	61 [1.0]	0.415 (0.017)	−0.041 (0.004)	0.052 (0.001)	60.70	49.73	0.73 (0.71 [a]) (0.015)
2,5-Dimethyl-	59 [1.0]	0.619 (0.021)	−0.035 (0.001)	0.059 (0.002)	66.71	50.19	0.90 (0.01)
2,6-Dimethyl-	51 [1.0]	0.524 (0.026)	−0.041 (0.001)	0.021 (0.006)	63.72	48.85	0.85 (0.94 [a]) (0.015)
3,5-Dimethyl-	88 [2.0]	1.263 (0.038)	−0.056 (0.005)	0.117 (0.003)	83.81	50.94	1.27 (0.02)
4-Bromo-2,6-dimethyl-	100 [1.5] (32)	2.807 (0.033)	−0.340 (0.002)	0.100 (0.007)	175.07	58.14	2.39 (0.01)
2,6-Dimethyl-4-nitro-	(67—68)	15.319 (0.136)	−0.221 (0.009)	0.184 (0.014)	613.18	59.39	5.20 (0.02)
2,4,6-Trimethyl-	70 [1.5]	0.256 (0.011)	−0.025 (0.002)	0.012 (0.002)	62.31	53.93	0.64 (1.03 [b]) (0.01)
2,4,6-Tribromo-	143 [2.5]	0.496 (0.020)	−0.645 (0.006)	0.159 (0.008)	86.74	63.30	1.07 (1.05 [c]) (0.02)

[a] I. Fischer, *Acta. Chem. Scand.*, 1950, **4**, 1197; *Nature*, 1950, 165, 239. [b] Ref. 3. [c] Ref. 1*a*. [d] Figures in parentheses are standard deviations from the slopes, α, β, ν, of the regression lines and, in the last column, from μ.

---

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin II*, 1975, Index issue.

[1] (*a*) A. V. Few and J. W. Smith, *J. Chem. Soc.*, 1949, 2663; (*b*) H. B. Watson, *Ann. Reports*, 1939, **36**, 219.

[2] J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955, (*a*) p. 216; (*b*) p. 215.

[3] C. E. Ingham and G. C. Hampson, *J. Chem. Soc.*, 1939, 981.

[4] J. D. Hepworth, J. A. Hudson, D. A. Ibbitson, and G. Hallas, *J.C.S. Perkin II*, 1972, 1905.

[5] J. D. Hepworth, D. A. Ibbitson, A. J. Williams, and G. Hallas, *J.C.S. Perkin II*, 1972, 2298.

[6] G. J. Fox G. Hallas, J. D. Hepworth, and K. N. Paskins, *Org. Synth.*, 1975, **55**, 20.

[7] M. Gillois and P. Rumpf, *Bull. Soc. chim. France*, 1954, 112.

[8] J. H. Billman, A. Radike, and B. W. Mundy, *J. Amer. Chem. Soc.*, 1942, **64**, 2977; W. A. Sheppard, *Org. Synth.*, 1969, **49**, 111.

with trimethyl phosphate,[8] any remaining primary or secondary amines being removed by reaction with acetic anhydride, and had the b.p.s indicated in the Table.

DISCUSSION

Inhibition of the mesomeric effect of the dimethylamino-group by *ortho*-methyl groups is illustrated by a comparison of the moments of *NN*-dimethylaniline (1.57 D) [9] and 2,4,6,*NN*-pentamethylaniline (1.03 D).[3] Such a reduction in moment must be due to a twisting of the dimethylamino-group from its position of maximum conjugation with the ring. The present value of 0.64 D for the dipole moment of the latter compound seems more reasonable, however, in that the moments of *NN*-dimethylaniline (1.57 D), 2,4,6,*NN*-pentamethylaniline (0.64 D), and 2,4,6-tribromo-*NN*-dimethylaniline (1.05 D) [2b] are now more consistent with those of aniline (1.53 D), 2,4,6-trimethylaniline (1.40 D), and 2,4,6-tribromoaniline (1.73 D).[2b] In each series, the effect of *ortho*-bromine atoms is to cause an increase in moment relative to the analogous methyl-substituted compound. The discrepancy in the literature value for the dipole moment of 2,4,6,*NN*-pentamethylaniline could be explained if the previous sample [3] contained secondary amine as impurity. In this connection, we experienced considerable difficulty in preparing samples of this compound which gave satisfactory n.m.r. spectra and g.l.c. traces. Although not resolving the question of purity, some discrepancy in literature b.p. is observed. Whereas Nomura and Takeuchi [10] recorded a value of 186°, we, like Ingham and Hampson [3] used samples of b.p. 213°, which in addition gave consistent values for α, the slope of the dielectric constant *vs.* weight fraction plot.

In an attempt to assess the effect of *ortho*-methyl-groups on the magnitude and direction of the *NN*-dimethylaniline moment as a whole, a value for the angle (γ) between the direction of this moment and the major axis of the ring in *NN*-dimethylaniline was first calculated. Vector addition [11] of the moments of *NN*-dimethylaniline (1.57 D), toluene (0.37 D), and 3,5,*NN*-tetramethylaniline (1.27 D) gave a value of 31° 39′ for γ, whereas Smith,[12] using two alternative procedures, obtained values of 30° and 29° 30′. Polarisability studies by Aroney *et al.*[13] indicated that real values for the *NN*-dimethylaniline semi-axes eventuate only if $\gamma < 20°$.

It is now accepted that under steric influences of groups situated *ortho* to the dimethylamino-group the latter group is twisted from its position of maximum conjugation with the ring.[14,15] By using the observed moments of 2,*NN*-trimethylaniline (0.92 D) and 2,4,*NN*-tetramethylaniline (0.73 D) and a moment of 0.90 D for the dimethylamino-group (from the moment of 2,5,*NN*-tetramethylaniline) it is calculated vectorially that γ increases from 31° 39′ as in *NN*-dimethylaniline to 61° 55′, and simultaneously the dimethylamino-group twists through 30° [*cf.* angles of twist of 17° and 50° (refs. 15*a* and 10)]. It is assumed in this calculation that no in-plane displacement of the *o*-methyl group occurs, the C(ring)–CH_3 bond moment being 0.37 D. The increase in γ can be explained by diminished conjugation of the dimethylamino-group with the ring giving rise to a reduction in magnitude and even a change in sign of the vector moment which acts towards the ring carbon atom and in the direction of the N–C(ring) bond in *NN*-dimethylaniline. We have calculated an angle of twist of the dimethylamino-group of 30° by using an alternative procedure, assuming (i) a regular tetrahedral geometry of the dimethylamino-group in which all CNC angles are equal, and the group is close to planarity with the ring, and (ii) that the change in moment of this group as it rotates from its position of maximum conjugation with the ring is explained by a vector moment change in the direction of the C(ring)–N bond. It is likely that a buttressing effect caused by adjacent methyl groups would reduce the *NN*-dimethylaniline group moment in 2,3,*NN*-tetramethylaniline below 0.90 D, and increase both γ and the angle of twist of the dimethylamino-group. In terms of this alternative procedure, an angle of twist of 45° explains the dipole moment of this compound.

With regard to the di-*ortho*-methyl-substituted compounds, by taking the observed moments of 2,6,*NN*-tetramethylaniline and 2,4,6,*NN*-pentamethylaniline as 0.85 and 0.64 D respectively, a value of γ of 68° 11′ may be calculated. An even greater reduction in the vector moment acting in the direction of the N–C(ring) bond is thereby implied, and brought about, presumably, by further twisting, and loss of conjugation with the ring, of the dimethylamino-group. By assuming a moment of 0.64 D for the *NN*-dimethylaniline group, acting at an angle of 68° 11′, it is possible to calculate the moments of 2,6-dimethyl-4-bromo- and 2,6-dimethyl-4-nitro-*NN*-dimethylaniline as 2.25 and 4.66 D, respectively, taking C(ring)–Br and C(ring)–NO_2 group moments as 1.56 and 4.01 D, respectively. These calculated moments are smaller than the respective observed moments (2.39 and 5.20 D), suggesting that *para*-substitution by electron-withdrawing groups restores some conjugation between the dimethylamino-group and the ring; the nitro-group has a greater effect than bromine.

The solvent used in the above dipole moment measurements, benzene, is not the most ideal and certainly is not the least interacting of solvents, but it does not produce the solubility difficulties often experienced with cyclo-

---

[9] A. L. McClellan, ' Tables of Experimental Dipole Moments ' Freeman, San Francisco and London, 1963.

[10] Y. Nomura and Y. Takeuchi, *Org. Magnetic Resonance*, 1969, **1**, 213.

[11] R. A. Y. Jones, A. R. Katritzky, and A. V. Ochkin, *J. Chem. Soc.* (*B*), 1971 1795.

[12] J. W. Smith, *J. Chem. Soc.*, 1961, 81.

[13] M. J. Aroney, R. J. W. LeFèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*) 1968, 507.

[14] T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J.C.S. Perkin II*, 1974, 289; L. V. Vilkov and T. P. Timasheva, *Doklady Akad. Nauk S.S.S.R.*, 1965, **161**, 351.

[15] (*a*) S. A. Cowling and R. A. W. Johnson, *J. Electron Spectra and Related Phenomena*, 1973, **2**, 161; (*b*) M. L. Filleux-Blanchard, J. Fieux, and J. C. Halk, *Chem. Comm.*, 1971, 851; (*c*) R. K. MacKenzie and D. D. MacNicol, *ibid.*, 1970, 1299.

hexane, hexane, and heptane. However, changes in the electrical environment of the dimethylamino-group may lead to changes in solution geometry which alone may or may not produce important dipole moment changes. Since the magnitudes of such changes are unknown, it is impossible to include them in the above analysis.

[6/678 *Received, 7th April,* 1976]