Dipole Moment Study of the *ortho*-Effect in 4-Substituted *NN*-Dimethyl-2-trifluoromethylanilines

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Apparent dipole moments in benzene of a series of eight 4-substituted derivatives of *NN*-dimethyl-2-trifluoromethylaniline have been determined. Vector moments in the direction of the major axis of the ring have been calculated in order to explain the observed dipole moments. These vector moments are compared with corresponding values calculated for 4-substituted derivatives of *NN*-dimethylaniline. The influence of the 2-trifluoromethyl group on the extent to which *para*-substitution restores conjugation between the dimethylamino-group and the ring is noted.

In a previous study [1] of the *ortho*-effect in some 2-methyl- and 2,6-dimethyl-*NN*-dimethylanilines, attention was drawn to the effect brought about by the *para*-substitution of electron-withdrawing groups in partly restoring conjugation between the dimethylamino-group and the ring. A nitro-group was found to have a greater effect than bromine. In view of speculation about the nature of the electrical effect operative in the trifluoromethyl group,[2] it was considered of interest to study the influence of this group, when substituted *ortho* to the dimethylamino-group, on the extent to which *para*-substituents restored conjugation. Consequently, apparent dipole moments in benzene of a series of eight 4-substituted *NN*-dimethyl-2-trifluoromethylanilines have now been determined.

EXPERIMENTAL

The apparent dipole moments were calculated as described previously [3] from experimental measurements at 25.0 °C of dielectic constant, specific volume, and refractive index to sodium D line [listed in Supplementary Publication No. 22454 (10 pp.)] † of a series of dilute solutions of graded concentration of each solute in benzene. The range of weight fractions employed was generally 0.001—0.01. The slopes, α, β, and ν, respectively, of 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 Table 1. N.m.r. spectra were obtained with a Varian HA 100 spectrometer for solutions in deuteriochloroform at the Physicochemical Measurements Unit, Harwell.

Table 1

Polarisation data and dipole moments (μ) at 25 °C for solutions of 4-substituted derivatives of *NN*-dimethyl-2-trifluoromethylaniline in benzene

4-Substituent	α	β	ν	$P_{2,\infty}$/cm³	${}_{\mathrm{E}}P_2$/cm³	μ/D
H	5.031	−0.283	−0.136	227.64	42.90	3.01 ± 0.015
Me	5.113	−0.262	−0.134	255.70	47.36	3.19 ± 0.016
Cl	4.639	−0.368	−0.069	246.93	48.01	3.12 ± 0.011
Br	3.799	−0.451	−0.056	246.98	51.61	3.09 ± 0.012
I	3.214	−0.574	0.044	244.15	55.37	3.04 ± 0.020
CN	14.270	−0.354	0.035	624.50	51.03	5.30 ± 0.007
NO_2	15.392	−0.470	0.149	654.33	52.94	5.42 ± 0.021
NMe_2	7.064	−0.245	−0.025	370.80	60.13	3.90 ± 0.006
NH_2	7.391	−0.335	−0.014	333.22	47.94	3.74 ± 0.006

Materials.—Benzene was purified as previously.[2] The solutes, which were prepared as previously described or as indicated below, gave satisfactory microanalyses and n.m.r. spectra and were shown to be pure by g.l.c. 4-Dimethylamino-3-trifluoromethylaniline had m.p. 39—40 °C; [4] 4-bromo-*NN*-dimethyl-2-trifluoromethylaniline had b.p. 136—137 °C at 20 mmHg; [4] *NN*-dimethyl-2-trifluoromethylaniline had b.p. 169—170 °C; [4] *NN*-dimethyl-4-nitro-2-trifluoromethylaniline had m.p. 44.5—45 °C.[4]

4-*Chloro*-NN-*dimethyl*-2-*trifluoromethylaniline*.—An ice-cold solution of 4-dimethylamino-3-trifluoromethylaniline (10.2 g) in concentrated hydrochloric acid (40 cm³) and water (20 cm³) was diazotised by the dropwise addition of a solution of sodium nitrite (3.7 g) in water (25 cm³). The diazonium salt solution was poured into a solution of freshly prepared copper(I) chloride [from copper(II) sulphate (16 g)] in concentrated hydrochloric acid (60 cm³). When the initial reaction had subsided, the mixture was heated at 60—70° for 1 h, basified, and distilled in steam. From the distillate, there was obtained 4-*chloro*-NN-*dimethyl*-2-*trifluoromethylaniline* (74%), b.p. 92 °C at 25 mmHg (Found: C, 48.2; H, 4.0; Cl, 15.9; F, 25.6; N, 6.4. $C_9H_9ClF_3N$ requires C, 48.3; H, 4.1; Cl, 15.8; F, 25.5; N, 6.3%), τ 7.30 (6 H, s, NMe_2), 2.78 (1 H, d, $J_{5,6}$ 8.5 Hz, 6-H), 2.59 (1 H, dd, $J_{5,6}$ 8.5, $J_{3,5}$ 2.5 Hz, 5-H), and 2.45 (1 H, d, $J_{3,5}$ 2.5 Hz, 3-H).

4-*Iodo*-NN-*dimethyl*-2-*trifluoromethylaniline*.—The diazonium salt solution prepared from 4-dimethylamino-3-trifluoromethylaniline (8 g) was added to potassium iodide (7 g) in water (20 cm³). After 4 h at 60—70°, the mixture was kept at room temperature overnight. The organic material was extracted into chloroform and the usual

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† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

work-up gave the *iodo-compound* (86%), b.p. 128 °C at 25 mmHg (Found: C, 34.5; H, 3.1; F, 17.9; I, 40.4; N, 4.1. $C_9H_9F_3IN$ requires C, 34.6; H, 2.8; F, 18.1; I, 40.2; N, 4.3%), τ 7.29 (6 H, s, NMe_2), 2.98 (1 H, d, $J_{5,6}$ 8.5 Hz, 6-H), 2.27 (1 H, dd, $J_{5,6}$ 8.5, $J_{3,5}$ 2.0 Hz, 5-H), and 2.13 (1 H, d, $J_{3,5}$ 2.0 Hz, 3-H).

4-*Dimethylamino*-3-*trifluoromethylbenzonitrile*.—A mixture of 4-dimethylamino-3-trifluoromethylbenzaldehyde[5] (21.8 g), hydroxylamine hydrochloride (9.0 g) in water (12 cm^3), sodium hydroxide (4.5 g) in water (12 cm^3), and ethanol (200 cm^3) was boiled under reflux for 3 h. The solid which separated on pouring the mixture into ice–water was recrystallised from light petroleum (b.p. 40—60 °C) to give the *oxime* (94%), m.p. 65.5—66 °C (Found: C, 51.8; H, 4.9; F, 24.5; N, 12.2. $C_{10}H_{11}F_3N_2O$ requires C, 51.7; H, 4.8; F, 24.5; N, 12.1%).

A mixture of the oxime (20 g) and acetic anhydride (85 cm^3) was boiled under reflux for 4 h, whereupon it was poured into ice–water and extracted with chloroform. The extracts were washed with sodium hydroxide solution and then with water. Removal of the solvent and distillation of the residue gave 4-*dimethylamino*-3-*trifluoromethylbenzonitrile* (80%), b.p. 90 °C at 1 mmHg (Found: C, 55.7; H, 5.3; F, 26.7; N, 13.0. $C_{10}H_9F_3N_2$ requires C, 56.1; H, 4.2; F, 26.6; N, 13.1%), τ 7.06 (6 H, s, NMe_2), 2.92 (1 H, d, $J_{5,6}$ 9.0 Hz, 5-H), 2.41 (1 H, dd, $J_{5,6}$ 9.0, $J_{2,6}$ 2.0 Hz, 6-H), and 2.21 (1 H, d, $J_{2,6}$ 2.0 Hz, 2-H).

4,NN-*Trimethyl*-2-*trifluoromethylaniline*.—Reaction between 4-dimethylamino-3-trifluoromethylphenyl-lithium [prepared from the bromo-compound (6.7 g) and n-butyllithium] and dimethyl sulphate (2.0 g), followed by the usual work-up afforded 4,NN-*trimethyl*-2-*trifluoromethylaniline* (82%), b.p. 88 °C at 25 mmHg (Found: C, 58.9; H, 5.9; F, 28.4; N, 6.8. $C_{10}H_{12}F_3N$ requires C, 59.1; H, 5.9; F, 28.1; N, 6.9%), τ 7.67 (3 H, s, 4-Me), 7.32 (6 H, s, NMe_2), and 2.46—3.03 (3 H, collapsed spectrum).

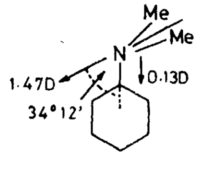
1,4-*Bisdimethylamino*-2-*trifluoromethylbenzene*.—A well stirred mixture of 4-dimethylamino-3-trifluoromethylaniline (12 g) and trimethyl phosphate (14 cm^3) was heated at 190° for 2 h. The usual work-up[6] gave the *di-tertiary amine*, m.p. 53—54 °C, b.p. 190 °C at 26 mmHg (Found: C, 57.0; H, 6.3; F, 24.2; N, 12.2. $C_{11}H_{15}F_3N_2$ requires C, 56.9; H, 6.5; F, 24.5; N, 12.1%), τ 7.38 (6 H, s, 1-NMe_2), 7.08 (6 H, s, 4-NMe_2), 3.16 (1 H, dd, $J_{5,6}$ 8.5, $J_{3,5}$ 3.0 Hz, 5-H), 3.09 (1 H, d, $J_{3,5}$ 3.0 Hz, 3-H), and 2.70 (1 H, d, $J_{5,6}$ 8.5 Hz, 6-H).

DISCUSSION

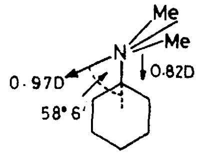
Inhibition of the mesomeric effect of the dimethylamino-group by *o*-methyl groups is illustrated by a comparison of the moments of *NN*-dimethylaniline (1.57 D)[7] and 2,4,6,*NN*-pentamethylaniline (0.64 D).[1] This evidence, together with that available from the measurements of a range of properties of *o*-substituted dimethylanilines,[8] has given rise to the suggestion that the dimethylamino-group is twisted from its position of maximum conjugation with the ring under the steric influence of the *ortho*-substituents.[9,10] This suggestion has received recent support from the magnitude of the upfield ^{15}N chemical shifts induced by *ortho*-methyl substitution in *NN*-dimethylaniline.[11] The difference between the π_4 and π_2 ionisation potentials, ΔIP,[11] reflecting the extent of lone-pair delocalization, has been correlated with the torsional angle about the C(1)–N bond and gives values of 55 and 69° for *o*-methyl- and di-*o*-methyl-*NN*-dimethylaniline, respectively. Values of 77 and 80° are calculated for the torsional angles appropriate to di-*o*-ethyl- and di-*o*-isopropyl-*NN*-dimethylaniline, respectively.[11] Using dipole moment data,[1] an angle of 30° is calculated for the torsional angle about the C(1)–N bond in *o*-methyl-*NN*-dimethylaniline [*cf*. angles of twist of 17 and 50° (refs. 10*a* and 12)].

It is to be expected that an *o*-trifluoromethyl group would similarly affect the dimethylamino-group. Being of greater size than a methyl group,[13] it might be imagined that the torsional angle would be greater than that caused by the latter substituent.

In order to calculate the torsional angle of the dimethylamino-group about the C(1)–N bond and the vector moments in the direction of this bond which are required to explain the observed dipole moments of the compounds studied, a vector model of the C(1)–NMe_2 group must be constructed. Using a literature value[9] of 116° for the C(1)NC angle, the angle, α, between the C(1)–N bond and the bisector of the CNC angle is calculated from geometry to be 145° 48′. Using this angle and a value[1] for the angle between the C(1)–N bond and the direction of the resultant moment of the C(1)–NMe_2 group in *NN*-dimethylaniline of 31° 39′, directional vector moments $\mu[\overset{-}{N}\text{–}\overset{+}{C}(1)]$ and $\mu(\overset{-}{N}\text{–}\overset{+}{b})$ are calculated to be −0.13 D and 1.47 D, respectively; $\mu(\overset{-}{N}\text{–}\overset{+}{b})$ refers to the moment along the bisector of the CNC angle. The vector model (a) of *NN*-dimethylaniline then becomes as shown. The effect on the model of changing the C(1)NC angle to the tetrahedral value of 109° is illustrated in (b).



(a)



(b)

On the basis of model (a), and using simple vector analysis, the moments of *NN*-dimethyl-2-trifluoromethylaniline and 4,*NN*-trimethyl-2-trifluoromethylaniline can be explained by a $\overset{-}{N}\text{–}\overset{+}{C}(1)$ bond moment of 1.26 D and an angle of twist, β, of the dimethylamino-group of 28° from its position of maximum conjugation with the ring. In this analysis, the NMe_2 group moment is kept constant at 1.47 D, it being argued that the polarity of N–C σ bonds will be little affected by group rotation. The CH_3 and CF_3 group moments are taken to be 0.37 and 2.56 D, respectively, the latter being the value of the dipole moment of trifluoromethylbenzene.[3,14] On the basis of model (b), β is again calculated as 28°, but the $\overset{-}{N}\text{–}\overset{+}{C}(1)$ bond moment is changed to 0.56 D. It is interesting to observe that loss of conjugation between the dimethylamino-group and the ring causes the moment in the direction of the major axis of the ring to change sign, the nitrogen atom now being at the negative end of the dipole. That the torsional angle of the dimethylamino-group of 28° is a little less than the value [1] of 30° obtaining when the latter group is hindered by an *o*-methyl group may at first sight appear anomalous. However, attractive effects between dipoles residing in the adjacent dimethylamino- and trifluoromethyl groups may be responsible for negating the influence of the larger size of the latter group. Such attractions can be anticipated in view of recent work [5] on the ^1H n.m.r. spectra, which implies a through space coupling [15] between the *ortho* groups arising from the proximity of the coupled nuclei.

Assuming constancy of the NMe_2 group moment and the angle β, vector moments in the direction of the C(1)–N bond required to explain the observed moments of the 4-substituted *NN*-dimethyl-2-trifluoromethylanilines have been calculated and are recorded in Table 2. In the vector calculations, *p*-substituent group moments were taken to be [16] Cl (1.58 D), Br (1.56 D), I (1.40 D), CN (4.03 D), NO_2 (4.01 D). Interactions between the trifluoromethyl group and the 4-substituent * could affect the magnitudes of these group moments, but insufficient literature data prevents a realistic assessment of the effect. It is noted that a value [7] for the moment of 3-chlorotrifluoromethylbenzene of 2.14 D is rather smaller than that calculated by vector addition (2.24 D). Similar differences in the observed and calculated moments of 3-chloronitrobenzene (3.40 and 3.50 D) and 3-bromonitrobenzene (3.44 and 3.50 D) occur, and yet, in the case of 3-iodonitrobenzene almost identical values arise (3.54 and 3.53 D).[7] In view of the uncertainty concerning the magnitude of this interaction between electron-withdrawing groups situated *meta* to each other, the possible small changes in the two group moments which might arise have been ignored in the current work. In any case, the likelihood is that interactions of this kind would merely alter the absolute, rather than the relative magnitudes of the values quoted in Table 2.

TABLE 2

Vector moments in the direction of the $\overset{-}{C}(1)-\overset{+}{N}$ bond required to explain observed dipole moments

4-Substituted derivatives of *NN*-dimethyl-2-trifluoromethylaniline

4-Substituent	Cl	Br	I	CN	NO_2
Model (a)	0.04	0.00	0.05	0.59	0.75
Model (b)	0.75	0.71	0.76	1.30	1.46
Δa	1.30	1.26	1.31	1.85	2.01
Δb	1.31	1.27	1.31	1.86	2.02
σ	0.23	0.23	0.28	1.00	1.27

4-Substituted derivatives of *NN*-dimethylaniline

4-Substituent	Cl	Br	I	CN	NO_2
Model (a)	0.42	0.50	0.53	1.30	1.64
Model (b)	1.14	1.22	1.07	2.02	2.34

It was considered too speculative to evaluate the $\overset{+}{N}-\overset{-}{C}(1)$ bond moments in the case of those compounds with *p*-dimethylamino- and *p*-amino-substituents, since the conformation of these groups relative to the displaced dimethylamino-group is not known with any certainty. For comparison purposes, it is instructive to calculate the moments in the direction of the major axis of the ring required to explain the dipole moments of the corresponding series of 4-substituted *NN*-dimethylanilines in which conjugation is at a maximum. In these calculations, the dipole moments of the dimethylanilines were taken as Me (1.30 D),[17] Cl (3.32 D),[17] Br (3.40 D),[17] I (3.25 D),[17] CN (6.60 D),[18] and NO_2 (6.92 D).[17] These moments, based on both models (a) and (b), are presented in Table 2. It is clear that restoration of conjugation is considerable on substituting electron-withdrawing groups in the *p*-position of *NN*-dimethyl-2-trifluoromethylaniline, although the $\overset{-}{C}(1)-\overset{+}{N}$ moment does not reach the value corresponding to maximum conjugation. A measure of the extent of this restoration of conjugation is given by the magnitudes of Δa and Δb, which represent the change in C(1)–N moments in models (a) and (b), respectively, brought about by *para*-substitution in the parent *NN*-dimethyl-2-trifluoromethylaniline. It is interesting to observe the almost identical Δa and Δb values for each compound, which reflect an independence of the geometry of the NMe_2 group. Also, the change in Δa or Δb with variation in the *para*-substituent is in accord with the Hammett σ constant of the latter group.

A comparison of the data in Table 2 with the magnitude of the restoration of conjugation on substituting electron-withdrawing groups in the *para*-position of 2,6,*NN*-tetramethylaniline is also of interest. The moment of this compound has been previously determined [1] as 0.85 D. Using model (a) for *NN*-dimethylaniline, this value can be explained by a value for $\mu[\overset{-}{N}-\overset{+}{C}(1)]$ of 1.05 D, assuming that the C(1)–Me bond moment is 0.37 D and the component moment $\mu(\overset{-}{N}-\overset{+}{b})$ is 1.47 D. The values of $\mu[\overset{-}{N}-\overset{+}{C}(1)]$ necessary to explain the observed moments [1] of 4-bromo-2,6-dimethyl- and 2,6-dimethyl-4-nitro-*NN*-dimethylaniline (2.39 and 5.20 D) are calculated to be 0.47 and 0.09 D, respectively. Corresponding values of Δa are 0.58 and 0.96 D. A comparison with the respective values in Table 2 of 1.26 and 2.01 D demonstrates that *para*-substitution is more effective in restoring conjugation of the dimethylamino-group with the ring in the case of the *o*-trifluoromethyl-*NN*-dimethylanilines.

A final point of discussion concerns the effect which a twisting of the N–C(1) bond has upon the pyramidal angle of the dimethylamino-group and the vector components $\mu(\overset{-}{N}-\overset{+}{b})$ and $\mu[\overset{-}{N}-\overset{+}{C}(1)]$ of this group. In the preceding analysis, it is shown that conjugation between the dimethylamino-group and the ring is reduced by the twisting of this group through 28°. Partial restoration of conjugation on *para*-substitution is explained by vector analysis on the basis that both the torsional and

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* We thank a referee for suggesting that some discussion of this interaction be inserted.

pyramidal angles remain unchanged. Alternatively, it may be suggested that on *para*-substitution, the torsional angle, β, decreases. If this is mechanically possible, then it is likely that a simultaneous change in hybridisation of the nitrogen atom occurs, the lone-pair orbital developing more sp^2 character. The pyramidal angle would also increase and affect the value of $\mu[\overset{-}{N}-\overset{+}{C}(1)]$. The magnitude of these changes would be dependent on the nature of the *para*-substituent. Unfortunately, too many unknown parameters preclude a determining vector analysis. It is considered that whereas the magnitudes of Δa or Δb would differ from those presented in Table 2, the sequence would remain the same.

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