A Dipole Moment Study of the Electrical Effect of the Trifluoromethyl Group

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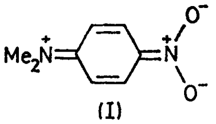
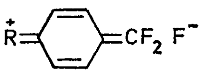
Apparent dipole moments in benzene of a series of substituted trifluoromethylbenzenes and related compounds have been determined. The magnitude of the differences between the observed moments and those calculated by vector analysis are most appropriately explained, principally, in terms of a π electron inductive effect of the trifluoromethyl group.

THE electronic effect of the trifluoromethyl group has been a controversial issue for some time and has been reviewed recently by Sheppard and Sharts[1] and by Holtz.[2] Alternative interpretations include fluorine hyperconjugation or no-bond resonance,[3] *p*–π electron interaction,[4] and π-electron induction.[2,5,6] Dewar[7] and Stock[8] consider that the trifluoromethyl group operates mainly by a field effect. One of the classical methods of studying electronic effects is by means of dipole moments. Differences in observed and calculated dipole moments of 1,4-disubstituted benzenes are often explained by resonance interaction between the two groups, and in many cases this is undoubtedly the dominant effect. For example, whereas the observed dipole moment in benzene of *NN*-dimethyl-4-nitroaniline is 6·87 D, the value calculated from the moments of nitrobenzene (4·01 D) and dimethylaniline (1·58 D) by simple vector analysis is 5·39 D.[9] In this calculation,[9] the inclination of the dipole axis of the dimethylamino-group to the ring C–N bond is taken as 34°. It is reasonable to attribute the large value of the interaction moment (1·48 D) to the important contribution of resonance structure (I) to the ground state of the molecule. Dipole moments, in benzene, of trifluoromethylbenzene[10] (2·56 D) and *NN*-dimethyl-4-trifluoromethylaniline[3a] (4·62 D) necessitate an interaction moment, in the direction of the major axis of the molecule, of 0·66 D.



(I)



(II) R = NMe$_2$
(III) R = Cl

It could be argued that resonance structure (II) contributes to the ground state of the molecule. The difference in the vapour dipole moments[11] of trifluoromethylbenzene (2·86 D) and 1,1,1-trifluoroethane (2·34 D) as well as that observed[3a] in benzene for trifluoromethylbenzene (2·60 D) and trifluoromethylcyclohexane (2·40 D) has been used as evidence[3a,11] in support of no-bond

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[1] W. A. Sheppard and C. M. Sharts, 'Organic Fluorine Chemistry,' Benjamin, New York, 1969, p. 35.

[2] D. Holtz, *Chem. Rev.*, 1971, **71**, 139.

[3] (*a*) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Amer. Chem. Soc.*, 1950, **72**, 408; (*b*) J. Bornstein, S. A. Leone, W. F. Sullivan, and O. R. Bennett, *ibid.*, 1957, **79**, 1745; (*c*) L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1960, p. 314; (*d*) J. Hine, *J. Amer. Chem. Soc.*, 1963, **85**, 3239.

[4] (*a*) W. A. Sheppard, *J. Amer. Chem. Soc.*, 1965, **87**, 2410; (*b*) L. M. Stock and J. Suzuki, *ibid.*, p. 3909; (*c*) E. G. Janzen and J. L. Gerlock, *ibid.*, 1967, **89**, 4902; (*d*) F. A. Cotton and R. M. Wing, *J. Organometallic Chem.*, 1967, **9**, 511; (*e*) K. Kosman and L. M. Stock, *J. Amer. Chem. Soc.*, 1970, **92**, 409; (*f*) W. A. Sheppard, *Tetrahedron*, 1971, **27**, 945.

[5] (*a*) M. J. S. Dewar, 'Hyperconjugation,' Ronald Press, New York, 1962, p. 155; (*b*) A. Streitwieser and H. F. Koch, *J. Amer. Chem. Soc.*, 1964, **86**, 404; (*c*) A. Talvik, P. Zuman, and O. Exner, *Collect. Czech. Chem. Comm.*, 1964, **29**, 1266.

[6] A. R. Katritzky and R. D. Topsom, *J. Chem. Educ.*, 1971, **48**, 427.

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[8] F. W. Baker, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, 1967, **89**, 5677.

[9] J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955, p. 209.

[10] (*a*) H. Freiser, M. E. Hobbs, and P. M. Gross, *J. Amer. Chem. Soc.*, 1949, **71**, 111; (*b*) G. Kraus and A. B. Conciatori, *ibid.*, 1950, **72**, 2283; (*c*) A. H. Boud and J. W. Smith, *J. Chem. Soc.*, 1956, 4507.

[11] J. J. Conradi and N. C. Li, *J. Amer. Chem. Soc.*, 1953, **75**, 1785.

resonance structures for trifluoromethylbenzene. Again, the calculated moment of 4-trifluoromethylchlorobenzene is appreciably lower (0·48 D) than the observed value,[11] and in explanation a contribution from structure (III) is contemplated. Before concluding that structures (II) and (III) contribute significantly to the ground state of the respective molecules, it seemed necessary to measure the dipole moments of analogous *meta*-disubstituted compounds in which resonance is impossible, and additional appropriate *para*-substituted trifluoromethylbenzenes and related compounds.

EXPERIMENTAL

Materials.—Benzene, dried by prolonged refluxing over sodium, was distilled and the fraction of b.p. 80·1° at 760 mmHg was collected. Commercial samples of methyl benzoate, b.p. 198—199°, and trifluoromethylbenzene, b.p. 102—103°, were purified and distilled immediately prior to use. Other solutes, which were also purified immediately before use, were prepared as indicated and had the following constants: methyl 4-methylbenzoate, m.p. 32—33°, and methyl 4-dimethylaminobenzoate, m.p. 101—102°; from the acid using boron trifluoride and methanol,[12] methyl 4-trifluoromethylbenzoate, b.p. 197—198°; from the acid and diazomethane, *NN*-dimethyl-3-trifluoromethylaniline, b.p. 84—85° at 12 mmHg, and *NN*-dimethyl-3,5-bistrifluoromethylaniline, m.p. 59·5—60°; from the primary amine and trimethyl phosphate.[13]

TABLE 1

Polarisation data and dipole moments (μ) at 25·0 °C in benzene solution

Compound	α	β	ν	$P_{2.\infty}/\mathrm{cm}^3$	$R_{2.\infty}/\mathrm{cm}^3$	μ/D	μ/D (lit)
Methyl benzoate	2·968	−0·227	0·035	113·22	37·52	1·93	1·94[a]
Methyl 4-methylbenzoate	3·258	−0·163	0·045	136·03	44·47	2·12	
Methyl 4-dimethylaminobenzoate	8·770	−0·245	0·281	343·56	56·84	3·75	3·90[b]
Trifluoromethylbenzene	4·495	−0·271	−0·227	161·75	31·28	2·56	2·54[c] 2·56[d–f] 2·60[g]
Methyl 4-trifluoromethylbenzoate	3·097	−0·367	−0·145	166·21	40·89	2·48	
NN-Dimethyl-3,5-bistrifluoromethylaniline	8·653	−0·294	−0·176	483·54	55·49	4·58	
NN-Dimethyl-3-trifluoromethylaniline	7·976	−0·290	−0·066	331·86	45·03	3·75	

[a] Ref. 18. [b] V. N. Vasil'eva, V. P. Bazov, and M. A. Geiderikh, *Zhur. Fiz. Khim.*, 1959, **33**, 1516. [c] P. E. Brown and T. De Vries, *J. Amer. Chem. Soc.*, 1951, **73**, 1811. [d–f] Ref. 10(*a*), (*b*), and (*c*). [g] Ref. 3(*a*).

Dipole Moments.—Dielectric constants, ε, and specific volumes, v, of at least six dilute solutions of graded concentrations of each compound in benzene were determined at 25·0°. Refractive indices of selected solutions were also measured at the wavelength of the sodium D-line. The range of weight fractions employed was generally 0·001—0·017.

Dielectric constants, accurate to 0·0001, were measured with an internally thermostatted, heterodyne-beat dipolemeter, type D.M. 01, manufactured by the Wissenschaftlich-Technische Werkstatten G.m.b.H. The thermostatted dielectric cell, type D.F.L.I., of 20-ml capacity, had gold-coated interior plates. Refractive indices were measured with an Abbé refractometer of high accuracy. Specific volumes were determined with a 25-ml capacity Warden's density bottle. To prevent vapour losses, the bottle was fitted with a cap, ground on over the capillary stopper. The results are summarised in Table 1, where the symbols have their usual significance.

The total molar polarisation at infinite dilution, $P_{2,\infty}$, was calculated from equation (1) in which ε_1 and v_1 are the di-

$$P_{2,\infty} = \frac{3M_2\alpha v_1}{(\varepsilon_1 + 2)^2} + M_2(v_1 + \beta)\,\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \qquad (1)$$

electric constant and specific volume respectively of the solvent, and M_2 is the molecular weight of the solute. $\alpha = (\mathrm{d}\varepsilon/\mathrm{d}w)_{w=0}$, $\beta = (\mathrm{d}v/\mathrm{d}w)_{w=0}$.

The molar electron polarisation, ${}_{\mathrm{E}}P_2$, is identified with the molar refraction $R_{2.\infty}$, given by equation (2) in which

$$R_{2,\infty} = \frac{3M_2 v_1 \nu}{(n_1^2 + 2)^2} + M_2(v_1 + \beta)\,\frac{n_1^2 - 1}{n_1^2 + 2} \qquad (2)$$

$\nu = (\mathrm{d}n^2/\mathrm{d}w)_{w=0}$ and n_1 is the refractive index of the solvent.

Neglecting the atom polarisation, ${}_{\mathrm{A}}P_2$, the molar orientation polarisation at infinite dilution, ${}_{\mathrm{O}}P_{2.\infty}$, was calculated from equation (3) and the dipole moment, μ, was evaluated

$${}_{\mathrm{O}}P_{2.\infty} = P_{2,\infty} - {}_{\mathrm{E}}P_2 \qquad (3)$$

from equation 4.

$$\mu = 0{\cdot}012812({}_{\mathrm{O}}P_{2.\infty} \times T)^{\frac{1}{2}} \qquad (4)$$

The values of α, β, and ν were calculated from the experimental data by the method of least squares.

Dielectric constants, specific volumes, and refractive indices are given in Supplementary Publication No. SUP 20484 (6 pp.).*

DISCUSSION

In order to calculate the dipole moments of the compounds studied, it is first necessary to consider the geometry of the dimethylamino- and methoxycarbonyl groups relative to the plane of the benzene ring. In the case of the former group, the C(ring)–N component lies in the plane of the ring and the NMe_2 component in a plane angularly disposed to the ring. The moment of 4,*NN*-trimethylaniline is computed vectorially from the moments of dimethylaniline and toluene,[9] the angle subtended by the C–NMe_2 group moment to the major axis of the ring being taken as 34°. The geometry of the ester group has been discussed by Eucken and

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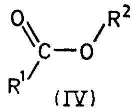
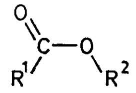
* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[12] G. Hallas, *J. Chem. Soc.*, 1965, 5770.

[13] D. E. Grocock, T. K. Jones, G. Hallas, and J. D. Hepworth, *J. Chem. Soc.* (*C*), 1971, 3305.

Meyer,[14] Marsden and Sutton,[15] Zahn,[16] and O'Gorman *et al.*[17] with the conclusion that the group is planar, conformation (IV) being preferred to (V). Electron diffraction studies by the latter workers suggests the possibility of rotatory oscillation about the C–O bond.


(IV)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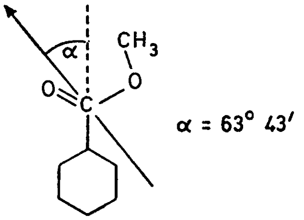

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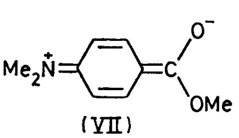

(VII)

Assuming that the ester group is coplanar with the benzene ring, then the angle, α, which the ester group moment makes with the major axis of the ring may be found by combining the moments of toluene (0·37 D) and methyl benzoate (1·93 D) vectorially to give the observed moment of methyl 4-methylbenzoate (2·12 D). This angle is found to be 63° 43′, the ester group dipole being directed away from the ring as in (VI). Jones *et al.*[18] have calculated an angle of 66° by vectorial combination of the 3,5-dichlorophenyl group moment with the moment of methylbenzoate to give their observed moment of 1·93 D for methyl 3,5-dichlorobenzoate. The agreement between these two calculated Ar–CO_2Me group moment angles is considered to be remarkably good and within the experimental error of dipole moment measurement.

Assuming that the methoxycarbonyl group moment and the dimethylamino-group moment make angles of 63° 43′ and 34°, respectively, with the major axis of the ring, it becomes possible to calculate vectorially, using substituent group moments, the dipole moments of the compounds studied. Calculations of the interaction moments, $\mu_{\text{int.}}$ along the major axis of the ring which explain the observed moments are also possible. The results are recorded in Table 2. It is noted that the difference of 2° 17′ in the chosen methoxycarbonyl group moment angle makes only small differences in $\mu_{\text{calc.}}$ and $\mu_{\text{int.}}$ and in no way affects the conclusions drawn from this study.

In the case of methyl 4-dimethylaminobenzoate, the dipole moment of the molecule is calculated from equation (5) to be 2·91 D. The additional (interaction)

$$\mu^2_{\text{calc.}} = (1{\cdot}58 \cos 34° + 1{\cdot}93 \cos 63° 43')^2 + (1{\cdot}93 \sin 63° 43')^2 + (1{\cdot}58 \sin 34°)^2 \quad (5)$$

moment, $\mu_{\text{int.}}$, along the major axis of the ring and necessary to explain the observed moment of 3·75 D is calculated to be 1·04 D in the sense $\mathrm{Me_2N}\ \overset{\text{ring}}{+\!\!\!\longrightarrow}\ \mathrm{CO_2Me}$. It seems reasonable to explain the magnitude of this interaction moment by conjugation from the nitrogen atom of the dimethylamino-group to the carbonyl oxygen atom of the ester group, giving rise to contributory structure (VII).

TABLE 2

Observed, calculated, and interaction moments (μ) of some trifluoromethyl-substituted benzenes and related compounds

	$\mu_{\text{obs.}}$/D	$\mu_{\text{calc.}}$*/D	$\mu_{\text{int.}}$*/D
Trifluoromethylbenzene	2·56		
Methyl 4-dimethylamino-benzoate	3·75	2·91 (2·88)	+1·04 (+1·10)
Methyl 4-trifluoromethyl-benzoate	2·48	2·43 (2·50)	−0·07 (+0·03)
NN-Dimethyl-3,5-bistri-fluoromethylaniline	4·58	3·97	+0·62
NN-Dimethyl-3-trifluoro-methylaniline	3·75	3·52	+0·30

* Dipole moments in parentheses were calculated using a methoxycarbonyl group moment angle of 66°.[18]

Dipole moments of *NN*-dimethyl-3,5-bistrifluoromethylaniline and *NN*-dimethyl-3-trifluoromethylaniline were calculated from equations (6) and (7), respectively

$$\mu^2_{\text{calc.}} = 1{\cdot}58^2 + 2{\cdot}56^2 + 2(1{\cdot}58)(2{\cdot}56) \cos 34° \quad (6)$$

$$\mu^2_{\text{calc.}} = (1{\cdot}58 \cos 34°)^2 + 2{\cdot}56^2 + 2(2{\cdot}56)(1{\cdot}58 \cos 34°) \cos 60° + (1{\cdot}58 \sin 34°)^2 \quad (7)$$

and found to be 3·97 and 3·52 D. Interaction moments, $\mu_{\text{int.}}$, along the major axis of the ring and necessary to explain the observed moments of 4·58 and 3·75 D are found to be 0·62 and 0·30 D, respectively in the sense $\mathrm{Me_2N}\ \overset{\text{ring}}{+\!\!\!\longrightarrow}\ \mathrm{CF_3}$. Since resonance is impossible in these compounds, it seems probable that these interaction moments are a consequence of a π electron inductive effect, particularly as the C–F bonds are appreciably polarised as a result of the high electronegativity of fluorine. The previously quoted interaction moment in *NN*-dimethyl-4-trifluoromethylaniline of 0·66 D is almost identical to the value of 0·62 D found in *NN*-dimethyl-3,5-bistrifluoromethylaniline. It appears then, that in the latter compound, the two *meta*-substituted trifluoromethyl groups each respond to the enhanced π electron displacement caused by the +*M* effect of the dimethylamino-group to the same extent as a *para*-substituted trifluoromethyl group.

It is concluded that enhancement of no-bond resonance in the trifluoromethyl group by the +*M* effect of the dimethylamino-group must be small. Further evidence for this conclusion is provided by the small interaction moment [+0·07 in the sense $\mathrm{C(ring)} \longleftarrow\!\!\!+ \mathrm{CF_3}$] calculated from equation (8) and necessary to explain

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[14] A. Eucken and I. Meyer, *Z. Physik.*, 1929, **30**, 397.

[15] R. J. B. Marsden and L. Sutton, *J. Chem. Soc.*, 1936, 1383.

[16] C. T. Zahn, *Z. Physik.*, 1932, **33**, 730.

[17] J. M. O'Gorman, W. Shand, and V. Schomaker, *J. Amer. Chem. Soc.*, 1950, **72**, 4222.

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

the observed moment of methyl 4-trifluoromethylbenzoate.

$$2{\cdot}48^2 = (2{\cdot}56 - \mu_{\text{int.}})^2 + 1{\cdot}93^2 - 2(2{\cdot}56 - \mu_{\text{int.}})(1{\cdot}93)\cos 63^\circ 43' \quad (8)$$

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