Dipole Moments of Methyl- and Trifluoromethyl-substituted Methyl Benzoates

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Apparent dipole moments in benzene of 1,3-bistrifluoromethylbenzene and of the methyl esters of 2,4-dimethyl-, 2,5-dimethyl-, 3,5-dimethyl-, 2,4-bistrifluoromethyl-, 2,5-bistrifluoromethyl-, 3,5-bistrifluoromethyl-, and 3-trifluoromethyl- benzoic acid have been determined. The values obtained can be explained either by rotation of the ester group out of the plane of the ring or, in the case of the 3-, and 2,4-substituted esters, by the existence of *cis*- and *trans*-isomers.

In a recent study[1] of the mechanism of the *ortho*-effect in *o*-methyl- and *o*-trifluoromethyl-substituted methyl benzoates, the values of apparent dipole moments were explained by rotation of the ester group out of the plane of the benzene ring. Support for the applicability of this model and, alternatively, the existence of *cis–trans*-isomerism is now provided by a comparison of calculated and measured moments in benzene of 1,3-bistrifluoromethylbenzene and the methyl esters of 2,4-dimethyl-, 2,5-dimethyl-, 3,5-dimethyl-, 2,4-bistrifluoromethyl-, 2,5-bistrifluoromethyl-, 3,5-bistrifluoromethyl-, and 3-trifluoromethyl-benzoic acid.

EXPERIMENTAL

The apparent dipole moments were calculated as described previously[2] from experimental measurements at 25.0 °C of dielectric constant, specific volume, and refractive index to sodium D-line [listed in Supplementary Publication No. SUP 21472 (9 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 the linear graphs of dielectric constant, specific volume, and refractive index squared against weight fraction, together with polarisation

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† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin II*, 1974, Index issue.

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

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

data, in which the symbols have their usual significance, and the computed dipole moments (μ), are given in Table 1.

Materials.—Benzene was purified as previously.[1] The solutes, which were prepared by esterification of the appropriately substituted benzoic acid with dimethyl sulphate [3] or were commercially available, gave satisfactory microanalyses and n.m.r. spectra [4] and were shown to be pure by g.l.c. 1,3-Bistrifluoromethylbenzene had b.p. 116 °C; methyl 2,4-dimethylbenzoate had b.p. 233 °C; methyl 2,5-dimethylbenzoate had b.p. 232 °C; methyl 3-trifluoromethylbenzoate had b.p. 198 °C; methyl 2,4-bistrifluoromethylbenzoate had b.p. 193—194 °C; methyl 2,5-bistrifluoromethylbenzoate had b.p. 195—196 °C; methyl 3,5-bistrifluoromethylbenzoate had b.p. 183—184 °C; and methyl 3,5-dimethylbenzoate had b.p. 236—237 °C.[4]

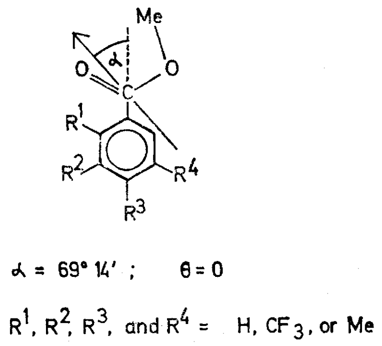
DISCUSSION

In an unhindered ester, the ester group is coplanar with the benzene ring.[5] A suggestion by Jones *et al.*[6] was used for the calculation of the angle, α, which the ester group moment makes with the major axis of the ring: vector combination of the moments of toluene (—0.37 D), methyl benzoate [2] (1.93 D), and methyl 3,5-dimethylbenzoate (2.09 D) gave a value of α of 69° 14′ (Figure).

TABLE 1

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

Compound	α	β	ν	$P_{2\infty}$/cm^3	$_EP_2$/cm^3	μ/D
Methyl 2,4-dimethylbenzoate	2.372	—0.183	0.053	120.28	47.93	1.89
Methyl 2,5-dimethylbenzoate	2.295	—0.190	0.043	117.59	47.29	1.85
Methyl 3,5-dimethylbenzoate	2.906	—0.223	0.041	134.89	45.81	2.09
Methyl 3-trifluoromethylbenzoate	3.390	—0.352	—0.152	178.41	41.51	2.59
Methyl 2,4-bistrifluoromethylbenzoate	3.007	—0.434	—0.204	211.58	46.12	2.85
Methyl 2,5-bistrifluoromethylbenzoate	1.148	—0.437	—0.223	116.15	44.92	1.87
Methyl 3,5-bistrifluoromethylbenzoate	2.464	—0.420	—0.237	184.89	45.54	2.61
1,3-Bistrifluoromethylbenzene	2.963	—0.408	—0.293	166.23	50.76	2.38



Conformation of a substituted methyl benzoate in which R^1 and R^2 are disposed *cis* to the C=O group

If the ester group remains coplanar with the ring on substitution of a trifluoromethyl group in the *meta*-position, then the observed moment of methyl 3-trifluoromethylbenzoate (2.59 D) should agree reasonably either with that calculated for the conformation in which the CF_3 group is disposed *cis* to the carbonyl group or with that for the corresponding *trans* situation. These moments, calculated by simple vector analysis by use of a value of 2.56 D for the moment of the C(ring)–CF_3 group, are 4.07 and 0.72 D, respectively. If free rotation of the plane of the ester group around the major axis of the ring is assumed, however, a value of 2.92 D is calculated. Since these three calculated values are considerably different from the observed moment of 2.59 D, it may be that a decrease in interaction between the methoxycarbonyl group and the π-system occurs, giving rise to a preferred conformation in which the ester group is disposed at an angle θ to the plane of the ring. Broxton *et al.*[7] have suggested that a change in the interaction between a functional group and the ring can be brought about by a polar *meta*-CF_3 group acting directly through space. The angle, θ, necessary to explain the observed moment of methyl 3-trifluoromethylbenzoate is calculated by using equation (i) to be 95° 52′.

$$\mu^2(\text{obs.}) = (1.93 \cos 69^\circ 14' - 2.56 \cos 60^\circ)^2 + (1.93 \sin 69^\circ 14' \cos \theta + 2.56 \sin 60^\circ)^2 + (1.93 \sin 69^\circ 14' \sin \theta)^2 \quad \text{(i)}$$

The moment of methyl 2-trifluoromethylbenzoate has been previously determined [1] as 3.09 D and this necessitates a value for θ of 108° 5′, calculated in a similar manner. This angle is greater than that appropriate to the 3-trifluoromethyl derivative, presumably owing to the closer approach of an *ortho*-group to the ester group. The presence of a methyl group *ortho* to the methoxycarbonyl group may be expected to have an opposite effect and cause a decrease in θ. If we take a value for the moment of the group C(ring)–CH_3 as —0.37 D, θ is calculated to be 40°, the previously determined moment of methyl 2-methylbenzoate being 1.65 D.[1] In this connection it is relevant that the steric effect of an *ortho*-methyl group is less than that of a trifluoromethyl group.[1]

Whereas the moment of trifluoromethylbenzene [2] is 2.56 D, that of 1,3-bistrifluoromethylbenzene is observed to be 2.38 D. Some interaction between two CF_3 groups situated *meta* to each other is apparent. In relation to

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[3] G. Hallas and J. D. Hepworth, *Chem. and Ind.*, 1972, 691.

[4] K. D. Bartle, G. Hallas, and J. D. Hepworth, *Org. Magnetic Resonance*, 1973, **10**, 479; D. E. Grocock, T. K. Jones, J. D. Hepworth, and G. Hallas, *J. Chem. Soc.* (*C*), 1971, 3305.

[5] A. Euken and I. Meyer, *Phys. Z.*, 1929, **30**, 397; R. J. B. Marsden and L. Sutton, *J. Chem. Soc.*, 1936, 1383; C. T. Zahn, *Phys. Z.*, 1932, **33**, 730; J. M. O'Gorman, W. Shand, and V. Schomaker, *J. Amer. Chem. Soc.*, 1950, **72**, 4222.

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

[7] T. J. Broxton, D. G. Cameron, R. D. Topsom, and A. R. Katritzky, *J.C.S. Perkin II*, 1974, 256.

values for the CF_3 group moments of 2.38 D, the observed moment of methyl 2,4-bistrifluoromethylbenzoate (2.85 D) can be explained if the ester group is twisted through an angle of 87° 12′ from its planar conformation. The decrease in this angle from that caused by one CF_3 group situated either *ortho* or *meta* to the methoxycarbonyl group could be due to the mutual interaction between the CF_3 groups reducing the effectiveness of both in causing rotation of the CO_2Me group. If this were so, it might be imagined that two CF_3 groups situated *para* to each other would be self-eliminating electrically, as in 1,4-bistrifluoromethylbenzene which has zero dipole moment. It would then be expected that the moments of methyl 2,5-bistrifluoromethylbenzoate (1.87 D) and methyl 2,5-dimethylbenzoate (1.85 D) would approach that of methyl benzoate (1.93 D), as is the case. Further, if interaction between CH_3 groups disposed *meta* to each other reduces the effectiveness of each in enhancing conjugation between the methoxycarbonyl group and the ring, then the value of θ for methyl 2,4-dimethylbenzoate should be greater than 40°. The angle calculated, by using an equation of the form of equation (i), is 62°.

Finally, and consequent upon the above argument, it could be reasoned that 3,5-bistrifluoromethyl substitution of methyl benzoate would allow free rotation of the methoxycarbonyl group about the major axis of the ring. The dipole moment of this compound, calculated on the basis of this assumption from equation (ii), is 2.48 D, to be compared with the observed value of 2.61 D. It is therefore possible, by taking reasonable values for group

$$\mu^2(\text{calc}) = 1.93^2 + 2.38^2 - 2(2.38)(1.93)\cos 69^\circ\,14' \quad \text{(ii)}$$

moments, and for angles which the groups make with the major axis of the ring, to explain by simple vector analysis the observed moments of a number of trifluoromethyl- and methyl-substituted benzoic acid esters in terms of the rotation of the plane of the ester group out of the plane of the benzene ring. Changes in group moments arising from the presence of nearby groups are not, in the main considered. Also it must be anticipated that the methoxycarbonyl group moment would alter slightly on rotation of the group out of the plane of the ring.

Two other possible models remain to be discussed. First, consideration is given to the effect of a change in the preferred conformation of the methoxy-group (Figure) in the methoxycarbonyl group itself on *ortho*-trifluoromethyl substitution in methyl benzoate. If the group skeleton $CF_3{\cdot}C_6H_4{\cdot}CO_2$ remains planar, but rotation of the OMe group around the C–O bond occurs, then calculated values of the moment of methyl-2-trifluoromethylbenzoate range from 4.48 D, corresponding to the conformation shown in the Figure, to 6.85 D. The conformation corresponding to this latter value is, however, impossible because of steric hindrance between the OMe group and the *ortho*-hydrogen atom. Thus the observed moment [1] of 3.09 D cannot be explained by rotation of the OMe group from the conformation shown in the Figure. The planar conformation in which the OMe group is adjacent to the CF_3 group (*trans*-form) has a calculated moment of 2.01 D. On rotation of the OMe group from this conformation, the calculated moment changes through a range of values to 4.54 D, so that an observed moment of 3.09 D could be explained by a displacement of the methoxy-group from the plane of the ring. However, steric hindrance between the OMe and the adjacent CF_3 group is so severe that such a displacement is considered unlikely. This view is reinforced on carrying out a similar vector analysis in the case of methyl 3-trifluoromethylbenzoate. The range of calculated moments for this molecule, on rotation of the OMe group round the C–O axis is 4.07—5.53 D in the *cis*-form (figure) and 0.72—2.05 D in the *trans*-form. In this case the observed moment of 2.59 D cannot be explained by such a rotation. In the calculations appropriate to the above discussion it is assumed that the C–O–Me group angle is 110° and the $O \leftarrow Me$ group moment is 1.5 D.

TABLE 2

Calculated dipole moments, polarisation data, and % *cis*- and *trans*-isomers in mixture

	μ(calc.)			Mole %	
	cis	*trans*	$_0P_2/\text{cm}^3$	*cis*	*trans*
Methyl 3-trifluoromethylbenzoate	4.07	0.72	136.9	38.5	61.5
Methyl 2-trifluoromethylbenzoate [1]	4.48	2.01	194.6	34.2	65.8
Methyl 2,4-bistrifluoromethylbenzoate	4.07	0.72	165.5	47.2	52.8
Methyl 2-methylbenzoate [1]	1.57	2.18	55.5	89.1	10.9
Methyl 2,4-dimethylbenzoate	1.72	2.30	72.4	75.1	24.9

The remaining possibility is that an unsymmetrically substituted methyl benzoate exists in solution as a mixture of *cis*- and *trans*-isomers in that ratio which gives the observed moment. Moments corresponding to *cis*- and *trans*-conformations for each appropriate ester, together with molar orientation polarisations and proportions (mole per cent) of *trans*- and *cis*-isomer in mixtures are given in Table 2. These results are consistent with those obtained from the first model considered. For example, in order to explain the observed moment of methyl 3-trifluoromethylbenzoate, the methoxycarbonyl group may either twist through an angle of 108° 5′ from the *cis*-conformation, giving rise to a disposition of this group which is transoid, or the molecules of ester could exist as a *cis*–*trans*-mixture, the *trans*-form being more stable. A similar and consistent alternative arises with each of the other esters given in Table 2.

It seems impossible to determine therefore, on the basis of our dipole moment evidence, whether the first or the third model discussed is the most appropriate in explaining the configurations of these substituted esters. Our tendency to favour the first model is based on the greater steric hindrance operative between the *ortho*-groups in the *trans*-conformation, the group angle[8] C(ring)–C–O being somewhat less than 120°, and that of C(ring)–C=O somewhat greater.

We thank Dr. A. M. Jones and M. S. J. Twiselton for discussions, and a referee for advocating the inclusion of an analysis of the two latter models.

[5/553 *Received*, 21*st March*, 1975]

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[8] 'Interatomic Distances,' *Chem. Soc. Special Publ.*, 1958.