A Dipole Moment Study of the *ortho*-Effects of Methyl and Trifluoromethyl Groups

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Apparent dipole moments in benzene of the methyl esters of 2-methyl-, 2,6-dimethyl-, 2-trifluoromethyl-, and 2,6-bistrifluoromethyl-benzoic acid have been determined. The moments of the 2-substituted esters are explained by disturbance of the conjugation between the ester and phenyl groups (i) by the electronic effects of the *ortho*-groups and (ii) by a twisting of the ester group out of the plane of the benzene ring. The moments of the 2,6-disubstituted esters are independent of the angular displacement of the ester group and the important contribution of lone-pair repulsions between the substituents in methyl 2,6-bistrifluoromethylbenzoate to the dipole moment is established.

In a recent dipole moment study of the electrical effect of the trifluoromethyl group [1] it was concluded that the magnitudes of the differences between the observed moments and those calculated by vector analysis of a series of substituted trifluoromethylbenzenes are most appropriately explained principally in terms of a π-electron inductive effect of the trifluoromethyl group.

In the light of this analysis it was considered of interest to investigate the mechanism of the *ortho*-effect in *o*-methyl- and *o*-trifluoromethyl-substituted methyl benzoates. Consequently, apparent dipole moments in benzene of the methyl esters of 2-methyl-, 2,6-dimethyl-, 2-trifluoromethyl-, and 2,6-bistrifluoromethyl-benzoate have been determined, together with that of methyl 2,2-dimethylpropanoate as an aliphatic reference standard.

EXPERIMENTAL

The apparent dipole moments were calculated as described previously [1] from experimental measurements at 25·0° of dielectric constant, specific volume, and refractive index to Na-D radiation [listed in Supplementary Publication SUP No. 20564 (4 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 to 0·018. The slopes α, β, and ν respectively of the linear graphs of dielectric constant, specific volume, and refractive index squared against weight fraction, the polarisation data in which the symbols have their usual significance, and the computed dipole moments (μ) are given in the Table.

Materials.—Benzene, dried by prolonged refluxing over sodium, was distilled and the fraction of b.p. 80·1° at 760 mmHg was collected. The solutes, which were purified immediately before use, were prepared as indicated and had the following constants: methyl 2-methylbenzoate, b.p. 108—109° at 25 mmHg and methyl 2,6-dimethylbenzoate, b.p. 52—53° at 1 mmHg from the acid using boron trifluoride and methanol; [2] methyl 2-trifluoromethylbenzoate, b.p. 104—105° at 25 mmHg, and methyl 2,6-bistrifluoromethylbenzoate, m.p. 31—32° [3] from the acid and diazomethane; methyl 2,2-dimethylpropanoate, b.p. 102—103° from the acid chloride and methanol.

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

Compound	α	β	ν	$P_{2,\infty}$/cm^3	${}_{E}P_2$/cm^3	μ/D
Methyl 2,2-dimethylpropanoate	2·445	0·008	−0·347	93·26	31·53	1·93
Methyl 2-methylbenzoate	1·992	−0·207	0·050	98·18	42·69	1·65
Methyl 2,6-dimethylbenzoate	1·882	−0·171	0·010	105·74	47·16	1·69
Methyl 2-trifluoromethylbenzoate	4·909	−0·364	−0·128	236·35	41·73	3·09
Methyl 2,6-bistrifluoromethylbenzoate	3·300	−0·412	−0·209	228·26	47·56	2·97

DISCUSSION

For the purposes of this discussion, it is assumed that in an unhindered ester, the ester group is coplanar with the benzene ring.[4] The angle α which the group moment makes with the major axis of the ring is calculated from equation (1), by taking the resultant moment μ_R for methyl 4-methylbenzoate as 2·12 D [1] and component moments μ_X and μ_Y for toluene and methyl benzoate as 0·37 and 1·93 D,[1] respectively. This angle is found to be 63° 43′.

$$\mu_R^2 = \mu_X^2 + \mu_Y^2 + 2\mu_X\mu_Y \cos \alpha \qquad (1)$$

In explaining the experimentally observed moments of the hindered esters studied, two models are considered. In one, the ester group is assumed to be coplanar with the ring and the C–Me, C–CF$_3$, and C–CO$_2$Me group moments necessary to explain the observed moments are calculated from equation (1). In the second model, the ester group

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

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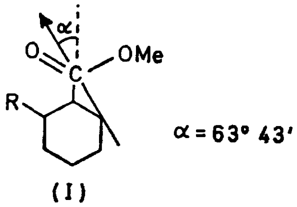
is assumed to be twisted through an angle θ from the planar arrangement of conformers (Ia) and (Ib).



(I)

{a; R = Me, μ(calc.) = 1·56 D [equation (1)]}
{b; R = CF_3, μ(calc.) = 4·49 D [equation (1)]}

It is also assumed that the ester group moment is independent of θ, although McRae and Goodman[5] have shown that the group moment depends on $\cos^2\theta$. However, the observed moments of methyl 2,2-dimethylpropanoate (1·74 D) and methyl benzoate (1·93 D) are sufficiently alike in magnitude to imply only a small mesomeric moment in the latter compound. The angles θ appropriate to the monosubstituted esters are calculated from equation (2), in which μ_X for the methyl and trifluoromethyl groups is —0·37 and 2·56 D,[1] respectively.

$$\mu_R^2 = 1{\cdot}93^2 + \mu_X^2 + 2(1{\cdot}93)\mu_X(\cos 60° \sin 26° 17' + \sin 60° \cos 26° 17' \cos \theta) \quad (2)$$

The observed moments of methyl 2-methylbenzoate and methyl 2-trifluoromethylbenzoate can be explained by reducing the C–Me group moment in the conformer (Ia) and the C–CF_3 group moment in (Ib) from the literature values of 0·37 and 2·56 D to 0·28 and 1·16 D, respectively. Alternatively, rotation of the dipole of the ester group through angles of 42° 1′ and 112° 21′ would account for the observed moments. The larger size of the trifluoromethyl group, covalent diameter 3·3 Å compared with 2·8 Å for the methyl group,[6] coupled with the strong lone-pair repulsive forces between the trifluoromethyl and ester groups could be responsible for the more pronounced displacement of the ester group in (Ib). Rotation of the ester group and the electronic effects of the 2-methyl and 2-trifluoromethyl groups will affect the conjugation between the phenyl and ester groups, thereby causing changes in the *ortho*-group–C(ring) bond moments. The probable orientation of the ester group, relative to that of the benzene ring, would be between that of a fully conjugated planar molecule and that corresponding to complete steric repulsion.

The observed moments of the 2,6-disubstituted esters cannot be explained by rotation of the ester group because of the symmetry of the *ortho*-groups about the C(ring)–C(substituent) axis and that of the molecule as a whole about the major axis of the ring. However, reductions in ester group moment from 1·93 to 1·82 D, and in C–CF_3 group moment from 2·56 to 1·56 D in the 2,6-dimethyl and 2,6-bistrifluoromethyl esters, respectively, satisfy the vector analysis. The large reduction in the C–CF_3 group moment in the latter ester must arise from an appreciable lone-pair repulsion effect.

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