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ORTHO EFFECT OF ONE METHYL GROUP: CONFORMATION OF METHYL 5-NITRO-2-METHYLBENZOATE IN CRYSTAL AND IN SOLUTION

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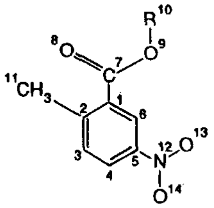
The x-ray structure of methyl 5-nitro-2-methylbenzoate was determined [$M_r = 195{\cdot}17$, monoclinic, $P2_1/c$, $a = 7{\cdot}265(1)$, $b = 7{\cdot}749(1)$, $c = 16{\cdot}526(3)$ Å, $\alpha = 91{\cdot}50(2)^\circ$, $V = 930{\cdot}0(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}39$ g cm^{-3}, Cu Kα, $\lambda = 1{\cdot}5418$ Å, $\mu = 9{\cdot}56$ cm^{-1}, $F(000) = 408$, $T = 291$ K, $R = 0{\cdot}081$ for 1295 observed reflections]. In contrast to the planar molecule of the corresponding acid, studied previously, the carboxylate group in the ester molecule is twisted through an angle 25° from the ring plane. This torsion angle was estimated to be 65° in benzene solution; the estimation was based on the dipole moment and that of methyl 2-methylbenzoate. For the corresponding ethyl esters a value of 79° was found in a similar way. Although these results are expressed in terms of one non-planar conformation, the alternative explanation of an equilibrium of two planar forms is not excluded in solution. The only safe conclusion is that the energy differences are small and the conformation is sensitive both to the conditions and to small changes in structure; a large part of the observed effects of an *ortho*-methyl group are due to reasons other than to the hindered resonance.



1 R = H
2 R = CH$_3$
3 R = C$_2$H$_5$

Ortho effects in substituted benzoic acids were observed on their dissociation constants,[1–4] IR spectra,[2,5] NMR spectra[6–8] and dipole moments,[9] and also on the IR spectra,[5,10] electronic spectra,[11] NMR spectra[6,8,12] and dipole moments[13,14] of their esters. The results were interpreted mostly in terms of the twisted carboxyl group and sterically hindered conjugation. They served even to evaluate the steric effect of the methyl group and the resonance effect of the carboxyl group.[2,15] Although this reasoning is undoubtedly correct for bulky substituents or for 2,6-disubstitution, it was recently questioned by us in the case of a single *ortho*-methyl group.[16] The reason was that the molecules of 5-nitro-2-methylbenzoic acid[16] (**1**) and 2,3-dimethylbenzoic acid[17] are planar in the crystalline state. Instead of twisting, two other effects were observed, relieving the steric strain: stretching of the C(1)—C(2) bond and in-plane deformation of the C(7)—C(1)—C(2) and C(11)—C(2)—C(1) angles.

In this work we extended the investigation to the corresponding ester, methyl 5-nitro-2-methylbenzoate (**2**). In addition to its x-ray structure, we examined also its conformation in solution, using dipole moment measurements in benzene on **2** and **3**, together with the

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simple compounds methyl 2-methylbenzoate (**4**) and ethyl 2-methylbenzoate (**5**). No crystal structure has been reported to date for a 2-methylbenzoic acid ester with the second *ortho* position unoccupied. The solution conformation of **4** was investigated previously by dipole moments,[13] in addition to some IR and NMR studies.[6,8,10,12]

The model compounds chosen here are characterized by the presence of a nitro group, which has two merits: a higher melting point is important for x-ray work, and an additional known moment is exploited in the analysis of dipole moments.[18]

EXPERIMENTAL AND RESULTS

Methyl 5-nitro-2-methylbenzoate,[19] $C_9H_9NO_4$ (**2**), m.p. 69 °C, and ethyl 5-nitro-2-methylbenzoate (**3**), m.p. 30 °C (benzene–hexane) were prepared from the acid.[16]

Crystals of **1** were obtained by slow cooling of a heptane solution, D_m was not measured. Its properties were as follows: parallelepiped crystal with dimensions $0{\cdot}42 \times 0{\cdot}36 \times 0{\cdot}04$ mm, lattice parameters refined using 20 reflections in the range $5° \leqslant 2\theta \leqslant 50°$; Huber four-circle diffractometer, RU200 rotating anode generator, graphite monochromatized Cu Kα radiation; 1681 $hk \pm l$ independent reflections with $\sin\theta/\lambda \leqslant 0{\cdot}60$ Å^{-1}; $0 \leqslant h \leqslant 8$, $0 \leqslant k \leqslant 9$, $-18 \leqslant l \leqslant 19$, 1295 with $I \leqslant 2{\cdot}5\sigma(I)$. Some degradation of the crystal during x-ray exposure was observed: a standard reflection (2–23) was checked every 50 reflections, and the data in each block were rescaled to take into account the decay. The structure solved using SHELX86.[20]

H atoms of the phenyl ring were obtained from difference Fourier synthesis and those of the methyl groups were calculated (C—H = 1·08 Å, H—C—H = 109·5°). Anisotropic least-squares refinement[21] using F; H isotropic with common refined temperature factor; $w = 1/(\sigma^2 + 0{\cdot}35131^2)$, $R = 0{\cdot}081$, $R_w = 0{\cdot}097$ for 1295 observed reflections. The high values of the R indices probably result from the poor quality and degradation of the crystal. The final maximum shift to error = 0·12, $S = 0{\cdot}24$. Maximum and minimum heights in the final difference Fourier synthesis were 0·47 and −0·52 e Å^{-3}. Atomic scattering factors were obtained from the International Tables.[22]

The atomic parameters are given in Table 1, bond distances and angles in Tables 2 and 3 and torsion angles in Table 4.

Table 1. Atomic coordinates (×10^4) and equivalent temperature factors for methyl 5-nitro-2-methylbenzoate (**2**)

Atom	x/a	y/b	z/c	B^a_{eq}(Å^2)
C(1)	7232(4)	1528(3)	−299(2)	3·68(5)
C(2)	7434(4)	3305(4)	−99(2)	4·41(5)
C(3)	8101(5)	3677(4)	684(2)	5·23(6)
C(4)	8555(5)	2446(4)	1244(2)	4·88(6)
C(5)	8353(4)	731(3)	1014(2)	3·78(5)
C(6)	7707(4)	273(3)	257(2)	3·67(5)
C(7)	6456(4)	994(4)	−1106(2)	4·33(5)
O(8)	5447(5)	1843(4)	−1524(2)	7·74(7)
O(9)	6976(4)	−578(3)	−1292(1)	5·72(5)
C(10)	6288(6)	−1283(5)	−2057(2)	6·48(8)
C(11)	7017(7)	4762(5)	−675(2)	6·50(8)
N(12)	8860(4)	−632(3)	1594(1)	4·58(5)
O(13)	9019(4)	−2103(3)	1347(1)	6·17(5)
O(14)	9132(5)	−208(4)	2296(1)	7·06(6)

[a] $B_{eq} = (8/3)\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 2. Bond distances in compound **2**

Bond	Distance (Å)	Bond	Distance (Å)
C(1)—C(2)	1·422(4)	C(2)—C(11)	1·503(4)
C(2)—C(3)	1·399(5)	C(7)—O(8)	1·192(4)
C(3)—C(4)	1·363(5)	C(7)—O(9)	1·314(4)
C(4)—C(5)	1·389(4)	O(9)—C(10)	1·453(4)
C(5)—C(6)	1·371(4)	C(5)—N(12)	1·466(4)
C(6)—C(1)	1·376(4)	N(12)—O(13)	1·218(3)
C(1)—C(7)	1·492(4)	N(12)—O(14)	1·218(4)

Table 3. Bond angles in compound **2**

Angle	Value (°)	Angle	Value (°)
C(6)—C(1)—C(2)	120·4(0·3)	C(7)—C(1)—C(2)	120·7(0·3)
C(7)—C(1)—C(6)	118·9(0·2)	C(3)—C(2)—C(1)	116·5(0·3)
C(11)—C(2)—C(1)	124·1(0·3)	C(11)—C(2)—C(3)	119·4(0·3)
C(4)—C(3)—C(2)	123·7(0·3)	C(5)—C(4)—C(3)	117·5(0·3)
C(6)—C(5)—C(4)	121·9(0·3)	N(12)—C(5)—C(4)	119·1(0·2)
N(12)—C(5)—C(6)	119·0(0·2)	C(5)—C(6)—C(1)	120·0(0·3)
O(8)—C(7)—C(1)	125·3(0·3)	O(9)—C(7)—C(1)	111·2(0·2)
0(9)—C(7)—0(8)	123·4(0·3)	C(10)—0(9)—C(7)	117·2(0·3)
O(13)—N(12)—C(5)	118·6(0·2)	O(14)—N(12)—O(5)	117·5(0·3)
O(14)—N(12)—O(13)	123·9(0·3)		

Table 4. Torsion angles ($\sigma = 1$) in compound **2**

Angle	Value (°)	Angle	Value (°)
C(6)—C(1)—C(2)—C(3)	−1	C(2)—C(3)—C(4)—C(5)	0
C(6)—C(1)—C(2)—C(11)	178	C(3)—C(4)—C(5)—C(6)	0
C(7)—C(1)—C(2)—C(3)	177	C(3)—C(4)—C(5)—N(12)	179
C(7)—C(1)—C(2)—C(11)	−4	C(4)—C(5)—C(6)—C(1)	0
C(2)—C(1)—C(6)—C(5)	1	N(12)—C(5)—C(6)—C(1)	180
C(7)—C(1)—C(6)—C(5)	−177	C(4)—C(5)—N(12)—O(13)	−166
C(2)—C(1)—C(7)—O(8)	−25	C(4)—C(5)—N(12)—O(14)	12
C(2)—C(1)—C(7)—O(9)	157	C(6)—C(5)—N(12)—O(13)	13
C(6)—C(1)—C(7)—O(8)	153	C(6)—C(5)—N(12)—O(14)	−168
C(6)—C(1)—C(7)—O(9)	−25	C(1)—C(7)—O(9)—C(10)	179
C(1)—C(2)—C(3)—C(4)	0	O(8)—C(7)—O(9)—C(10)	1
C(11)—C(2)—C(3)—C(4)	−179		

Table 5. Polarization and dipole moment data for 2-methylbenzoates (benzene, 25 °C)

Compound	α^a	β^a	P_2^0 (cm^3 mol^{-1})	R_D^b (cm^3 mol^{-1})	$\mu^c_{(D)}$	$\mu_{calc.}{}^d(\tau)$ (D)	x^e (%)
4	2·19	−0·262	101·2	42·5	1·67[f]	1·70 (63°)	73
2	7·48	−0·428	315·8	48·8	3·60	3·57 (63°)	73
5	2·13	−0·119	116·0	47·2	1·81	1·80 (77°)	61
3	8·27	−0·420	369·9	53·5	3·92	3·94 (77°)	61

[a] Slopes of the plots of ε_{12} and d_{12}^{-1}, respectively, versus the weight fraction w_2.
[b] Calculated from increments; see Experimental.
[c] Correction for the atomic polarization taken as 5% of the R_D value.
[d] Calculated according to equation (1) with the value of τ as given in parentheses.
[e] The population of the sp rotamer which gives the same $\mu_{calc.}$ as in the preceding column [according to equation (2)].
[f] Literature[13] gives 1·65 D.

Dipole moments were determined by the Halverstadt–Kumler method;[23] some details of the procedure have been reported.[24] The molar refractions were calculated from Vogel's increments.[25] The polarization data and dipole moments are listed in Table 5. The dipole moments expected for the individual conformations were calculated by vector addition of the standard group moments:[26] C_{ar}—CH_3 0·3 D, C_{ar}—NO_2 4·0 D, C_{ar}—$COOCH_3$ 1·86 D at an angle of 64° to the C(1)—C(7) bond (experimental determination[27]); for the C_{ar}—$COOC_2H_5$ group the value is greater[28] (1·9 D, 62°) and less accurate. The bond angles were either assumed to be hexagonal or taken from the x-ray geometry, with almost identical results.

DISCUSSION

As the first task, all the bond lengths, bond angles and torsion angles of **2** (Tables 2–4) were compared with the corresponding values[16] for the parent acid **1**. In several cases the differences significantly exceeded the combined standard deviations, but their reliability is affected by the relatively high *R*-factor. Therefore, the similarity of molecules **1** and **2** can be better estimated with reference to the two molecules of **1** present in one crystal cell.[16] It turned out that the differences between **1** and **2** are similar in magnitude to those between the two molecules of **1**; this is true both for bond lengths (standard deviations 0·014 and 0·015 Å, respectively) and bond angles (0·9° and 1·1°, respectively). Note also that the internuclear bond angles in **1** are only in qualitative agreement with the value predicted by summing the standard substituent effects.[29] Certain differences in the geometries of the COOH and $COOCH_3$ groups are evident and need not be discussed: particularly the longer C(7)=O(8) and the shorter C(7)—O(9) bond and the smaller C(1)—C(7)—O(8) angle in the acid molecule may be caused by hydrogen bonding. In conclusion, there is only one actually important difference between **1** and **2**, viz. in the torsion angles. Whereas the molecule of the acid **1** is planar, within the experimental accuracy, the molecule of the ester **2** is not. As both the ester and nitro groups are twisted from the ring plane, the reason can be seen merely in different crystal environments rather than in the potential energy curves. The only safe conclusion is that these curves are rather flat with small energy differences.

Of the other deformations observed in the acid **1**, two were found also in the ester **2**: stretching of the C(1)—C(2) bond and widening of the C(1)—C(7)—C(11) angle. Note that the three observed effects, twisting, bond stretching and angle deformation, would be connected with comparable energies[30] as estimated roughly within the framework of the MMP2 force field.[31] However, these estimated energies are still too low to explain completely the experimental energy of destabilization[32] of 2-methylbenzoic acid (in comparison with benzoic acid).

Essentially concordant results were obtained for the conformation in solution. The dipole moment data (Table 5) were processed by the well established graphical method.[18] The expected dipole moments were calculated from bond moments for the two planar conformations, sp (C=O *cis* to CH_3 as in **2**) and ap (C=O *trans* to CH_3). They were plotted as μ^2 (Figure 1), with values for the unsubstituted compound **4** or **5** on the abscissa and for the nitro derivative **2** or **3** on the ordinate. Any point on the connecting line may represent either a single conformer with a given torsion angle τ, or a mixture of the two planar forms, ap and sp, in a given molar fraction x. The graphical picture thus represents the mathematical expressions:

$$\mu^2_{\text{exp}} = \mu^2_{\text{sp}}(1 + \cos\tau)/2 + \mu^2_{\text{ap}}(1 - \cos\tau)/2 \qquad (1)$$

or

$$\mu^2_{\text{exp}} = x\mu^2_{\text{sp}} + (1 - x)\mu^2_{\text{ap}} \qquad (2)$$

The fundamental assumption is that the substituent (NO_2) does not influence the conformation.[33] In our case this assumption is fulfilled very well, since the experimental points lie on the connecting lines with surprising accuracy; see also the agreement of the calculated and experimental values in Table 5.

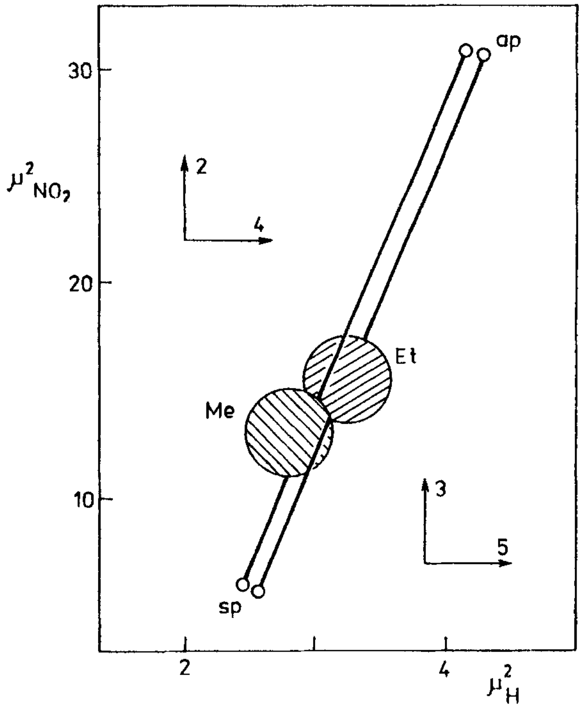

Figure 1. Comparison of squared dipole moments of compounds **4** and **5** (abscissa) and **2** and **3** (ordinate). Open points, calculated for ap and sp conformations; hatched points, experimental

The 'effective' torsion angles – somewhat different for the methyl and ethyl esters – may be compared with literature data obtained from the dipole moment[13] of the single compound **4** ($\tau = 42°$), from its ^{13}C and ^{17}O NMR spectra[8,12] (18°, 29°), and further with the corresponding values for 2-methylbenzoic acid, either experimental[7,16] (21° or 36°, almost 0°), theoretically[8,34] calculated (29°, 37°) or obtained by interpolation[1] (11°).

Our values in the crystalline phase and in solution are near to the two ends of the whole scale. Most of the workers cited assumed only a non-planar conformation, and an explanation based on an equilibrium of the ap and sp forms was only occasionally taken into account[14] or preferred.[10] Several times the opinion was offered that the molecule is planar,[5,35] without considering a conformational equilibrium. In our opinion, such an equilibrium has not been disproved and would be in agreement with many experimental findings. A critical factor might be the presence of doubled IR bands, but the spectral observations are controversial.[10,36] In our opinion, the problem may not be considered to have been solved. Note also that an equilibrium of planar forms with a well defined energy barrier was proved in the case of 2-halobenzoic acid esters.[37,38] It is not clear why this barrier should be absent with 2-methyl derivatives, since the steric hindrance of the methyl group cannot been larger than that of the heavier halogens.

CONCLUSIONS

The conformation of (substituted) 2-methylbenzoic acids and their esters has not be definitely established: a non-planar form may represent either an energy minimum or a maximum. Further progress may be expected mainly from more sophisticated theoretical calculations. For the time being, only two conclusions seem safe: (i) the conformation is hardly rigid and may change appreciably with the phase and conditions, and also with further substitution; and (ii) of the two planar conformations, the sp form is more stable, probably for steric reasons:[37] if an equilibrium is assumed, the sp form prevails, whereas if a non-planar conformation is assumed, it is nearer to sp ($\tau < 90°$). Under these conditions, it is not justifiable to use these compounds in the correlation analysis when evaluating the resonance or steric effects.[2,15] Most observed facts, particularly in aqueous solution, might be explained by reasons other than the steric hindrance of resonance, e.g. induction within the methyl group[4] or steric hindrance to solvation (note, e.g., the reversal of substituent effects with the solvent composition[3]). To separate these effects, additional models would be needed.

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