STRUCTURE OF 5-NITRO-2-METHYLBENZOIC ACID:
ortho EFFECT OF THE METHYL GROUP

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The X-ray structure of the title compound was determined: $M_r = 181.15$, triclinic, $P\bar{1}$, $a = 7.628(2)$ Å, $b = 10.475(3)$ Å, $c = 10.522(2)$ Å, $\alpha = 90.61(2)°$, $\beta = 98.19(2)°$, $\gamma = 76.41(2)°$, $V = 808.6(4)$ Å^3, $Z = 4$, $D_x = 1.49$ g cm^{-3}, CuK$_\alpha$, $\lambda = 1.5418$ Å, $\mu = 10.57$ cm^{-1}, $F(000) = = 376$, $T = 291$ K, $R = 0.049$ for 1 713 observed reflections. The deformations induced by the steric effect of the *ortho*-methyl group are discussed in some detail. They are partly different from those commonly considered, in particular the carboxyl group is coplanar with the benzene ring.

Steric arrangement of *ortho*-substituted benzoic acids is of importance for discussing their dissociation constants[1,2], electronic spectra[3], or dipole moments[4]. The problem reappears with their esters which should possess very similar conformations[5-7]. While the carboxyl group is evidently twisted out of the aromatic plane in the presence of bulky *ortho* substituents, some doubts persist just about the simple 2-methylbenzoic acid[1-4,8] since the steric strain can be relieved also by deformations of another kind. An X-ray study of this compound[8] was not sufficiently precise for a decision. Searching in the Cambridge Structural Database[9] has not revealed any substituted benzoic acid, or its ester, with one *ortho*-methyl group and the other *ortho* position unoccupied, except 2,3-dimethylbenzoic acid[10] in which strengthening of the steric effect may occur (buttressing effect). For these reasons we investigated the title compound, more favourable than 2-methylbenzoic acid due to its higher melting point.

EXPERIMENTAL

5-Nitro-2-methylbenzoic acid, m.p. 179°C, was prepared according to the literature[11]. Crystals obtained by evaporation from dichloromethane. D_m not measured. Parallelepiped crystal with dimensions $0.12 \times 0.20 \times 0.25$ mm. Lattice parameters refined using 15 reflections in the range $5° \leqq 2\Theta \leqq 45°$. Huber four circle diffractometer, graphite monochromatized CuK$_\alpha$ radiation. 2 920 $h \pm k \pm l$ independent reflections with $\sin \Theta/\lambda \leqq 0.599$ Å^{-1}; $0 \leqq h \leqq 9$, $-12 \leqq k \leqq 12$,

$-12 \leqq l \leqq 12$, 1 713 with $I \geqq 2 \cdot 5\sigma(I)$. Standard reflection $(2,2,-3)$ checked every 50 reflections: no significant deviation. Structure solved by MULTAN80[12]. H atoms from difference Fourier synhtesis. Anisotropic least squares refinement (SHELX76)[13] using F; H isotropic with common refined temperature factor; $w = 1/(\sigma^2 + 0 \cdot 01314F^2)$, $R = 0 \cdot 049$ $R_w = 0 \cdot 061$ for 1 713 observed reflections. Final maximum shift to error $= 0 \cdot 4$ (U_{12} of C(1B)); $S = 0 \cdot 65$. Maximum and minimum heights in final difference Fourier synthesis 0·28 and $-0 \cdot 31$ e . Å^{-3}. Atomic scattering factors from *International Tables for* X-ray *Crystallography*[14].

RESULTS AND DISCUSSION

The atomic parameters are given in Table I. Figure 1 is a view of molecule A, showing the numbering of the atoms (Programme PLUTO[15]). Bond distances and angles are given in Tables II and III, torsion angles in Table IV.

The two independent molecules in the unit cell differ mainly by their orientation; as shown in Tables II—IV their geometrical parameters are very similar. For the following discussion the average values will be sufficient.

The steric interaction between the two *ortho*-standing groups may produce particularly the following distortions which may be present or absent in the case under consideration: *a*) Rotation of the carboxyl group out of the ring plane is practically absent (torsion angle O(1)—C(8)—C(1)—C(6) only $3 \pm 1°$). *b*) Out-of-plane deflection of the CH_3 and COOH groups to opposite sides is not observed (torsion angle C(8)—C(1)—C(6)—C(7) only 1·5°). *c*) In-plane deformation (splaying-out) appears as an important mechanism of the steric strain relief. Quantitatively it is expressed as deviations of the exocyclic C—C bond from the angle bisector of the opposite internal ring angle. It amounts 3° for each group. *d*) The latter effect is supported by the deformation of the ring angles themselves. At the atoms bearing substituents these are contracted by 1·5° as compared to the values anticipated from the additive effects[16] of the two groups. *e*) Deformations within the carboxylic group seem to be insignificant. *f*) A remarkable effect, often neglected in conformation analysis, is lengthening of the aromatic C—C bond between the substituents. It may be estimated from the difference between this bond length and the average of all bonds in the ring. The value of 0·026 Å is approximately double of the highest values found in monosubstituted benzenes[17].

Qualitatively the same results were found[10] for 2,3-dimethylbenzoic acid, in spite of the lower accuracy $(R = 0 \cdot 091)$ and of the possible buttressing effect. In both compounds the practically coplanar carboxyl group is in the *sp* conformation (the carbonyl oxygen near to methyl). This conformation was interpreted in the case of 2-halogenobenzoic acids[6] by the larger O=C—C angle as compared to O—C—C. The effect is operative also in their esters in competition with the electrostatic effect[5].

Summarizing, the steric effect of the methyl group causes several deformations, partly different from those commonly considered. In particular, it seems that the torsional energy was often underestimated and stretching energy overestimated.

Hence the reasoning based on twisting out the carboxyl group should be reevaluated in the case of 2-methylbenzoic acid[2-4] and its esters[7,18] in favour of alternative explanations[1,19]. Although the conformation in solution need not be exactly the same as in crystal, the calculated torsion angles of 11°, 21°, or even 40° (ref[2,7,18], respectively) obtained from various physical quantities, are certainly not trustworthy; interpolation procedures may be misleading in the case of weak steric

TABLE I

Atomic coordinates (. 10^4) and equivalent temperature factors (Å^2).

$$B_{eq} = (8/3) \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	y	z	B_{eq}
		Molecule A		
C(1)	4 261(5)	4 043(3)	7 929(3)	3·22(6)
C(2)	5 827(5)	3 616(4)	8 823(3)	3·31(6)
C(3)	5 672(5)	3 224(3)	10 027(3)	3·53(6)
C(4)	4 006(6)	3 219(4)	10 408(4)	4·08(7)
C(5)	2 461(5)	3 637(4)	9 506(4)	4·29(7)
C(6)	2 517(5)	4 069(3)	8 265(3)	3·56(6)
C(7)	770(6)	4 536(5)	7 395(5)	4·62(8)
C(8)	4 521(5)	4 474(4)	6 627(3)	3·64(6)
N(1)	7 335(5)	2 815(3)	10 964(3)	3·93(6)
O(1)	3 267(4)	4 830(4)	5 768(3)	5·73(6)
O(2)	6 198(4)	4 410(4)	6 509(3)	6·06(7)
O(3)	7 154(5)	2 563(3)	12 064(3)	5·78(6)
O(4)	8 807(4)	2 755(3)	10 612(3)	5·39(6)
		Molecule B		
C(1)	2 309(5)	884(3)	7 130(3)	3·34(6)
C(2)	3 205(5)	1 224(4)	6 175(4)	3·52(6)
C(3)	2 216(5)	1 711(4)	4 997(3)	3·63(6)
C(4)	349(5)	1 869(4)	4 755(4)	3·98(7)
C(5)	−519(5)	1 503(4)	5 707(4)	3·84(6)
C(6)	400(5)	1 016(4)	6 902(4)	3·50(6)
C(7)	−677(6)	668(5)	7 873(5)	4·43(9)
C(8)	3 455(5)	424(3)	8 375(3)	3·34(6)
N(1)	3 188(5)	2 083(4)	4 005(3)	4·90(7)
O(1)	2 796(4)	202(3)	9 339(3)	4·81(5)
O(2)	5 174(4)	312(3)	8 403(3)	5·18(6)
O(3)	4 842(5)	1 970(4)	4 276(4)	7·10(8)
O(4)	2 312(5)	2 479(4)	2 979(3)	7·16(8)

effects. The lowered dipole moments[18] can be possibly explained by induction within the *ortho* methyl group[20], similar explanation may be advanced also for ^{13}C NMR shifts[7]. In the case of dissociation constants such polarization seems to be the most probable explanation[19]. It is true that twisting out may occur in the anion[1], but the resulting effect would be acid weakening instead of acid strengthening. The supposed symmetry effect was not confirmed[21].

Figure 2 shows the packing in the unit cell (Programme PLUTO[15]). Both molecules form dimers by hydrogen bonds between the carboxylic acid groups. The distances are as follows: $O \cdots O$ 2·648 or 2·630 Å, $H \cdots O$ 1·642 or 1·615 Å in the molecules A and B, respectively. These values are well in the expected range.

TABLE II

Bond distances (Å) in molecules A and B

Bond	A	B	Bond	A	B
C(2)—C(1)	1·396(5)	1·387(5)	C(6)—C(5)	1·397(5)	1·388(5)
C(6)—C(1)	1·419(5)	1·415(4)	C(7)—C(6)	1·486(5)	1·497(6)
C(8)—C(1)	1·501(4)	1·483(5)	O(1)—C(8)	1·210(4)	1·242(4)
C(3)—C(2)	1·366(5)	1·389(5)	O(2)—C(8)	1·288(4)	1·285(4)
C(4)—C(3)	1·387(5)	1·381(5)	O(3)—N(1)	1·223(4)	1·230(4)
N(1)—C(3)	1·470(5)	1·469(5)	O(4)—N(1)	1·220(4)	1·207(5)
C(5)—C(4)	1·389(6)	1·380(5)			

TABLE III

Bond angles (°) in molecules A and B

Angle	A	B	Angle	A	B
C(6)—C(1)—C(2)	120·4(3)	120·2(3)	C(5)—C(6)—C(1)	117·0(3)	117·7(3)
C(8)—C(1)—C(2)	117·0(3)	116·2(3)	C(7)—C(6)—C(1)	124·5(3)	123·9(3)
C(8)—C(1)—C(6)	122·6(3)	123·6(3)	C(7)—C(6)—C(5)	118·5(3)	118·4(3)
C(3)—C(2)—C(1)	119·6(3)	119·7(3)	O(1)—C(8)—C(1)	122·7(3)	122·4(3)
C(4)—C(3)—C(2)	122·6(3)	121·4(3)	O(2)—C(8)—C(1)	113·8(3)	115·6(3)
N(1)—C(3)—C(2)	118·6(3)	118·8(3)	O(2)—C(8)—O(1)	123·5(3)	122·0(3)
N(1)—C(3)—C(4)	118·7(3)	119·9(3)	O(3)—N(1)—C(3)	117·6(3)	117·8(3)
C(5)—C(4)—C(3)	117·1(3)	118·3(3)	O(4)—N(1)—C(3)	118·7(3)	117·8(3)
C(6)—C(5)—C(4)	123·2(3)	122·7(3)	O(4)—N(1)—O(3)	123·7(3)	124·4(4)
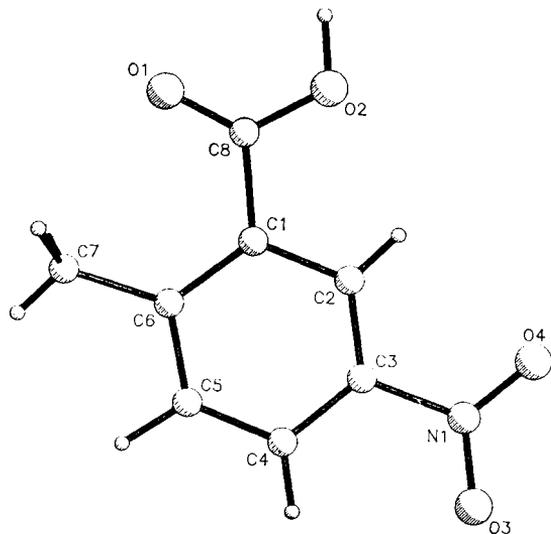
Fig. 1

View of 5-nitro-2-methylbenzoic acid (molecule *A*) showing the atom numbering[15]
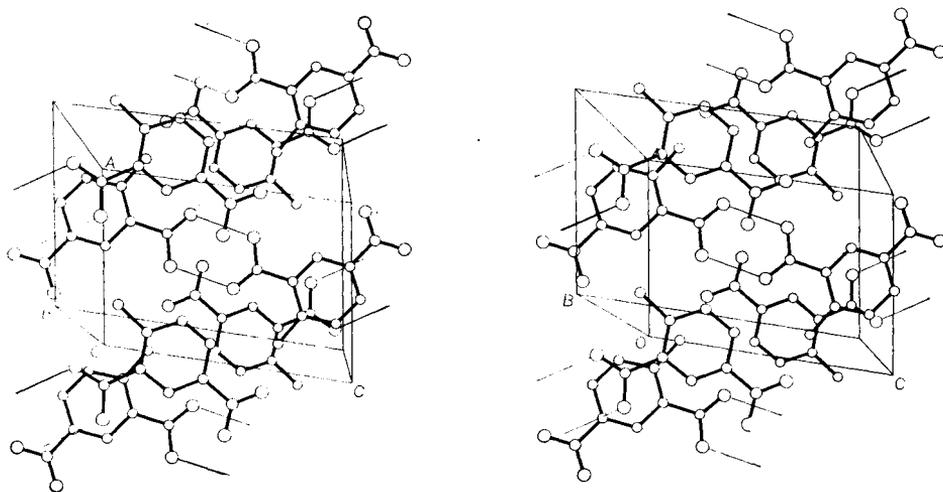
Fig. 2

Stereoscopic view of the packing in the unit cell and hydrogen bonding[15]

TABLE IV

Torsion angles (°) ($\sigma = 1$) in molecules A and B

Angle	A	B	Angle	A	B
C(6)—C(1)—C(2)—C(3)	0	1	C(1)—C(2)—C(3)—N(1)	−178	179
C(8)—C(1)—C(2)—C(3)	180	−178	C(2)—C(3)—C(4)—C(5)	0	−1
C(2)—C(1)—C(6)—C(5)	−1	0	N(1)—C(3)—C(4)—C(5)	179	180
C(2)—C(1)—C(6)—C(7)	178	180	C(2)—C(3)—N(1)—O(3)	174	−1
C(8)—C(1)—C(6)—C(5)	180	178	C(2)—C(3)—N(1)—O(4)	−5	178
C(8)—C(1)—C(6)—C(7)	−1	−2	C(4)—C(3)—N(1)—O(3)	−4	177
C(2)—C(1)—C(8)—O(1)	178	173	C(4)—C(3)—N(1)—O(4)	176	−3
C(2)—C(1)—C(8)—O(2)	−1	−4	C(3)—C(4)—C(5)—C(6)	−1	2
C(6)—C(1)—C(8)—O(1)	−2	−5	C(4)—C(5)—C(6)—C(1)	1	0
C(6)—C(1)—C(8)—O(2)	178	177	C(4)—C(5)—C(6)—C(7)	−178	179
C(1)—C(2)—C(3)—C(4)	0	0			

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