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Structure of *m*-Fluorobenzoic Acid, $C_7H_5FO_2$

BY TOORU TAGA, NORIKO YAMAMOTO AND KENJI OSAKI

Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606, *Japan*

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Abstract. $M_r = 140\cdot1$, monoclinic, $P2_1/c$, $a = 6\cdot809\ (2)$, $b = 3\cdot808\ (1)$, $c = 25\cdot904\ (6)$ Å, $\beta = 109\cdot20\ (2)°$, $V = 634\cdot3$ Å^3, $Z = 4$, $D_x = 1\cdot268$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot54178$ Å, $\mu = 0\cdot743$ mm^{-1}, $F(000) = 288$, $T = 296$ K. $R(F) = 0\cdot045$ for 859 unique observed reflexions. The benzene ring is significantly distorted, the C—C bond lengths varying from 1·364 (2) to 1·388 (3) Å, and the internal bond angle of the ring being 122·9 (2)° at the F-substituted position. The C—F bond length is 1·358 (3) Å. The molecules form hydrogen-bonded dimers, and they are stacked along the *b* axis. The shortest intermolecular F···F contact is 3·146 (2) Å.

Introduction. The benzene ring is usually distorted from $D_{6h}(6/mmm)$ symmetry by the substitution of the H atom with a strongly electronegative atom or group (Domenicano, Murray-Rust & Vaciago, 1983). The significant distortions of the benzene ring in fluorobenzoic acid have been observed in the *p*-substituted isomer (Colapietro, Domenicano & Ceccarini, 1979) and the *o*-substituted isomer (Ferguson & Islam, 1975). The structure of *m*-fluorobenzoic acid has been studied in order that it may be compared with those of the fluorobenzoic acid isomers and other F-substituted aromatic compounds.

Experimental. Transparent plate-like crystal from benzene solution. Crystal $0\cdot1 \times 0\cdot1 \times 0\cdot3$ mm mounted on a Rigaku AFC-5 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Cell parameters refined by least squares with 18 2θ values, $35 < 2\theta < 50°$. Intensities measured using 2θ–ω scan, scan width $\Delta(\omega) = 0\cdot8° + 0\cdot5°\tan\theta$. 972 reflexions with $2\theta < 120°$, h 0–7, k 0–6, l −26–26, 859 observed with $F_o > 3\sigma(F_o)$. No significant intensity variation for three standard reflexions. No absorption correction. Structure solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least squares with anisotropic thermal parameters for non-H atoms, isotropic parameters for H atoms. H positions determined by difference Fourier synthesis. $\sum w|F_o - kF_c|^2$ minimized with $w^{-1} = \sigma^2(F_o) + (0\cdot0023F_o)^2$; $R = 0\cdot045$, $R_w = 0\cdot063$. $(\Delta/\sigma)_{\max} = 0\cdot07$. Max. and min. height in final difference Fourier map 0·12 and −0·16 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic parameters are listed in Table 1.* The atomic numbering and thermal ellipsoids of the non-H atoms are shown in Fig. 1. Bond lengths and bond angles are given in Table 2. The C—F bond length of 1·358 (3) Å is in good agreement with the lengths of the corresponding bond in other F-substituted benzenes. The C hexagon of the benzene ring is planar within 0·001 Å. However, the bond lengths C(2)—C(3) 1·363 (3) Å and C(4)—C(5) 1·367 (4) Å are significantly

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* Lists of atomic parameters for H atoms, anisotropic thermal parameters for non-H atoms and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39764 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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shorter than the average distance 1·388 (6) Å for the C—C bonds of the benzene ring in benzoic acid (Bruno & Randaccio, 1980). The internal angles of the benzene ring are increased from 120° by 2·9° (14σ) at C(2)—C(3)—C(4), and decreased by 2·0° (10σ) at C(1)—C(2)—C(3) and by 1·4° (7σ) at C(3)—C(4)—C(5). Since the F atom has the highest electronegativity of all atoms, it may give the dominant effects for the ring deformation. The ring distortion, except for the shortening of the C(4)—C(5) bond, may be well explained by the σ-electron effects of the F substituent as revealed in the cases of monosubstituted benzenes by Domenicano *et al.* (1983). A similar trend of the ring distortions has been observed in the *p*- and *o*-isomers. The shortening of the C(4)—C(5) bond cannot, however, be explained by the σ effects of the F substituent, and must be related to the resonance effects (Domenicano & Murray-Rust, 1979) unique to the *m*-isomer.

Table 1. *Atomic parameters and their e.s.d.'s for m-fluorobenzoic acid*

$B_{\rm iso}$ is the isotropic equivalent of the anisotropic thermal parameter in Å^2. ($B_{\rm iso} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.)

	x	y	z	$B_{\rm iso}$
F(3)	0·6804 (2)	0·1455 (5)	0·7474 (<1)	7·36 (4)
C(1)	0·4510 (2)	0·2016 (4)	0·6010 (1)	4·27 (4)
C(2)	0·4708 (3)	0·1346 (5)	0·6551 (1)	4·72 (4)
C(3)	0·6561 (3)	0·2105 (5)	0·6941 (1)	5·07 (5)
C(4)	0·8227 (3)	0·3506 (6)	0·6820 (1)	5·52 (5)
C(5)	0·8013 (3)	0·4154 (6)	0·6285 (1)	5·54 (5)
C(6)	0·6157 (3)	0·3422 (5)	0·5874 (1)	5·00 (5)
C(7)	0·2534 (3)	0·1143 (5)	0·5572 (1)	4·47 (4)
O(1)	0·1122 (2)	−0·0412 (4)	0·5692 (1)	5·78 (4)
O(2)	0·2355 (2)	0·2041 (4)	0·5087 (1)	6·17 (5)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

F(3)—C(3)	1·358 (3)	C(1)—C(2)	1·387 (4)
C(1)—C(6)	1·389 (3)	C(1)—C(7)	1·485 (2)
C(2)—C(3)	1·363 (3)	C(3)—C(4)	1·380 (3)
C(4)—C(5)	1·367 (4)	C(5)—C(6)	1·387 (3)
C(7)—O(1)	1·252 (3)	C(7)—O(2)	1·269 (4)
C(2)—C(1)—C(6)	120·6 (2)	C(2)—C(1)—C(7)	119·6 (2)
C(6)—C(1)—C(7)	119·8 (2)	C(1)—C(2)—C(3)	118·0 (2)
F(3)—C(3)—C(2)	119·2 (2)	F(3)—C(3)—C(4)	117·8 (2)
C(2)—C(3)—C(4)	122·9 (2)	C(3)—C(4)—C(5)	118·6 (2)
C(4)—C(5)—C(6)	120·5 (2)	C(1)—C(6)—C(5)	119·4 (2)
C(1)—C(7)—O(1)	119·5 (2)	C(1)—C(7)—O(2)	117·7 (2)
O(1)—C(7)—O(2)	122·8 (2)		

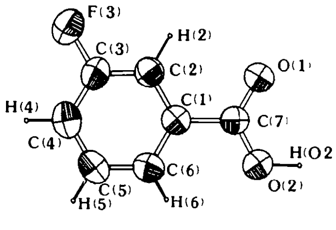

Fig. 1. *m*-Fluorobenzoic acid: atomic numbering and thermal ellipsoids at 50% probability.

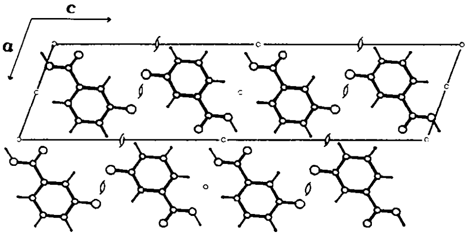

Fig. 2. Projection of the structure along the *b* axis.

The projection of the molecular packing along the *b* axis is shown in Fig. 2. The molecules are packed as centrosymmetric hydrogen-bonded dimers with an O···O distance of 2·631 (2) Å, and they are stacked along the *b* axis. The COOH group is rotated by 6·0 (1)° about the exocyclic C(1)—C(7) bond out of the plane of the benzene ring. The plane normals of the benzene ring and COOH group are tilted by 22·7 (1) and 27·0 (1)°, respectively, from the direction of the *b* axis. The mean separation between the parallel-packed benzene rings is 3·512 (7) Å, and that between the COOH groups is 3·392 (7) Å. The short intermolecular non-bonding contacts are 3·513 (3) Å for C(3)···C(4′), 3·514 (3) Å for C(1)···C(6′), and 3·400 (3) Å for O(1)···C(7′). The intermolecular contacts of the face-to-face benzene rings resemble those of the other fluorobenzoic acid isomers. The F atoms are arranged along the *b* axis with a period of 3·808 (1) Å. The shortest intermolecular F···F contact of 3·146 (2) Å is observed between the F atoms related by the twofold screw symmetry. The shortest C—H···F and C—H···H—C distances are 2·50 (2) and 2·67 (3) Å, respectively, for the H(4) atoms near the twofold screw axis.

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