The Crystal Structure of *o*-Fluorobenzamide

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Synopsis. The crystal of the title compound is monoclinic, with space group $P2_1/a$, $a=12.695$, $b=20.534$, $c=5.133$ Å, $\beta=97.80°$, $Z=8$. The molecules are connected by one pair of hydrogen bonds to form asymmetric dimers and these dimers are further linked by two kinds of hydrogen bonds into endless chains along the c axis.

The crystals of *m*- and *p*-fluorobenzamides[1,2] contain four molecules per unit cell and the molecules are connected by hydrogen bonds to form centrosymmetric dimers. These dimers are linked by two kinds of hydrogen bonds into one-dimensional chains (*m*-fluorobenzamide) and two-dimensional networks (*p*-fluorobenzamide). The present study was undertaken to determine the type of hydrogen bonds and the molecular arrangement in the crystal of *o*-fluorobenzamide which has eight molecules in a unit cell.

Experimental

Crystals were grown from a hot aqueous solution by slow cooling to room temperature. The cell dimensions and reflection intensities were measured on a Rigaku automated four-circle diffractometer using monochromatized Mo $K\alpha$ radiation. The crystal data are as follows: $a=12.695(2)$, $b=20.534(2)$, $c=5.133(1)$ Å, $\beta=97.80(1)°$, $P2_1/a$, $Z=8$.

The intensity data were collected by the 2θ-ω scan technique with a speed of $8°(2\theta)$ min^{-1} up to $2\theta=58°$. The crystal used had approximate dimensions of $0.4\times0.4\times0.5$ mm^3. A total of 1953 reflections were obtained, of which 1471 were non-zero reflections. No corrections for absorption and extinction were made.

Structure Determination and Refinement

The structure was solved by the direct method with the MULTAN program.[3] All the non-hydrogen atoms appeared clearly in the *E* map, and the hydrogen atoms were found on difference Fourier maps. The *R* value was finally reduced to 0.076 by the block-diagonal least-squares refinement using the program *HBLS V*[4] with anisotropic thermal parameters for non-hydrogen atoms and an isotropic one ($B=3.7$ Å^2) for hydrogen atoms. The weighting scheme of the type $w=1-\exp(-15s^2)$ with $s=\sin\theta/\lambda$ was used. The final positional parameters and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 1.[5]

Discussion

The bond lengths and bond angles are shown in Fig. 1. The molecular arrangement projected along the c axis is shown in Fig. 2. The least-squares plane through the six carbon atoms of the benzene ring and the plane through the C, N, and O atoms of the carbamoyl group for molecules I and II are given by the following equations:

molecule I

benzene ring $0.577X+0.612Y-0.541Z=1.864$,

carbamoyl group $0.588X+0.808Y-0.032Z=1.583$,

molecule II

benzene ring $0.527X+0.471Y+0.707Z=0.240$,

carbamoyl group $0.813X+0.555Y+0.179Z=1.064$,

where X, Y, and Z are coordinates measured in Å

Table 1. Final positional parameters with their standard deviations ($\times10^4$) and B_{eq}[a] for non-hydrogen atoms

	x	*y*	*z*	B_{eq}/Å^2
F (1)	3531 (3)	0213 (2)	3094 (5)	6.0
O (1)	1417 (3)	0196 (2)	−3505 (7)	4.5
N (1)	1413 (4)	0346 (2)	0788 (8)	4.6
C (11)	1820 (4)	0092 (2)	−1260 (9)	3.4
C (12)	2777 (4)	−0332 (2)	−0759 (9)	3.3
C (13)	3581 (4)	−0276 (3)	1327 (10)	4.0
C (14)	4459 (4)	−0678 (3)	1680 (12)	5.1
C (15)	4520 (4)	−1170 (3)	−0052 (12)	5.2
C (16)	3743 (5)	−1251 (3)	−2184 (12)	4.9
C (17)	2897 (4)	−0830 (3)	−2550 (10)	4.3
F (2)	−0226 (3)	2522 (2)	−6347 (9)	6.6
O (2)	−0376 (4)	1286 (2)	−0381 (7)	5.2
N (2)	−0180 (3)	1237 (2)	−4655 (9)	4.0
C (21)	−0546 (4)	1506 (2)	−2627 (9)	3.7
C (22)	−1199 (4)	2117 (2)	−3106 (10)	3.7
C (23)	−1031 (4)	2592 (2)	−4939 (11)	4.5
C (24)	−1633 (6)	3149 (3)	−5252 (15)	6.1
C (25)	−2450 (7)	3225 (4)	−3846 (17)	7.5
C (26)	−2659 (6)	2768 (4)	−2050 (16)	7.2
C (27)	−2028 (5)	2213 (3)	−1682 (12)	5.5

a) $B_{eq}=8\pi^2(u_1^2+u_2^2+u_3^2)/3$, where u_i is the root-mean-square deviation in the *i*-th principal axis of the thermal ellipsoid.

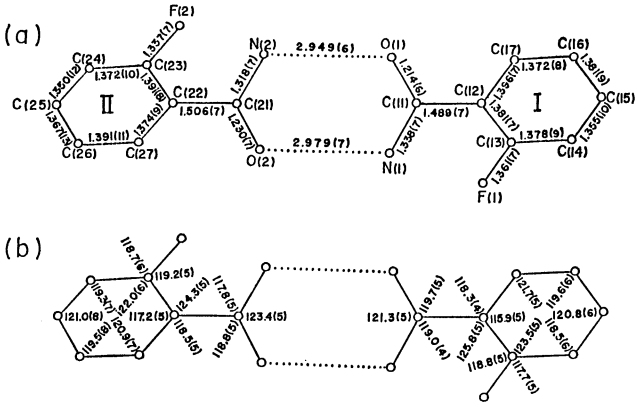

Fig. 1. a) Bond lengths (l/Å) and b) bond angles (ϕ/°).

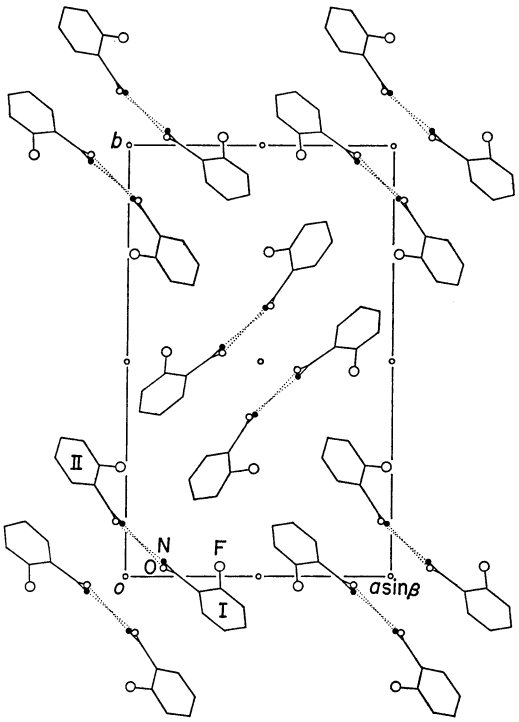

Fig. 2. The crystal structure viewed along the c axis.

along the orthogonal axes a, b, and c* respectively. The dihedral angles between the plane of the carbamoyl group and the mean plane of the benzene ring are 31.7° for molecule I and 35.4° for molecule II, which are rather small as compared with those of other ortho-substituted benzamides.[6] This can be explained from the fact that the van der Waals radius of the F atom is close to that of the H atom. It is interesting that the F atom lies on the side of N atom of the carbamoyl group for both of molecules I and II, while in the crystals of other *o*-halogenobenzamides[6] the halogen atoms lie on the side of O atom of the carbamoyl group. It is also noticeable that in the crystal of *o*-fluorobenzamide the unit cell contains eight molecules, which are linked in pairs by NH···O hydrogen bonds (2.949, 2.979 Å) to form asymmetric dimers. These dimers are further linked by the other NH···O hydrogen bonds (2.917, 2.945 Å) to form one-dimensional chains along the c axis. A pair of such chains related by a center of symmetry forms a double-chain having an enantiometric configuration.

X-Ray data collection was carried out on a Rigaku automated four-circle diffractometer at Crystallographic Research Center, Institute for Protein Research, Osaka University.

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