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Topochemical Studies. VIII. The Crystal and Molecular Structures of two Polymorphs of 4-Formylbenzoic Acid

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Form I of 4-formylbenzoic acid is stable at low temperature and transforms into form II at about 140 °C. The heat of transition (0·9 kcal mole^{-1}) corresponds to the entropy change of Rln4. The crystals of form I are monoclinic, space group $P2_1/a$, $Z=4$ with $a=7·28$ (3), $b=29·21$ (3), $c=3·74$ (1) Å, $\beta=121·5$ (2)°, and those of form II are triclinic, space group $P\bar{1}$, $Z=1$ with $a=6·43$ (1), $b=7·30$ (1), $c=3·81$ (1) Å, $\alpha=97·4$ (2), $\beta=91·3$ (2), $\gamma=83·2$ (2)°. The structures were solved by the Patterson method, and refined by the block-diagonal least-squares method using visually estimated Cu $K\alpha$ data. The final R values are 0·100 for 369 and 0·079 for 389 non-zero reflexions for forms I and II respectively. The structure of form I consists of a dimer linked by hydrogen bonds [2·57 (1) Å] between the carboxylic groups. The dimers are held together by C–H···O interactions to form a sheet on the (001) plane. The structure of form II contains fourfold disorder in the arrangement of the carboxylic and aldehydic groups, which results in an apparent centre of symmetry. Infinite chains of molecules linked by hydrogen bonds [2·608 (6) Å] along the [$\bar{1}$11] axis are held together side by side to form a sheet parallel to the (101) plane. This structure is similar to that of form I of terephthalic acid.

Introduction

In the course of studies of the crystal structure of bis(2-hydroxyethyl) terephthalate (Kashino & Haisa, 1975), it became of interest to determine the structure of 4-formylbenzoic acid (4-FBA), an important intermediate in the manufacture of terephthalic acid (TPA) from p-xylene. 4-FBA is known to constitute the principal impurity in TPA which is difficult to eliminate. In addition, polymorphism in aromatic aldehydes is of topochemical interest (Cohen, Schmidt & Sonntag, 1964; Ehrenberg, 1968; Coppens & Schmidt, 1964).

This paper reports the structures of two polymorphs of the compound obtained at room temperature from different solvents of recrystallization, and the structural relationship with TPA.

Experimental

Crystals of form I were grown, by cooling an acetonitrile solution in an autoclave at 150 °C, as very thin plates with developed {010} faces. Those of form II were obtained from an aqueous ethanol solution by slow evaporation as tiny needles elongated along the c axis. The dimensions of the crystals used were $1·20\times0·02\times0·30$ and $0·05\times0·09\times0·50$ mm for forms I and II respectively. Cell parameters were determined by the least-squares refinement using the reflexions recorded on oscillation photographs (Cu $K\alpha$, $\lambda=1·5418$ Å). The intensity data were collected on equi-inclination Weissenberg photographs. The intensities were estimated visually and corrected for Lorentz–polarization factors and spot shape. The crystal data and experimental details are listed in Table 1.

Structure determination and refinement

Form I

The structure was solved from a sharpened Patterson map. All the H atoms except that of the carboxylic

Table 1. *The crystal data and experimental details*

4-Formylbenzoic acid, $C_8H_6O_3$, M.W. 150·1

	Form I	Form II		
Crystal system	Monoclinic	Triclinic		
Space group	$P2_1/a$	$P\bar{1}$		
a (Å)	7·28 (3)	6·43 (1)	7·79*	7·55†
b	29·21 (3)	7·30 (1)	6·43	7·79
c	3·74 (1)	3·81 (1)	3·81	3·81
α (°)		97·4 (2)	91·3	68·4
β	121·5 (2)	91·3 (2)	111·6	121·6
γ		83·2 (2)	95·7	95·8
V (Å^3)	678 (4)	176 (1)		
Z	4	1		
D_x (g cm^{-3})	1·47	1·417		
D_m (by flotation in KI aqueous solution)	1·46	1·42		
μ (cm^{-1}) for Cu $K\alpha$	9·7	9·4		
F(000)	312	78		
Layers photographed	0kl to 5kl	hk0 to hk3		
Number of non-zero reflexions	369	389		

* Cell constants referred to the cell of form I of terephthalic acid (Bailey & Brown, 1967).

† Cell constants referred to the cell of form I of 4-formylbenzoic acid.

group were located by a difference Fourier synthesis. The structure was refined by the block-diagonal least-squares method. The weighting scheme used was: $w=1{\cdot}0$ for $0<F_o\le F_{\max}$ $(=8{\cdot}0)$ and $w=(F_{\max}/F_o)^2$ for $F_o>F_{\max}$. The contribution from the carboxyl H was not included. The final R value was 0·100 for 369 non-zero reflexions.*

Form II

The orientation of the molecule in the cell was found from a sharpened Patterson map. At first the space group was assumed to be $P1$ based on the molecular symmetry and $Z=1$. A Fourier synthesis, which was phased with all the heavy atoms except the O atom of the aldehydic group, revealed two peaks for the aldehydic O atom as if the molecule had a twofold axis along the long axis. Block-diagonal least-squares refinement of the disordered structure of the aldehydic group reduced R to 0·15 where anisotropic temperature factors were assigned to the heavy atoms and isotropic ones to the H atoms. The bond lengths in the benzene ring, however, continued to be abnormal (C–C, 1·2–1·5 Å) and the temperature factors of the carboxylic O atoms took considerably large values whereas those of aldehydic O atoms took small values. Thus additional disorder between the carboxylic and aldehydic groups in space group $P\bar{1}$ was postulated. The least-squares refinements reduced R to 0·085. A difference Fourier map revealed the carboxylic H atom as a single elongated peak of height 0·3 e Å^{-3}. The parameters of the disordered aldehydic and carboxylic H atoms were assumed (C–H; O–H 1·0 Å). The weighting scheme used was identical with that for form I, but here $F_{\max}$ was chosen to be 2·0. The final R value was 0·079 for 389 non-zero reflexions,* and the maximum parameter shift for heavy atoms was 0·2σ and that for H atoms, 0·9σ. A final difference map did not show any residual electron density greater than 0·3 e Å^{-3}.

The final atomic parameters are given in Tables 2 and 3. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computations were carried out on an NEAC 2200-500 computer at the Okayama University Computer Center. The main programs used were *HBLS*-5 and *DAPH* (Ashida, 1973).

Results and discussion

Projections of the crystal structures along the c axis for form I and on the bc plane for form II are shown

Table 3. *The final parameters of the hydrogen atoms*

	x	y	z	B(Å^2)
Form I				
H(1)	0·057 (12)	0·140 (2)	−0·026 (23)	1·2 (17)
H(2)	0·310 (13)	0·204 (3)	0·042 (25)	2·0 (19)
H(3)	0·777 (18)	0·115 (4)	0·172 (36)	7·5 (33)
H(4)	0·552 (11)	0·050 (2)	0·129 (21)	0·9 (17)
H(5)	0·619 (12)	0·241 (2)	0·149 (22)	0·9 (17)
Form II				
H(1)	0·422 (6)	0·173 (5)	0·483 (10)	3·7 (9)
H(2)	0·164 (5)	0·430 (5)	0·729 (9)	2·4 (7)
H(3)*	0·931	0·224	0·088	6·2
H(4)*	0·767	0·069	0·206	6·2
H(5)*	1·068	0·128	−0·044	6·2
H(6)*	0·866	−0·073	0·101	6·2

Atoms marked with an asterisk have an occupancy factor of 0·25.

Table 2. *The final positional and thermal parameters* (×10^4) *with standard deviations in parentheses*

The anisotropic coefficients have the form $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Form I									
C(1)	3018 (19)	903 (3)	500 (32)	562 (48)	13 (1)	1383 (162)	8 (13)	1261 (152)	−8 (23)
C(2)	2252 (19)	1346 (4)	236 (36)	413 (44)	18 (2)	1645 (163)	−6 (13)	1158 (141)	−27 (25)
C(3)	3500 (18)	1712 (4)	600 (36)	471 (46)	13 (1)	1913 (200)	−38 (13)	1061 (162)	4 (25)
C(4)	5520 (18)	1654 (3)	1106 (34)	471 (45)	12 (1)	1763 (192)	−41 (12)	1200 (158)	−10 (23)
C(5)	6341 (19)	1213 (4)	1408 (34)	509 (48)	15 (1)	1540 (160)	−25 (14)	1119 (147)	−11 (25)
C(6)	5054 (18)	837 (3)	1055 (33)	430 (40)	16 (1)	1401 (163)	22 (13)	951 (136)	−16 (24)
C(7)	1711 (18)	519 (3)	243 (33)	516 (47)	11 (1)	1621 (159)	−2 (12)	1115 (145)	−12 (23)
C(8)	6751 (19)	2058 (4)	1319 (41)	550 (50)	15 (2)	2193 (207)	0 (14)	1519 (165)	−27 (27)
O(1)	−53 (12)	570 (2)	114 (25)	426 (26)	16 (1)	2381 (126)	6 (8)	1387 (97)	5 (18)
O(2)	2380 (11)	110 (2)	197 (25)	480 (31)	16 (1)	2580 (140)	−6 (9)	1699 (112)	1 (19)
O(3)	8518 (13)	2039 (3)	1648 (29)	523 (32)	18 (1)	2791 (156)	4 (10)	1627 (120)	21 (20)
Form II									
C(1)	6449 (5)	3545 (5)	3564 (9)	279 (9)	252 (8)	728 (31)	−13 (14)	139 (26)	−47 (24)
C(2)	4534 (6)	3187 (5)	4811 (10)	331 (11)	232 (9)	899 (35)	−46 (16)	161 (30)	11 (26)
C(3)	3084 (6)	4645 (5)	6273 (10)	294 (10)	268 (9)	879 (35)	−77 (16)	184 (28)	25 (26)
C(4)	7983 (6)	1998 (6)	2028 (10)	318 (11)	268 (9)	981 (36)	−49 (17)	182 (30)	−10 (27)
O(1)*	9656 (5)	2334 (5)	658 (10)	345 (11)	249 (8)	1466 (41)	−19 (15)	528 (34)	−7 (28)
O(2)*	7581 (7)	356 (5)	2035 (12)	436 (13)	238 (9)	1675 (46)	−45 (17)	693 (39)	−50 (31)

Atoms marked with an asterisk have an occupancy factor of 0·75.

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* A list of structure factors for forms I and II has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31308 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

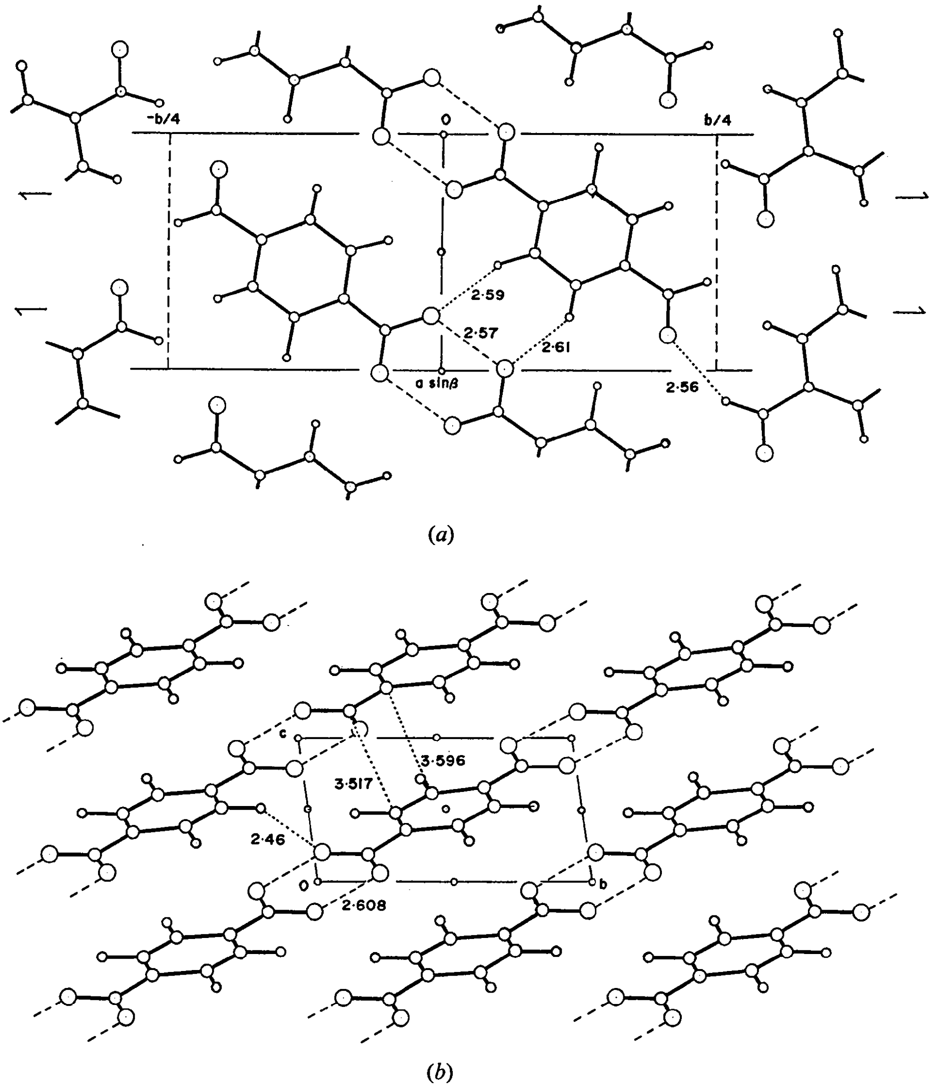


Fig. 1. Projections of the crystal structures (*a*) along the *c* axis for form I and (*b*) on the *bc* plane for form II. Broken lines show hydrogen bonds, and dotted lines intermolecular contacts.

in Fig. 1. The structure of form I consists of a dimer linked by hydrogen bonds [2·57 (1) Å] between the carboxylic groups. The dimers are held together by C–H···O interactions (H···O = 2·56 and 2·59 Å) to form a sheet on the (001) plane. The sheets are stacked along the *c* axis with a spacing of 3·43 Å.

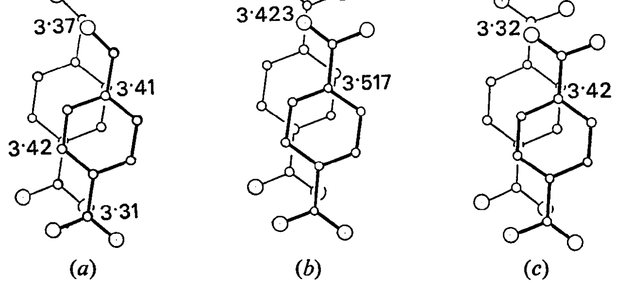
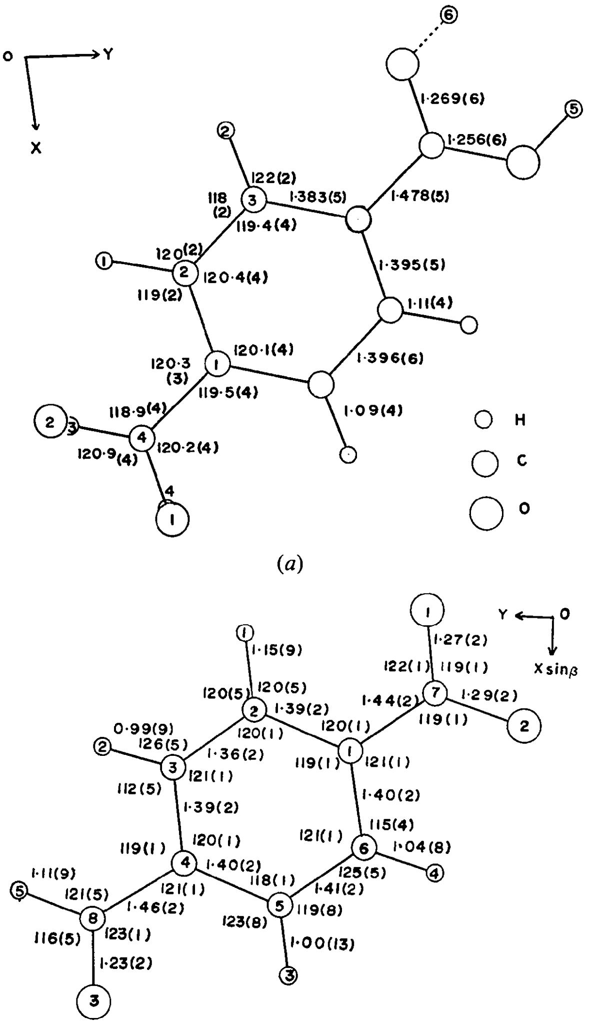


Fig. 2. Mode of overlapping of benzene ring planes (*a*) for form I of 4-FBA, (*b*) for form II of 4-FBA and (*c*) for form I of TPA.

The structure of form II contains fourfold disorder in the arrangement of the carboxylic and aldehydic groups. The structure is isomorphous with form I of TPA (Bailey & Brown, 1967). The molecules form an infinite chain along the [$\bar{1}$11] axis. The chains are held together side by side to form a sheet parallel to the (101) plane. The sheets are stacked along the *c* axis with a spacing of 3·47 Å, which is slightly longer than that in form I of TPA (3·40 Å). The intermolecular distance between O(1) and O(2) in the chain, 2·608 Å, is the same as the hydrogen-bond distance in form I of TPA. Although aldehydic and carboxylic groups appear to be different in chemical nature, the hydrogen-



(a)

(b)

Fig. 3. The bond lengths (Å) and bond angles (°) for (*a*) form I, τ[C(6)C(1)C(7)O(2)] = 5·5°, τ[C(5)C(4)C(8)O(3)] = 2·1°, and (*b*) form II, τ[C(2)C(1)C(4)O(2)] = 3·7°.

bond length is fairly close to the sum of the van der Waals radii of H and O, so that it is not surprising that the structure is disordered between the groups in view of the space-filling condition. The Kitaigorodsky (1973) packing coefficients of 4-FBA and TPA are 0·792 and 0·801 for form I and 0·763 and 0·775 for form II, and the similarity between them is remarkable.

In consequence of the disorder, appreciable diffuse scattering accompanied reflexions 110, $01\bar{1}$, 101, $1\bar{1}2$ and 202, where $h = k + l$. This indicates that the molecule oscillates around the molecular axis.

The modes of overlapping of benzene ring planes of the two forms of 4-FBA and of form I of TPA are compared in Fig. 2. The only difference among them is a slight increase of inter-ring spacing of form II of 4-FBA as reflected in the packing coefficients.

Form I of 4-FBA is stable at low temperature and transforms irreversibly into form II at about 140°C. The heat of transition is determined to be 0·9 kcal mole^{-1} by differential scanning calorimetry based on the heat of fusion for indium, 0·78 kcal mole^{-1}. This value corresponds to the entropy of the Frenkel (1935) model transition $R \ln 4$, in accordance with the fact that there are four possible orientations for form II. The crystals of form II become gradually opaque at about 220°C.

The infrared spectra taken with a KBr disc show coupling vibrations between O–H bending and C–O stretching at 1292 cm^{-1} for form I, and at 1292 and 1245 cm^{-1} for form II. The former corresponds to the hydrogen bonds between double carboxylic groups, whereas the latter corresponds to those between the carboxylic and aldehydic groups, in agreement with the structures described above.

The bond lengths and angles are shown in Fig. 3. In both forms the molecules are nearly planar. In form I, the benzene ring is planar within 0·01 Å. O(1), O(2) and O(3) deviate by 0·159, −0·053 and −0·105 Å, respectively, from the ring plane. The dihedral angles with respect to the benzene ring are 5·6° for the carboxylic group and 5·1° for the aldehydic group. The difference in the two C–O bond lengths of the carboxylic group is rather small as found in form I of TPA and *p*-toluic acid (Takwale & Pant, 1971).

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