

The Crystal Structure of Isophthalic Acid

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The crystal structure of isophthalic acid has been determined by direct methods. The crystals are monoclinic, space group $P2_1/c$, $a = 3.76 \text{ \AA}$, $b = 16.42 \text{ \AA}$, $c = 11.72 \text{ \AA}$, $\beta = 90^\circ \pm 30'$. There are 4 molecules per unit cell. Measurement was made of 809 reflexions by the multiple-film equi-inclination method using $\text{Cu K}\alpha$ radiation. An E -map was calculated, based on 160 phases developed by statistical methods. All the carbon and two of the oxygen atoms were located from this E -map. A three-dimensional Fourier synthesis, computed with the phase signs given by these atoms, revealed the locations of all the non-hydrogen atoms. The hydrogen atoms were located from a difference map. Refinement proceeded anisotropically for the heavier atoms and isotropically for the hydrogen atoms to a final discrepancy index $R = 0.05$. The molecules of isophthalic acid are strongly hydrogen-bonded between the carboxyl groups forming dimers related by screw axes.

Introduction

The crystal structure determination of isophthalic acid is a continuation of the work on the benzenecarboxylic acids and some of their derivatives already completed in some Departments of the Facultad de Ciencias of the Universidad de Zaragoza and of the Instituto Rocasolano of the C.S.I.C. in Madrid (González Sánchez, 1958; Gómez Beltrán & Forniés Marquina, 1965; Forniés Marquina 1969; Cano, Martínez-Carrera & García-Blanco, 1970; Anca, Martínez-Carrera & García-Blanco, 1967 *etc.*) and elsewhere (see later references).

The study by González-Sánchez of the O-H stretching vibrations in the infrared spectra of the twelve benzenecarboxylic acids suggested that they are all associated by intermolecular hydrogen bonding between carboxyl groups. This suggestion has been verified in benzoic, phthalic, trimesic and mellitic acids, whose structures have been determined, and so it was thought that the crystal structures of the twelve benzene-carboxylic acids would give more information about the hydrogen bond. With this purpose, the crystal structure determination of isophthalic acid was undertaken, in which the carboxyl groups are bonded by hydrogen bonds, as expected.

Crystal data

Single crystals of isophthalic acid were obtained by slow evaporation in ethyl alcohol of a purified specimen. The crystals were thin monoclinic plates. Cell dimensions were measured from Weissenberg photographs of the three zero layers, and gave $a = 3.76 \pm 0.01$, $b = 16.42 \pm 0.01$, $c = 11.72 \pm 0.01 \text{ \AA}$, $\beta = 90^\circ \pm 30'$, $D_m = 1.52$, $D_x = 1.53 \text{ g.cm}^{-3}$, $Z = 4$, $\mu = 10.60 \text{ cm}^{-1}$.

The systematic absences, $h0l$ when $l = 2n + 1$; $0k0$ when $k = 2n + 1$ are consistent with the space group $P2_1/c$.

Experimental

Intensity data were obtained with $\text{Cu K}\alpha$ radiation from multiple-film integrated Weissenberg photographs of three layers along $[100]$ and ten layers along $[010]$.

809 independent reflexions were estimated by means of a Joyce-Loebl microdensitometer, Mark IIIC type.

Non-observed reflexions were given values of half the intensity of the weakest observed spot of the same layer. Since the value of the absorption coefficient $\mu = 10.6 \text{ cm}^{-1}$ is small enough and the crystal used ($0.5 \times 0.1 \times 0.5 \text{ mm}$) was below the optimum size, absorption corrections were not made.

The data were reduced to structure amplitudes in the usual way, and were scaled according to the method of Rollett & Sparks (1960). All observed reflexions were included in the calculations.

Determination of the structure

As the molecule has two carboxyl groups it was thought that the structure would be formed with dimers of the isophthalic acid molecules joined by hydrogen bonds through a symmetry centre.

A three-dimensional Patterson function was calculated and from it the orientation of the molecule was found, but it was not possible to arrange it in the cell. Placing the hydrogen bond around the symmetry center, R -values were too high (the best value being $R = 0.60$).

Then it was supposed that the hydrogen bond could be asymmetric as in other benzenecarboxylic acids (Duchamp & Marsh, 1969; Pedone, Benedetti &

Allegra, 1970; and Darlow, 1961) and not situated around a symmetry centre.

Since it was not possible to continue by Patterson methods, Sayre's equation

$$S[E_h] \sim S[E_h'] S[E_{h-h'}]$$

was used in order to resolve the structure. The E_h were calculated in the usual way and Sayre's equation was applied to reflexions with E greater than 1.5. For this purpose a program called *REL* written by R. E. Long (UCLA 1965) for the IBM 7090 was used.

Three reflexions were chosen to fix the origin, $\bar{2}, 14, 3, \bar{1}, 14, 1$ and 375. A further four reflexions with high values of E also chosen (0, 14, 1, 178, 276 and 2, 13, 9). In this way $2^4 = 16$ combinations of phases were possible.

The method used was iterative; the phases determined after the first cycle were used in the second and so on. After each cycle a consistency index C was calculated as

$$C = \langle |E_h \sum_{h'} E_{h'} E_{h-h'}| \rangle / \langle |E_h| \sum_{h'} |E_{h'} E_{h-h'}| \rangle$$

(where $\langle \rangle$ represents the averaged mean value). Usually, the best phase determination corresponds to the group with the higher consistency index achieved in the smaller number of cycles. With this criterion, six groups were chosen with consistency index 0.897, 0.807, 0.832, 0.760, 0.732 and 0.748 and number of cycles 7, 9, 10, 8, 9, 11 respectively. With the phases assigned by each group a three-dimensional Fourier synthesis using E values was calculated.

In the synthesis corresponding to the 1st, 3rd, 4th and 6th groups, an atomic distribution resembling those used previously was found and was rejected. In the synthesis corresponding to the 2nd and 5th groups another atomic distribution was found, which was similar to those used previously with the hydrogen bond out of the symmetry centres. With this distribution only ten atoms were found, eight carbon atoms and two oxygen atoms. The R value was 0.48. The other two oxygen atoms were located by considerations about bond lengths, valence angles and the planarity of the carboxyl group.

With this configuration the R value was 0.30, and with the phases obtained in this calculation for F values with $\sin \theta < 0.8$ (581 reflexions) a three-dimensional Fourier synthesis was calculated where all non-hydrogen atoms were located. The R value with the coordinates of this map was 0.17 and all intra- and intermolecular distances were reasonable.

Refinement

Fig. 1 shows the electron density map from the last synthesis. Next, three cycles of differential synthesis were carried out using individual isotropic temperature factors, and another three cycles with anisotropic temperature factors. These syntheses were stopped when the shifts in the parameters were less than three times the value of the standard deviation. The new agreement index was 0.142 for the isotropic refinement and 0.086 for the anisotropic refinement.

With the coordinates of the last Fourier synthesis, the refinement by least-squares procedures was carried out (Busing, Martin & Levy, 1962), and using the weighting scheme of Hughes, R became 0.152 for the isotropic and 0.070 for the anisotropic refinement. The position coordinates from both refinements by difference maps and by least-squares were almost equal, the biggest differences being in the temperature factors. The R values obtained, together with the value of

Table 1. *Final atomic parameters*

Estimated standard deviations in parentheses.

(a) Fractional coordinates			
	x/a	y/b	z/c
C(1)	0.3530 (11)	0.2320 (3)	0.1706 (3)
C(2)	0.2688 (11)	0.1570 (3)	0.1234 (3)
C(3)	0.1079 (12)	0.1534 (3)	0.0156 (4)
C(4)	0.0352 (12)	0.2246 (3)	-0.0431 (4)
C(5)	0.1223 (12)	0.2998 (3)	0.0038 (3)
C(6)	0.2816 (11)	0.3034 (3)	0.1111 (3)
C(7)	0.3530 (12)	0.0816 (2)	0.1869 (4)
C(8)	0.3849 (12)	0.3819 (2)	0.1644 (4)
O(1)	0.2572 (10)	0.0143 (2)	0.1380 (3)
O(2)	0.5118 (9)	0.0835 (2)	0.2799 (2)
O(3)	0.2930 (11)	0.4470 (2)	0.1085 (3)
O(4)	0.5487 (9)	0.3833 (2)	0.2552 (3)

Table 1 (cont.)

(b) Thermal parameters in the form $f = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots + 2U_{13}hla^*c^* \cos \beta^*)]$.

	$10^3 \times U_{11}$	$10^3 \times U_{22}$	$10^3 \times U_{33}$	$10^3 \times U_{12}$	$10^3 \times U_{13}$	$10^3 \times U_{23}$
C(1)	36 (2)	29 (1)	30 (2)	-2 (2)	-3 (2)	1 (2)
C(2)	34 (3)	26 (3)	37 (2)	-2 (2)	-1 (2)	-1 (2)
C(3)	41 (3)	34 (3)	36 (2)	-3 (2)	-5 (2)	-5 (2)
C(4)	41 (2)	42 (3)	33 (2)	-2 (3)	-6 (2)	1 (2)
C(5)	40 (3)	38 (3)	38 (2)	1 (2)	-3 (2)	5 (2)
C(6)	35 (3)	26 (3)	37 (2)	-1 (2)	-3 (2)	1 (2)
C(7)	41 (3)	25 (3)	44 (2)	-2 (2)	-3 (2)	-2 (2)
C(8)	44 (3)	25 (3)	40 (2)	3 (2)	-5 (2)	3 (2)
O(1)	86 (3)	23 (1)	59 (2)	-4 (2)	-3 (2)	-4 (2)
O(2)	72 (2)	29 (1)	41 (1)	2 (2)	-2 (2)	-2 (2)
O(3)	84 (3)	25 (1)	61 (2)	-4 (2)	-3 (2)	8 (2)
O(4)	73 (2)	27 (1)	47 (2)	-4 (2)	-2 (2)	-1 (1)

inter- and intramolecular distances and bond angles obtained show the improvement of the structure model.

Finally a difference synthesis gave the positions of

the hydrogen atoms which were consistent with the coordinates of the carbon and oxygen atoms. They were included in a final cycle of least squares, where the temperature factors of the hydrogen atoms were made equal to those of the corresponding bonded atoms, but were not allowed to vary. The final *R* index was 0.050.

Table 2. Bond lengths and valence angles

C(1)–C(2)	1.387 (6) Å	C(1)–C(2)–C(3)	119.7 (4)°
C(2)–C(3)	1.402 (6)	C(2)–C(3)–C(4)	119.9 (4)
C(3)–C(4)	1.383 (6)	C(3)–C(4)–C(5)	120.4 (4)
C(4)–C(5)	1.391 (6)	C(4)–C(5)–C(6)	119.7 (4)
C(5)–C(6)	1.395 (6)	C(5)–C(6)–C(1)	119.9 (4)
C(6)–C(1)	1.392 (6)	C(6)–C(1)–C(2)	120.3 (4)
C(2)–C(7)	1.479 (6)	C(1)–C(2)–C(7)	119.6 (4)
		C(3)–C(2)–C(7)	120.7 (4)
C(7)–O(1)	1.297 (5)	C(2)–C(7)–O(1)	115.6 (4)
C(7)–O(2)	1.244 (5)	C(2)–C(7)–O(2)	121.5 (4)
		O(1)–C(7)–O(2)	122.9 (4)
C(6)–C(8)	1.483 (6)	C(1)–C(6)–C(8)	118.1 (4)
		C(5)–C(6)–C(8)	122.0 (4)
C(8)–O(3)	1.301 (6)	C(6)–C(8)–O(3)	115.6 (4)
C(8)–O(4)	1.230 (5)	C(6)–C(8)–O(4)	120.8 (4)
		O(3)–C(8)–O(4)	123.5 (4)

Table 3. Intermolecular distances less than 4 Å

The following roman numbers give the symmetry relationship of the atoms concerned.

I (x y z)	VIII ($1-x$ $-\frac{1}{2}+y$ $\frac{1}{2}-z$)
II ($1+x$ y z)	IX ($-x$ $\frac{1}{2}+y$ $\frac{1}{2}-z$)
III (x $\frac{1}{2}-y$ $\frac{1}{2}+z$)	X ($1-x$ $\frac{1}{2}+y$ $\frac{1}{2}-z$)
IV ($-1+x$ y z)	XI ($1-x$ $-y$ $-z$)
V ($-x$ $-y$ $-z$)	XII ($-x$ $-\frac{1}{2}+y$ $\frac{1}{2}-z$)
VI (x $\frac{1}{2}-y$ $-\frac{1}{2}+z$)	XIII ($-x$ $1-y$ $-z$)
VII ($-1+x$ $\frac{1}{2}-y$ $-\frac{1}{2}+z$)	XIV ($1-x$ $1-y$ $-z$)

Final parameters

Final atomic parameters and standard deviations are given in Table 1; bond lengths and bond angles are shown in Table 2. The mean standard deviations are 0.006 Å and 0.4° respectively.

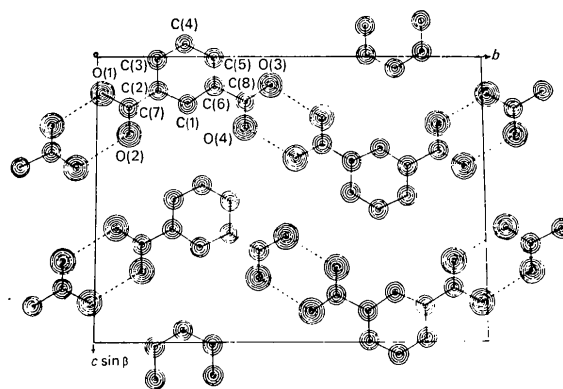


Fig. 1. Isophthalic acid. A composite diagram of the final electron density function.

Table 3 (cont.)

Atom <i>i</i>	Atom <i>j</i>	<i>d</i> (<i>ij</i>)	Atom <i>i</i>	Atom <i>j</i>	<i>d</i> (<i>ij</i>)
C(1) (I)	C(2) (II)	3.699 Å	C(6) (I)	O(4) (IV)	3.488
C(1) (I)	C(3) (II)	3.609	C(7) (I)	C(8) (VIII)	3.842
C(1) (I)	C(4) (II)	3.587	C(7) (I)	O(1) (II)	3.621
C(1) (I)	C(4) (III)	3.632	C(7) (I)	O(2) (IV)	3.346
C(1) (I)	C(5) (II)	3.664	C(7) (I)	O(3) (VIII)	3.522
C(1) (I)	C(6) (II)	3.749	C(7) (I)	O(4) (VIII)	3.347
C(2) (I)	C(3) (II)	3.399	C(8) (I)	O(1) (IX)	3.990
C(2) (I)	C(4) (II)	3.653	C(8) (I)	O(1) (X)	3.450
C(2) (I)	C(7) (IV)	3.734	C(8) (I)	O(2) (X)	3.396
C(2) (I)	O(2) (IV)	3.595	C(8) (I)	O(3) (II)	3.637
C(3) (I)	C(4) (II)	3.741	C(8) (I)	O(4) (IV)	3.319
C(3) (I)	C(7) (IV)	3.671	O(1) (I)	O(1) (V)	3.798
C(3) (I)	O(1) (V)	3.565	O(1) (I)	O(1) (XI)	3.744
C(3) (I)	O(2) (IV)	3.992	O(1) (I)	O(2) (IV)	3.451
C(3) (I)	O(4) (VI)	3.525	O(1) (I)	O(3) (XII)	3.785
C(3) (I)	O(4) (VII)	3.755	O(1) (I)	O(3) (VIII)	3.593
C(4) (I)	C(5) (IV)	3.689	O(1) (I)	O(4) (XII)	3.921
C(4) (I)	C(6) (IV)	3.601	O(1) (I)	O(4) (VIII)	2.594*
C(4) (I)	O(4) (VI)	3.529	O(2) (I)	O(3) (III)	3.970
C(4) (I)	O(4) (VII)	3.475	O(2) (I)	O(3) (XII)	3.986
C(5) (I)	C(6) (IV)	3.403	O(2) (I)	O(3) (VIII)	2.697*
C(5) (I)	C(8) (IV)	3.612	O(2) (I)	O(4) (VIII)	3.321
C(5) (I)	O(2) (VI)	3.564	O(3) (I)	O(3) (XIII)	3.788
C(5) (I)	O(2) (VII)	3.978	O(3) (I)	O(3) (XIV)	3.453
C(5) (I)	O(4) (IV)	3.900	O(3) (I)	O(4) (IV)	3.447
C(6) (I)	C(8) (IV)	3.663			

* Hydrogen bond.

Intermolecular distances less than 4 Å are shown in Table 3. Equations of the mean planes through (i) all atoms except hydrogen atoms and (ii) atoms in the aromatic ring are:

- (i) All atoms: $0.8910x' - 0.0439y' - 0.4518z' = 0.1494$
 (ii) Ring: $0.9022x' - 0.0446y' - 0.4291z' = 0.1750$.

Here $x'y'z'$ in Å are referred to the orthogonal axes abc' . Deviations of atoms from the mean planes are given in Table 4. It may be concluded that the molecule is fairly planar. A comparison between observed and calculated structure factors is given in Table 5. Table 6 gives the hydrogen atoms parameters. Bond lengths and valence angles with the hydrogen atoms are shown

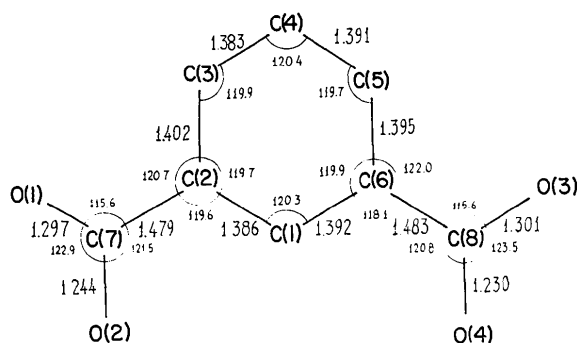


Fig. 2. Bond lengths and angles in the isophthalic acid molecule.

in Table 7; the estimated standard deviations are in parentheses.

Table 4. Displacements of the atoms from the various planes

	(i)	(ii)
C(1)	-0.035 Å	-0.003 Å
C(2)	-0.014	0.003
C(3)	0.019	0.001
C(4)	0.035	-0.003
C(5)	0.025	0.002
C(6)	-0.011	0.001
C(7)	-0.013	0.025
C(8)	-0.004	0.026
O(1)	-0.028	-0.006
O(2)	0.025	0.095
O(3)	-0.063	-0.053
O(4)	0.064	0.125

Discussion of the structure

The distances C-C in the aromatic ring show that there is no significant deviation from the hexagonal symmetry in the ring (See Table 2 and Fig. 2). The average value for the C-C distance in the ring is 1.392 Å, in good agreement with the value usually reported in the literature. The angles are also in good agreement, since the mean value is 120°. The bond distances C(ring)-C(carboxyl group) are 1.479 and 1.482 Å, also usual for sp^2 bonds.

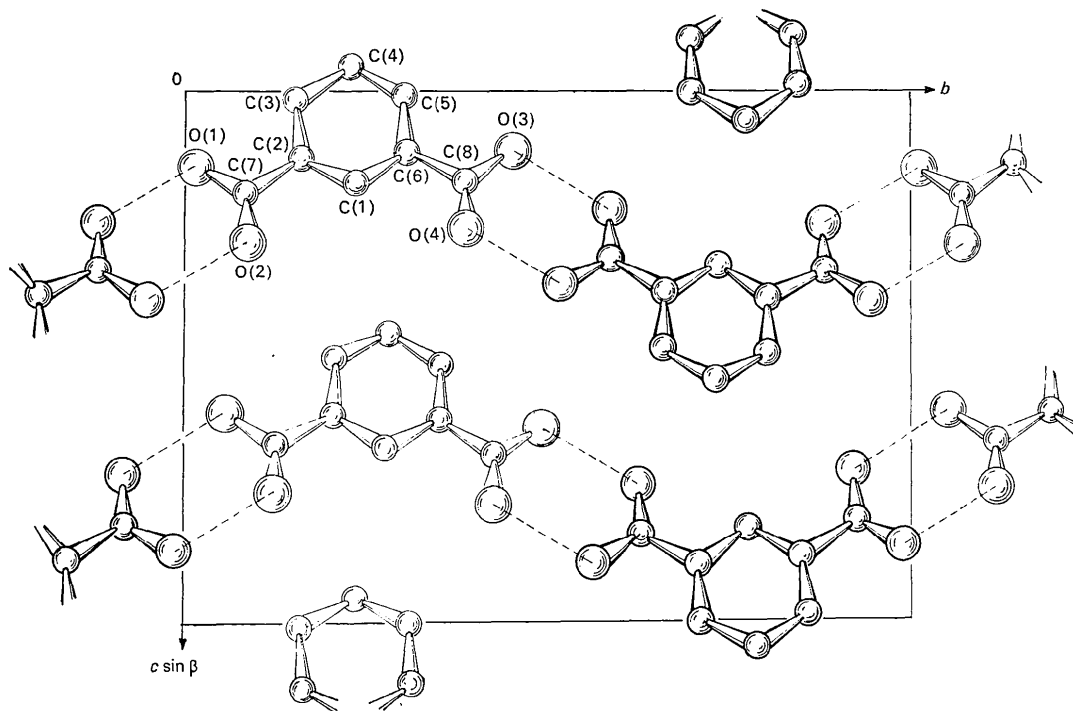


Fig. 3. Isophthalic acid. Projection of the structure along the a axis.

Table 5 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> O B S	<i>F</i> C A L	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> O B S	<i>F</i> C A L	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> O B S	<i>F</i> C A L	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> O B S	<i>F</i> C A L	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> O B S	<i>F</i> C A L
-3	2	10	4.07	4.51	-3	3	6	4.97	4.72	-3	6	3	6.36	5.71	-3	8	6	9.35	9.71	4	2	6	2.38	2.32
-3	2	7	3.13	3.38	-3	4	4	4.43	3.75	-3	6	2	13.44	12.34	-3	8	3	3.30	3.58	4	6	2	3.93	4.11
-3	2	5	3.03	2.90	-3	4	3	2.84	2.49	-3	6	1	5.19	3.50	-3	8	7	4.28	4.46	4	3	4	5.23	5.45
-3	2	4	5.37	4.96	-3	4	2	5.01	5.55	-3	6	0	5.10	4.77	-3	8	2	2.94	3.16	4	3	6	3.13	4.31
-3	2	3	8.31	8.54	-3	4	0	8.41	8.41	-3	6	2	5.34	4.01	-3	8	1	5.07	5.43	4	3	6	2.80	2.72
-3	2	2	3.17	3.13	-3	4	3	5.24	4.50	-3	6	3	6.18	6.18	-3	8	0	5.07	5.43	4	3	6	3.20	4.03
-3	2	0	5.02	4.30	-3	4	4	3.71	3.98	-3	6	4	12.08	12.59	-3	8	0	5.07	5.43	4	3	6	3.40	3.44
-3	2	2	5.06	4.53	-3	4	7	3.91	3.17	-3	6	5	11.22	11.48	-3	8	0	5.07	5.43	4	3	6	2.47	2.41
-3	2	8	6.02	6.42	-3	4	8	5.37	5.13	-3	6	6	16.90	13.80	-3	8	0	5.07	5.43	4	3	6	2.88	3.01
-3	2	10	4.16	4.36	-3	4	9	3.02	3.62	-3	6	6	5.11	4.96	-3	8	0	6.12	6.85	4	5	2	3.26	3.42
-3	2	6	3.63	3.36	-3	5	9	4.67	4.79	-3	6	8	4.80	4.77	-3	8	0	10.41	13.11	4	5	2	5.36	5.94
-3	2	5	3.76	3.90	-3	5	7	3.25	3.39	-3	6	9	3.69	3.66	-3	8	0	7.14	7.22	4	6	4	4.70	4.60
-3	2	3	4.48	3.06	-3	5	6	6.10	4.08	-3	6	9	4.27	4.42	-3	8	0	6.05	6.17	4	6	3	4.03	4.28
-3	2	3	5.99	5.51	-3	5	3	6.97	6.17	-3	6	7	4.64	4.44	-3	8	0	6.05	6.17	4	6	2	3.54	3.43
-3	2	3	4.14	3.62	-3	5	2	8.00	7.80	-3	6	4	4.63	4.13	-3	8	0	4.22	5.39	4	6	2	4.03	4.28
-3	2	0	6.16	6.06	-3	5	1	2.98	2.94	-3	6	3	5.91	4.30	-3	8	0	5.93	6.95	4	6	0	3.22	2.97
-3	2	6	6.47	6.12	-3	5	1	5.40	5.31	-3	6	1	14.35	13.35	-3	8	0	3.92	3.80	4	6	4	10.22	11.77
-3	2	3	3.87	3.38	-3	5	4	5.77	5.53	-3	6	0	6.89	6.67	-3	8	0	9.92	9.78	4	6	5	8.78	5.93
-3	2	4	6.89	6.75	-3	5	5	4.73	4.67	-3	6	3	6.89	6.67	-3	8	0	3.61	3.66	4	6	2	5.06	5.09
-3	2	3	10.96	11.45	-3	5	7	5.77	6.46	-3	6	4	21.01	21.13	-3	8	0	3.92	3.80	4	6	4	6.23	6.23
-3	2	8	8.05	8.64	-3	5	8	3.46	3.42	-3	6	5	27.30	28.07	-3	8	0	7.52	8.36	4	6	6	3.19	2.81
-3	2	9	3.56	3.93	-3	5	6	6.20	6.35	-3	6	6	8.34	8.34	-3	8	0	5.54	6.27	4	7	3	6.18	6.23
-3	2	10	6.21	6.87	-3	5	6	4.94	6.76	-3	6	8	10.09	10.73	-3	8	0	4.09	5.03	4	7	2	4.97	4.94
-3	2	8	3.23	3.20	-3	5	6	5.77	5.05	-3	6	8	9.22	9.60	-3	8	0	3.90	4.30	4	7	2	4.97	4.94

Table 6. Hydrogen atom parameters

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$10^3 \times U$
H(1)	0.457 (13)	0.234 (3)	0.236 (4)	22
H(2)	0.045 (13)	0.102 (3)	-0.013 (4)	26
H(3)	-0.081 (13)	0.223 (3)	-0.115 (4)	26
H(4)	0.071 (13)	0.354 (3)	-0.035 (4)	28
H(5)	0.325 (15)	-0.026 (3)	0.174 (4)	33
H(6)	0.387 (15)	0.483 (4)	0.133 (5)	36

In the carboxyl group O(1)-C(7)-O(2) the values found for the valence length C(7)-O(1), (1.297 Å) and for the bond angle C(2)-C(7)-O(1), (115.6°) clearly show that the hydrogen atom is attached to the O(1) atom. In the carboxyl group O(3)-C(8)-O(4), for the same reason, the hydrogen atom is attached to the O(3) atom. This is also in agreement with the positions found for the hydrogen atoms in the difference synthesis.

The molecule is basically planar. The rotations of the carboxyl groups around the C(2)-C(7) and C(2)-C(8) bonds being only 2.8° and 4.7° away from the plane of the ring respectively.

A feature which is common in most carboxyl derivatives is the dimerization or polymerization by double hydrogen bonds between two carboxyl groups around the symmetry centres. In the present structure there is also polymerization of the molecules by double hydrogen bonds but these bonds are not around the symmetry centres and so the two hydrogen bonds are

not symmetrical, as can be seen in Fig. 3. A similar asymmetry between the two H-bonds is found in other benzenecarboxylic acids [trimesic and mellitic acids: Duchamp & Marsh (1967); Darlow (1961)]. In phthalic acid the polymerization is produced by double hydrogen bonds around the symmetry centres: Nowacki & Jaggi (1957). In benzoic acid there is dimerization around the symmetry centres: Sim, Robertson & Goodwin (1955).

Among the intermolecular distances involving hydrogen atoms the smallest distance H-C is 2.66 Å and the smallest distance H-O is 2.66 Å, which can be considered normal.

All calculations were made on the IBM 7070 and 7090 computers of the Centro de Cálculo Electronico of the C.S.I.C. (Madrid, Spain). The present work is part of a Doctoral Thesis by one of us (R.A.).

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Table 7. Bond lengths and valence angles concerning the hydrogen atoms

The Roman numbers give the same symmetry relationships as in Table 3.

C(1) (I)-H(1) (I)	0.86 (5)	C(2) (I)-C(1) (I)-H(1) (I)	119.6° (3)
C(3) (I)-H(2) (I)	0.94 (5)	C(6) (I)-C(1) (I)-H(1) (I)	120.1° (3)
C(4) (I)-H(3) (I)	0.94 (5)	C(2) (I)-C(3) (I)-H(2) (I)	117.7° (3)
C(5) (I)-H(4) (I)	1.01 (5)	C(4) (I)-C(3) (I)-H(2) (I)	122.4° (3)
O(3) (I)-H(6) (I)	0.75 (6)	C(3) (I)-C(4) (I)-H(3) (I)	120.2° (3)
O(2) (X)-H(6) (I)	1.98 (6)	C(5) (I)-C(4) (I)-H(3) (I)	119.6° (3)
O(4) (I)-H(5) (X)	1.77 (6)	C(4) (I)-C(5) (I)-H(4) (I)	123.4° (3)
O(1) (X)-H(5) (X)	0.83 (6)	C(6) (I)-C(5) (I)-H(4) (I)	116.9° (3)
		C(8) (I)-O(3) (I)-H(6) (I)	109.4° (4)
		O(3) (I)-H(6) (I)-O(2) (X)	162.0° (4)
		H(6) (I)-O(2) (X)-C(7) (X)	121.6° (4)
		C(8) (I)-O(4) (I)-H(5) (X)	123.8° (4)
		O(4) (I)-H(5) (X)-O(1) (X)	175.9° (4)
		H(5) (X)-O(1) (X)-C(7) (X)	111.8° (4)

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The Crystal and Molecular Structure of δ -Pyrazincarboxamide

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δ -Pyrazincarboxamide crystallizes in the space group $P\bar{1}$ with unit-cell dimensions $a=5.728$ (2), $b=5.221$ (3), $c=9.945$ (6) Å, $\alpha=96.81$ (5), $\beta=97.27$ (4), $\gamma=106.22$ (4)°. The structure was first solved on the basis of a three-dimensional Patterson synthesis and later confirmed by the method of symbolic addition. Refinement was achieved by means of the full-matrix least-squares method, including anisotropic temperature factors and the use of a weighting scheme. The final value of the R_1 index is 0.061. The molecules are closely planar and connected by hydrogen bonds across the centres of symmetry to form dimers, which are held together in the lattice by van der Waals forces.

Introduction

Pyrazincarboxamide is known to appear in four different crystalline modifications, namely α -, β -, γ - and δ -pyrazincarboxamide (hereafter abbreviated α -, β -, γ - and δ -PCA) respectively, as shown by Tamura, Kuwano & Sasada (1961). The crystal structure of α -PCA was solved and refined by Takaki, Sasada & Watanabe (1960), and a report on a structure determination for β -PCA has recently been given by Rø & Sørum (1972). While the molecular structures of these two forms show relatively small differences only, distinct differences are found in the molecular packing and especially in the intermolecular hydrogen bonds. Some preliminary results on the γ and δ forms were given by Tamura & Kuwano (1962), by comparing the infrared absorption spectra of the four crystalline modifications. Takaki (1965) used an ellipsoid-model approach to the determination of the crystal structure of γ -PCA, but no detailed structure determination has yet appeared for the γ and the δ forms of PCA. The present paper reports the results of a structure determination of δ -PCA.

Experimental

Crystals of δ -PCA were obtained by recrystallization of commercial PCA in a mixture consisting of one

part of hexane and one part of absolute ethanol. The crystals were transparent plates showing a pronounced cleavage plane identified later as the (012) plane. The crystal chosen for the structure determination was a rectangular plate having the dimensions $0.12 \times 0.20 \times 0.04$ mm. The crystallographic a axis was mounted along the φ axis of a Picker FACS-1 four-circle automatic diffractometer and the cell dimensions together with the calculating matrix were refined by the method of least squares using Busing and Levy's notation. Twelve strong reflexions at high 2θ values were used in the refinement. The crystallographic data are:

δ -pyrazine-2-carboxamide;
 $C_5H_5N_3O$; F.W. 123.11; m.p. 188°C;
 Triclinic; $Z=2$; $\lambda(\text{Cu } K\alpha_1)=1.5405$ Å;

$$\begin{aligned} a &= 5.728 \pm 0.002 \text{ \AA} \\ b &= 5.221 \pm 0.003 \\ c &= 9.945 \pm 0.006 \\ \alpha &= 96.81 \pm 0.05^\circ \\ \beta &= 97.27 \pm 0.04 \\ \gamma &= 106.22 \pm 0.04. \end{aligned}$$

Volume of the unit cell $V=279.58$ Å³;
 Density, calculated with $Z=2$: $D_x=1.462$ g.cm⁻³;
 Absorption coefficient for $\lambda(\text{Cu } K\alpha)$ ($=1.5418$ Å):
 $\mu=9.25$ cm⁻¹.
 Space group $P\bar{1}$. $F(000)=128$.