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Isophthalic Acid

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Abstract. Benzene-1,3-dicarboxylic acid, $C_6H_4(COOH)_2$ $P2_1/c$, $a=3·758$ (2), $b=16·364$ (6), $c=11·703$ (4) Å, $\beta=90·30$ (2)°, $Z=4$; $D_c=1·533$, $D_m=1·530$ g cm^{-3}. The molecule has nearly C_{2v} symmetry and consists of a practically undistorted benzene ring with two hydrogen-bonded carboxyl groups, the two carbonyl oxygen atoms being adjacent. The crystal is built up from molecules connected by hydrogen bonds, forming infinite chains. The two hydrogen bonds are clearly not equivalent, as shown by their O···O hydrogen-bond lengths of 2·682 and 2·581 Å.

Introduction. Needle-shaped single crystals of isophthalic acid were grown by slow evaporation of a 1:1 acetic acid–water solution at room temperature. Reflexions were measured on an Enraf–Nonius CAD4 computer-automated four-circle diffractometer, using Mo $K\alpha$ radiation and a graphite monochromator ($2\theta=12·6°$). From the systematic extinctions $h0l$ for $l\neq 2n$ and $0k0$ for $k\neq 2n$ the space group $P2_1/c$ was inferred. The intensities of 992 reflexions up to $2\theta=53°$ were measured; 672 of these had an intensity ≥ 2 times their standard deviation based on counting statistics; another 493 very weak reflexions were not accurately measured because of time economy. No absorption or extinction corrections were applied. The structure was solved by direct methods using the program *AUDICE* (Spek, 1968). An E map calculated with 229 terms showed all C and O atoms, while the H atoms in the first instance were placed at expected positions.

The structure was refined by full-matrix least-squares calculations on the intensities of the 992 reflexions, with weights based on the counting statistics. The positional parameters for all atoms, anisotropic temperature parameters for the C and O atoms and isotropic temperature factors for the H atoms resulting from this procedure are presented in Table 1.*

The final R index thus obtained is 0·082. A more 'conventional' refinement on the structure factors of the 672 reflexions with $I\geq 2\sigma_I$ yielded $R=0·046$ and only slightly different parameter values. See the discussion of the refinement procedure of Hirshfeld & Rabinovich (1973) and of Derissen & Smit (1974).

Table 1. *Atomic parameters for isophthalic acid*

Positional parameters are given as fractional coordinates, thermal parameters for O and C according to the expression: $T=\exp[-2\pi^2\sum_i\sum_j U_{ij}h_ih_ja_i^*a_j^*]$. Positional parameters for O and C are $\times 10^4$. Hydrogen atom coordinates and thermal parameters for O and C are $\times 10^3$. The e.s.d.'s given in parentheses refer to the last significant digit(s) of the parameters. For hydrogen atoms the isotropic Debye–Waller factor B is given. δ is the distance of each atom from the least-squares plane through the six benzene-ring carbon atoms, in Å.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	δ
C(1)	7316 (8)	3431 (2)	3768 (2)	32 (2)	31 (2)	38 (2)	−0·1 (15)	−1·5 (15)	−1·1 (13)	−0·0012
C(2)	6457 (7)	2684 (2)	3298 (3)	37 (2)	34 (2)	32 (2)	−0·2 (16)	−5·5 (15)	0·2 (16)	−0·0005
C(3)	7175 (8)	1968 (2)	3890 (2)	30 (2)	34 (2)	37 (2)	−2·3 (15)	0·3 (15)	−0·7 (13)	0·0031
C(4)	8795 (8)	2006 (2)	4960 (2)	44 (2)	40 (2)	37 (2)	0·9 (16)	−4·7 (16)	8·3 (15)	−0·0040
C(5)	9628 (9)	2754 (2)	5425 (3)	46 (2)	47 (2)	33 (2)	−4·6 (18)	−7·1 (15)	−1·9 (16)	0·0023
C(6)	8915 (8)	3463 (2)	4842 (2)	42 (2)	34 (2)	40 (2)	−2·5 (17)	−3·8 (16)	−6·7 (15)	0·0004
C(7)	6445 (8)	4184 (2)	3132 (2)	46 (2)	28 (2)	43 (2)	0 (15)	−2·0 (16)	−4·5 (14)	0·027
C(8)	6153 (8)	1177 (2)	3360 (2)	41 (2)	33 (2)	42 (2)	0·3 (15)	−1·4 (15)	4·0 (15)	0·026
O(1)	7421 (7)	4860 (1)	3621 (2)	87 (2)	30 (1)	60 (2)	−0·8 (13)	−29·6 (14)	−3·9 (11)	−0·009
O(2)	4882 (6)	4166 (1)	2202 (2)	77 (2)	33 (1)	46 (1)	1·5 (11)	−22·0 (12)	−0·6 (10)	0·087
O(3)	4518 (6)	1168 (1)	2446 (2)	80 (2)	33 (1)	49 (1)	−3·6 (12)	−22·0 (12)	0·7 (10)	0·118
O(4)	7058 (7)	0527 (1)	3915 (2)	89 (2)	29 (1)	61 (2)	−3·1 (13)	−27·0 (13)	7·1 (11)	−0·048
H(1)	543 (7)	265 (2)	260 (2)	2·4 (6)						−0·008
H(2)	926 (7)	152 (1)	534 (2)	2·7 (6)						−0·001
H(3)	1075 (7)	279 (2)	614 (2)	4·2 (7)						−0·014
H(4)	940 (7)	399 (1)	513 (2)	2·5 (6)						0·017
H(5)	341 (9)	032 (2)	182 (3)	9·8 (13)						0·116
H(6)	380 (9)	504 (2)	149 (3)	8·1 (11)						0·160

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* The structure-factor tables are available on request and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30553 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

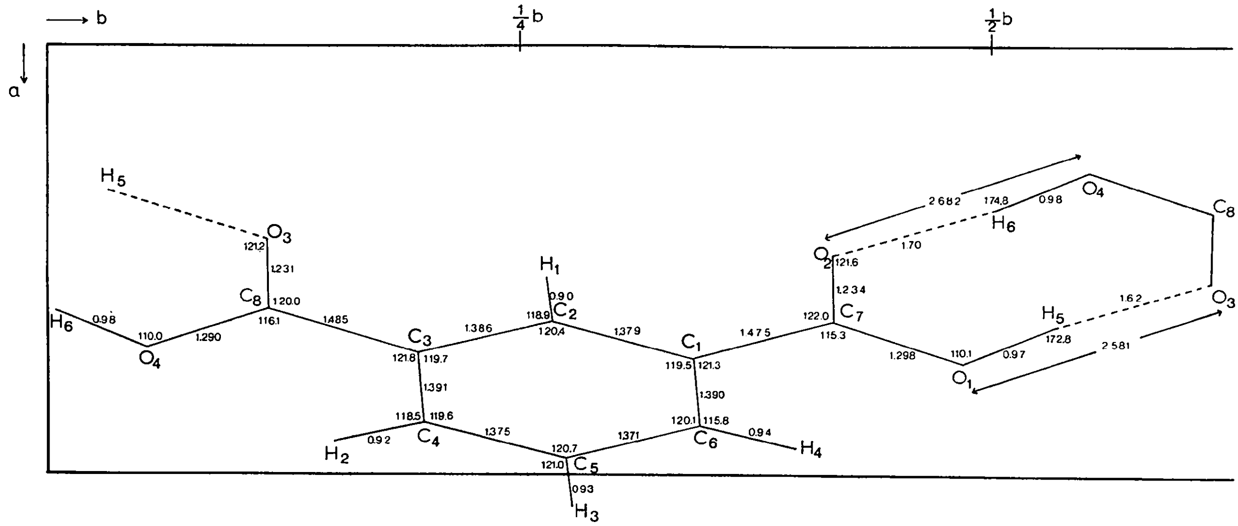

Fig. 1. Bond lengths and angles of isophthalic acid. The molecule is shown in the *ab* projection.

The molecular structure is shown in Fig. 1. The average standard deviations, including the uncertainties in the cell dimensions, for the bond lengths are: C–C 0·004, C–H 0·025, C–O 0·004, O–H 0·04 Å and for the bond angles: C–C–C 0·3, C–C–H 1·5, C–C–O 0·25, C–O–H 2·3°.

Discussion. This structure determination was undertaken within the framework of our research on intermolecular interactions in hydrogen-bonded molecular crystals.

We will attempt to calculate the lattice energies and the hydrogen-bond strengths of a number of dicarboxylic acids. For this purpose the crystal structures of a number of appropriate compounds have to be determined accurately, in addition to the few suitable structures already available in the literature. Isophthalic acid seems to be such a compound, as the molecules are expected not to show other structural differences in the crystalline and gaseous state than those due to hydrogen bonding.

The molecular packing of isophthalic acid molecules in the crystal follows the usual pattern of infinitely double hydrogen-bonded 'cyclic dimers', found in many carboxylic acids. As the two hydrogen-bonding groups in a molecule are not related by symmetry, a difference in the two O···O hydrogen-bond distances is expected, but we see no *a priori* reason for the unexpectedly large difference of 0·10 Å. The bond lengths and bond angles all have expected values. The distances of all atoms from the least-squares plane through the benzene ring carbon atoms are given in Table 1. The molecule is seen to be almost planar, although the small rotations of the carboxyl groups out of the benzene plane may have to be taken into account in a packing analysis.

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