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Structure of the γ Form of Bis(2-hydroxyethyl) Terephthalate, $C_{12}H_{14}O_6$

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Abstract. $M_r = 254{\cdot}2$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}644\ (3)$, $b = 5{\cdot}692\ (2)$, $c = 27{\cdot}136\ (5)$ Å, $V = 1180{\cdot}7\ (6)$ Å^3, $D_x = 1{\cdot}430\ (1)$ Mg m^{-3}, $Z = 4$, $F(000) = 536$, $\mu(\text{Mo}\ K\alpha) = 0{\cdot}108$ mm^{-1}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å. Refractive indices for the Na D line are $n_a = 1{\cdot}487\ (2)$, $n_b = 1{\cdot}626\ (4)$, $n_c = 1{\cdot}693\ (1)$, by Abbe refractometer. $R = 0{\cdot}036$ for 808 reflections with $I > 3\sigma(I)$. The benzene ring was constrained to a regular hexagon with C—C = 1·395 Å, and all C—H = 1·08 Å. The molecules have no centre of symmetry. Each carbonyl O atom is hydrogen-bonded to hydroxyl O atoms of the neighbouring molecule in the **b** direction, thus forming four hydrogen-bonded ribbons passing through each *ac* plane of the unit cell. The plane normals to these ribbons are parallel alternately to those of the (101) and $(10\bar{1})$ planes.

Introduction. Poly(ethylene terephthalate) (PET) is of great commercial importance. Much research has been carried out on its properties and on those of small molecules related to it ('model' compounds). PET is used in fibre form in textiles and in sheet form as a packaging material. For both uses the polymer is oriented by drawing so as to optimize its mechanical properties. Several methods have been developed for characterizing the molecular orientation. One of the more recent methods uses Raman spectroscopy (Purvis & Bower, 1976; Jarvis, Hutchinson, Bower & Ward, 1980). In order to reduce the uncertainties in this method a detailed study of Raman scattering from single crystals of model compounds for PET is being undertaken.

Bis(2-hydroxyethyl) terephthalate (BHET) is one of these, since in this molecule the environment of the benzene ring is similar to that of the ring in PET. In addition, four polymorphs of BHET exist (Miyake, 1957), and to interpret the Raman data from the crystals their structure must be known. The structure of one polymorph, Miyake's α form, is known (Kashino & Haisa, 1975), and the present paper is concerned with that of the γ form. Crystal structures for PET itself (Daubeny, Bunn & Brown, 1954) and a number of model compounds are also known; in particular, terephthalic acid (TA) (Bailey & Brown, 1967), dimethyl terephthalate (DMT) (Brisse & Pérez, 1976), and diethyl terephthalate (DET) (Bailey, 1949).

Experimental. The starting material was supplied by ICI Ltd, Fibres Division, Harrogate, England. When a 10% w/w solution in ethyl acetate was cooled from about 333 K to room temperature in 20–60 min, small crystals were formed which optical examination showed were orthorhombic. Powder X-ray diffraction studies showed that these crystals were of the γ form described by Miyake; the crystals were thin rectangular platelets and the largest measured about 3 × 0·8 × 0·05 mm.

Raman spectroscopy confirmed the preliminary powder X-ray studies. Fig. 1(*a*) shows the spectrum of the powdered α form and Fig. 1(*b*) that of a single crystal of the γ form. The γ form shows carbonyl stretching modes near 1695 cm^{-1}, which is characteristic of hydrogen-bonded carbonyl groups, whereas the α form shows modes both in this region and in the 1720 cm^{-1} region, which is characteristic of carbonyl groups which are not hydrogen-bonded. These spectra are in accord with Miyake's conclusion, based on IR spectroscopy, that the γ form contains hydrogen-bonded carbonyls whereas the other three structures have some or all carbonyls free.

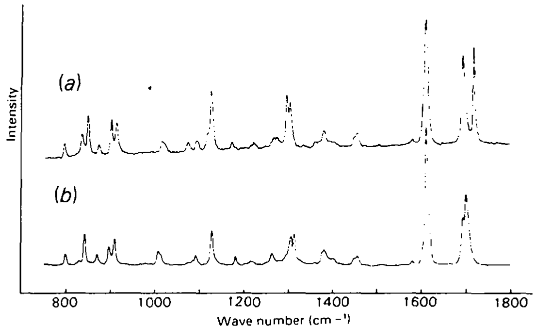

Fig. 1. Raman spectra of BHET: (*a*) the α form, powder; (*b*) the γ form, single crystal.

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Structure determination. X-ray measurements made on a Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation; cell dimensions and their e.s.d.'s obtained by least squares from the setting angles of 15 reflections having $30° < 2\theta < 40°$; all 955 independent reflections with $4° < 2\theta < 45°$ measured in the θ–2θ scan mode and corrected for Lorentz and polarization factors; of these, 808 having $I > 3\sigma(I)$ were used in the analysis. Structure solved using *MULTAN* 80 (Main *et al.*, 1980), and subsequent calculations carried out with *SHELX* (Sheldrick, 1976); non-hydrogen atoms refined with anisotropic temperature factors, H atoms given fixed $U_{\rm iso}$ values of 0·05 Å^2; the benzene ring was constrained as described in the *Abstract*; the two hydroxyl H atoms included as fixed contributions at their difference-map locations; other H-atom positions were calculated. Final $R = 0{\cdot}036$, $R_w = 0{\cdot}038$; least-squares weights were those obtained from counting statistics; scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic coordinates and their e.s.d.'s are given in Table 1,* and the bond lengths and angles in Table 2.

Table 1. *Atomic coordinates with e.s.d.'s, and equivalent isotropic temperature factors* (Å^2) *for the non-hydrogen atoms*

$$B_{\rm eq} = \frac{8\pi^2}{3} \textstyle\sum_i U_{ii}.$$

	x	y	z	$B_{\rm eq}$
C(1)*	0·2488 (3)	0·1909 (4)	0·23779 (7)	2·37 (11)
C(2)*	0·2986 (3)	0·4086 (4)	0·25683 (7)	2·80 (12)
C(3)*	0·2547 (3)	0·4687 (4)	0·30511 (7)	2·96 (12)
C(4)*	0·1610 (3)	0·3112 (4)	0·33435 (7)	2·49 (11)
C(5)*	0·1112 (3)	0·0936 (4)	0·31531 (7)	2·92 (12)
C(6)*	0·1551 (3)	0·0334 (4)	0·26703 (7)	2·78 (11)
C(7)	0·2916 (6)	0·1179 (8)	0·18644 (14)	2·79 (13)
C(8)	0·1158 (6)	0·3849 (8)	0·38556 (14)	2·94 (13)
C(9)	0·4020 (6)	0·2459 (7)	0·10897 (12)	3·34 (13)
C(10)	0·4982 (6)	0·4541 (6)	0·09036 (15)	3·61 (13)
C(11)	0·0124 (6)	0·2563 (6)	0·46355 (12)	3·06 (12)
C(12)	−0·0214 (6)	0·0261 (7)	0·48772 (14)	3·25 (13)
O(1)	0·3573 (3)	0·2953 (4)	0·16032 (9)	3·42 (9)
O(2)	0·2686 (4)	−0·0757 (6)	0·17107 (10)	4·22 (10)
O(3)	0·0553 (3)	0·2070 (4)	0·41220 (9)	3·26 (8)
O(4)	0·1359 (4)	0·5811 (4)	0·40063 (10)	4·52 (10)
O(5)	0·3909 (6)	0·6558 (6)	0·08646 (11)	5·49 (11)
O(6)	0·1315 (4)	−0·1181 (4)	0·48903 (10)	4·44 (10)

* Since the benzene ring has been treated as a rigid group, the relatively low e.s.d.'s in the coordinates of C(1) to C(6) reflect the error in the position and orientation of the ring as a whole.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(7)	1·491 (4)	C(4)–C(8)	1·492 (4)
C(7)–O(2)	1·191 (5)	C(8)–O(4)	1·199 (5)
C(7)–O(1)	1·332 (5)	C(8)–O(3)	1·327 (5)
O(1)–C(9)	1·462 (4)	O(3)–C(11)	1·459 (4)
C(9)–C(10)	1·483 (6)	C(11)–C(12)	1·488 (6)
C(10)–O(5)	1·415 (5)	C(12)–O(6)	1·428 (5)
O(5)–H(O5)	1·08	O(6)–H(O6)	0·93
H(O5)···O(2′)	1·89	H(O6)···O(4′)	2·04
O(5)···O(2′)	2·912 (4)	O(6)···O(4′)	2·947 (4)
C(2)–C(1)–C(7)	122·3 (2)	C(3)–C(4)–C(8)	117·9 (2)
C(6)–C(1)–C(7)	117·7 (2)	C(5)–C(4)–C(8)	122·1 (2)
C(1)–C(7)–O(2)	123·6 (4)	C(4)–C(8)–O(3)	111·9 (4)
C(1)–C(7)–O(1)	111·6 (4)	C(4)–C(8)–O(4)	123·4 (4)
O(2)–C(7)–O(1)	124·8 (4)	O(3)–C(8)–O(4)	124·7 (4)
C(7)–O(1)–C(9)	116·7 (3)	C(8)–O(3)–C(11)	116·9 (3)
O(1)–C(9)–C(10)	106·7 (3)	O(3)–C(11)–C(12)	106·9 (3)
C(9)–C(10)–O(5)	112·7 (4)	C(11)–C(12)–O(6)	112·0 (4)
C(10)–O(5)–H(O5)	114	C(12)–O(6)–H(O6)	119
O(5)–H(O5)···O(2′)	158	O(6)–H(O6)···O(4′)	163

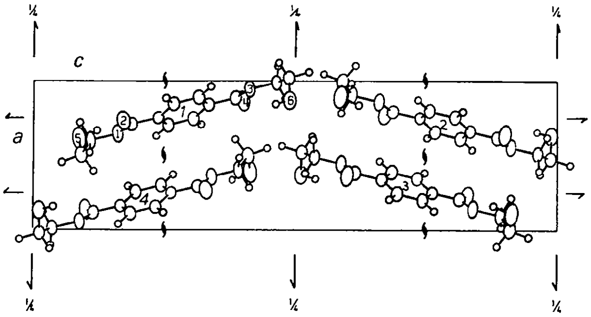

Fig. 2. *ORTEP* (Johnson, 1965) projection of the structure along **b**. Molecule 1 is the reference molecule; the others are derived from it by the operation of the screw axes. The numbered atoms are the O atoms in the reference molecule. The boundaries of the atoms are those of the thermal ellipsoids at the 50% probability level. Hydrogen bonds are not shown, as the bonded molecules form ribbons perpendicular to the paper.

The volume of the unit cell (1181 Å^3) is similar to that of the α form (1193 Å^3). The projection of the crystal structure parallel to **b** is shown in Fig. 2. (The projection parallel to the **a** axis has been deposited.)* Unlike the structure of the α form and those of TA, DMT, DET, and PET there are no centres of symmetry.

The molecule is approximately planar except for the hydroxyl groups and the aliphatic H atoms. The terephthaloyl residue is in the '*trans*' conformation and the C–CO–O–C and C–O–CH$_2$–CH$_2$ groups are approximately '*trans*', whereas the two O–CH$_2$–CH$_2$–O groups are approximately in '*gauche*' conformations of opposite handedness, which brings the two hydroxyl groups out of the mean plane of the rest of the molecule on opposite sides of it. Although there is no true centre of symmetry in the molecule it is not far from being centrosymmetric and, in broad outline, it is very similar in form to either of the two

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a figure showing a projection parallel to the *a* axis have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38267 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

types of molecule in the α form, which are, however, centrosymmetric.

The molecules are connected by two types of hydrogen bond: those linking O(4) in one molecule to O(6) in an adjacent molecule and those linking O(2) in the original molecule to O(5) in the adjacent molecule on the other side (Fig. 3), so that the structure consists of four hydrogen-bonded ribbons passing through the *ac* plane of each unit cell. The lengths of the hydrogen bonds (Table 2) suggest that the bonding is rather weak. Fig. 2 shows that the parallel ribbons are stacked so that the benzene rings are well separated and there is no simple relationship between their planes or their C(1)—C(4) directions, unlike the rings in crystals of PET or the α form of BHET. The angles between the mean planes of rings 2, 3 and 4 and that of ring 1 are 37·8 (2), 61·8 (2) and 47·0 (2)°, respectively. The four ribbons divide into two pairs, each pair related internally by the screw axis parallel to **b**, and the two pairs are approximately parallel to the (101) and (10$\bar{1}$) planes. The mean planes of the molecules are tilted by 3·8 (2)° with respect to the mean planes of the hydrogen-bonded ribbons, which may therefore be described as puckered.

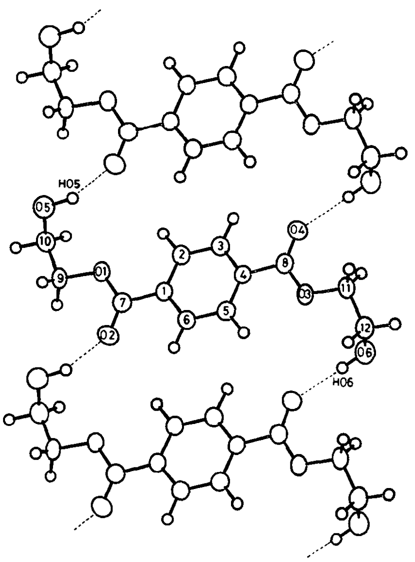

Fig. 3. The reference molecule viewed along **a**, hydrogen-bonded to its neighbours in the **b** direction, forming one of the four ribbons passing through each unit cell. Boundaries of atoms are as in Fig. 2, and hydrogen bonds are shown as broken lines.

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