Topochemical Studies. V. The Crystal Structure and Molecular Conformation of Bis-(2-hydroxyethyl) Terephthalate

By Setsuo Kashino and Masao Haisa

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan

The crystal structure of the stable form of bis-(2-hydroxyethyl) terephthalate has been determined from visually estimated Cu $K\alpha$ data. The crystals are monoclinic, space group $P2_1/a$, $Z=4$ with $a=25\cdot72$ (2), $b=5\cdot47$ (1), $c=8\cdot58$ (2) Å, $\beta=98\cdot9$ (2)°. The structure was solved by the symbolic addition procedure, and refined by the block-diagonal least-squares method to a final R value of $0\cdot072$ for 1559 non-zero reflexions. In the crystals there exist two kinds of molecules (A and B), and each occupies a centre of symmetry of the cell. The dihedral angle between the benzene rings of A and B is $178\cdot0°$ and the shortest $C\cdots C$ contact is $3\cdot385$ (5) Å. The molecules are held together by an $O-H\cdots OH$ hydrogen bond [$2\cdot839$ (5) Å] to form a chain along the c axis. Additional $O-H\cdots O=C$ hydrogen bonds [$2\cdot841$ (4) Å] connect the **b**-translated B molecules to form two-dimensional sheets parallel to the **bc** plane. The sheets are stacked by van der Waals forces. The only notable difference between the conformations of the two molecules is found in the internal rotation angle around the ethylenic C–C bond; $\tau(O-C-C-OH)=66\cdot0$ and $-73\cdot2°$ for molecules A and B, respectively.

Introduction

The crystal structure of poly(ethylene terephthalate) (PETP) has been studied by Daubeny, Bunn & Brown (1954), who have shown that the molecules are nearly planar and held together by van der Waals forces. The high melting point is attributed to the rigidity of the aromatic ring. Bateman, Richards, Farrow & Ward (1960) have shown by X-ray and n.m.r. studies that the high-temperature transition appears to be associated with the rotation of the aliphatic linkage of the molecules in the amorphous regions.

Bis-(2-hydroxyethyl) terephthalate (BHETP), a fragmental model substance of the polymer, has been found to have at least four polymorphs differing in configuration of the side chain (Miyake, 1957). This work was undertaken to confirm the conformational features of the ester and hydroxyethyl groups of the terephthalate and to examine the mode of molecular stacking in view of π-electron interaction.

Experimental

The material was kindly supplied by Mr Yuhiko Yamashita of the School of Engineering of this University. Crystals obtained from benzene–methanol solution were prisms elongated along the b axis. Crystallographic data are listed in Table 1. The cell constants are effectively identical with those reported by Bailey (1949). The intensity data were collected on equi-inclination Weissenberg photographs for the layers $h0l$ to $h4l$ and $hk0$ to $hk6$ by using specimens of dimensions $0\cdot1\times0\cdot4\times0\cdot3$ and $0\cdot2\times0\cdot4\times0\cdot6$ mm, respectively. In total, 1559 independent reflexions (58% of those in the Cu $K\alpha$ sphere) were observed as non-zero reflexions. The intensities were estimated

Table 1. *Crystallographic data*

Bis-(2-hydroxyethyl) terephthalate
$C_{12}H_{14}O_6$ M.W. 254·2 m.p. 112–113°C
Monoclinic, $a=25\cdot72$ (2), $b=5\cdot47$ (1), $c=8\cdot58$ (2) Å,
$\beta=98\cdot9$ (2)°
$D_m=1\cdot41$ g cm^{-3} by flotation in aqueous KI solution
$D_x=1\cdot415$ g cm^{-3} for $Z=4$ $F(000)=536$
$\mu=9\cdot9$ cm^{-1} for Cu $K\alpha$ ($\lambda=1\cdot5418$ Å)
Space group: $P2_1/a$

Table 2. *Starting set of phases*

h	k	l	$\|E\|$	Phases
16	1	4	3·50	0
5	2	6	3·16	0
8	3	7	3·45	0
28	0	4	4·10	A
19	1	2	4·52	B
24	0	0	3·96	C

visually and corrected for Lorentz and polarization factors and for spot shape.

Structure determination and refinement

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966). The starting set of phases is shown in Table 2. The phases of 50 reflexions out of 190 with $|E|>2\cdot0$ were assigned in terms of 0, π, A, B, and C based on the $\sum_2$ relationships. Each of eight sets of phases obtained by combinations of phases for A, B and C was used as a basic set for the application of the tangent formula. The minimum value of Karle's R ($0\cdot295$) was found to correspond to the combination $A=B=\pi$ and $C=0$. A three-dimensional E map computed from 262 terms with $|E|>1\cdot5$ revealed all the non-hydrogen atoms.

Block-diagonal least-squares refinements with aniso-

Table 3. *The final positional and thermal parameters* ($\times 10^4$) *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}
O(A1)	4124 (1)	3739 (6)	2129 (4)	20·7 (0·6)	341 (11)	263 (7)	−25 (4)	−31 (3)	135 (14)
O(A2)	3739 (1)	186 (5)	2511 (3)	11·6 (0·4)	405 (11)	178 (5)	−22 (4)	−19 (2)	85 (12)
O(A3)	2780 (1)	−2593 (7)	2072 (4)	15·0 (0·5)	676 (17)	167 (5)	−54 (5)	−10 (3)	110 (16)
O(B1)	4011 (1)	3175 (5)	7165 (4)	14·1 (0·5)	275 (9)	213 (5)	9 (4)	−42 (2)	81 (12)
O(B2)	3735 (1)	−640 (4)	7531 (3)	8·4 (0·3)	281 (9)	156 (4)	2 (3)	−20 (2)	28 (10)
O(B3)	3242 (1)	−4114 (5)	5139 (3)	15·9 (0·5)	304 (10)	157 (4)	20 (4)	−26 (2)	−6 (11)
C(A1)	5034 (1)	2213 (7)	4230 (4)	14·1 (0·6)	299 (13)	128 (6)	−17 (5)	10 (3)	−7 (14)
C(A2)	4576 (1)	828 (7)	3936 (4)	11·9 (0·6)	287 (13)	118 (5)	−4 (4)	6 (3)	−47 (14)
C(A3)	4546 (1)	−1394 (7)	4700 (5)	12·4 (0·6)	288 (13)	154 (6)	−27 (5)	13 (3)	−61 (15)
C(A4)	4133 (1)	1780 (7)	2771 (5)	12·3 (0·6)	320 (14)	145 (6)	−7 (5)	10 (3)	−38 (15)
C(A5)	3293 (2)	833 (8)	1344 (5)	13·5 (0·7)	435 (18)	175 (7)	1 (6)	−18 (4)	72 (19)
C(A6)	3006 (2)	−1502 (9)	871 (5)	14·9 (0·7)	538 (21)	155 (7)	−22 (6)	−18 (4)	−7 (20)
C(B1)	4970 (1)	2171 (6)	9147 (4)	9·8 (0·5)	259 (12)	123 (5)	2 (4)	−10 (3)	6 (13)
C(B2)	4554 (1)	529 (6)	8943 (4)	8·2 (0·5)	235 (11)	115 (5)	19 (4)	−8 (2)	−9 (12)
C(B3)	4580 (1)	−1636 (6)	9790 (4)	8·8 (0·5)	251 (12)	128 (6)	−5 (4)	−12 (3)	9 (13)
C(B4)	4079 (1)	1194 (6)	7789 (4)	9·3 (0·5)	260 (12)	130 (6)	18 (4)	−7 (3)	−18 (13)
C(B5)	3252 (1)	−168 (7)	6431 (5)	9·1 (0·5)	335 (14)	144 (6)	17 (4)	−22 (3)	−5 (15)
C(B6)	2985 (1)	−2572 (7)	6122 (5)	9·1 (0·5)	378 (15)	169 (7)	−10 (5)	−23 (3)	22 (17)

tropic thermal parameters reduced the R value to 0·12. A difference Fourier map revealed all the hydrogen atoms. Including all the atoms, further refinements were carried out using the weighting scheme:

$$w = 1\cdot0 \quad \text{for} \quad 0 < |F_o| \le F_{max}(= 11\cdot0),$$
$$w = (F_{max}/F_o)^2 \quad \text{for} \quad |F_o| > F_{max}.$$

The final R value was 0·072 for 1559 non-zero reflexions.* The final atomic parameters are listed in Tables 3 and 4.

Table 4. *The final parameters of the hydrogen atoms*

	x	y	z	B (Å²)
H(A1)	0·304	−0·312	0·294	7·1
H(A2)	0·505	0·378	0·365	2·6
H(A3)	0·425	−0·246	0·434	2·7
H(A4)	0·342	0·178	0·033	3·4
H(A5)	0·306	0·191	0·190	5·6
H(A6)	0·324	−0·270	0·049	3·6
H(A7)	0·275	−0·117	0·004	5·0
H(B1)	0·348	−0·506	0·580	4·0
H(B2)	0·493	0·379	0·849	2·0
H(B3)	0·428	−0·280	0·961	2·7
H(B4)	0·334	0·045	0·539	2·1
H(B5)	0·306	0·099	0·703	3·3
H(B6)	0·263	−0·229	0·560	3·6
H(B7)	0·297	−0·360	0·720	4·4

$\langle \sigma(x) \rangle = 0\cdot002$, $\langle \sigma(y) \rangle = 0\cdot009$, $\langle \sigma(z) \rangle = 0\cdot005$, $\langle \sigma(B) \rangle = 1\cdot1$ Å²

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computations were carried out on a NEAC 2200-700 computer at the Computation Center of Osaka University and a NEAC 2200-500 computer at the Okaya-

ma University Computer Center. The main programs used were *SIGM*, *TANG*, *HBLS*-5 and *DAPH* (Ashida, 1973).

Description and discussion of the structure

A projection of the crystal structure and some intermolecular contacts are shown in Fig. 1. There are two kinds of molecules (A and B), and each occupies a centre of symmetry of the cell, as has been reported for the white form of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (Byrn, Curtin & Paul, 1972). Both molecules lie nearly on ($\overline{4}$12) planes. A hydrogen bond from the hydroxyl group of molecule A to that of molecule B forms a chain along the c axis [O···O, 2·839 (5) Å; O–H···O, 151 (5); H···O–C 109 (2)°]. The other hydrogen bonds connect the hydroxyl groups and carbonyl oxygen atoms of **b**-translated B molecules on both their sides to form a ladder-like column along the b axis [O···O, 2·841 (4) Å; O–H···O, 175 (5); H···O=C, 139 (2)°]. These result in two-dimensional hydrogen-bonded sheets parallel to the bc plane. The sheets are stacked by the twofold screw axis in van der Waals contact. The carbonyl oxygen atoms of molecule A are free from hydrogen bonds in accordance with the infrared data (Miyake, 1957).

Fig. 2 illustrates the mode of overlap of the benzene ring planes in BHETP, diethyl terephthalate (DETP) (Bailey, 1949) and PETP. The respective molecules are symmetrically independent and hydrogen-bonded to each other in BHETP, while they are related by **c**-translation and free from hydrogen bonds in DETP. In spite of these differences both modes of stacking are very similar. On the other hand, the mode is of graphitic type in PETP and the shortest C···C distance, 3·7 Å, is longer than that in the other two, 3·385 (5) and 3·54 Å, respectively. Thus the mode of stacking in BHETP and DETP could be considered to reflect the existence of π-electron interaction.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30947 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
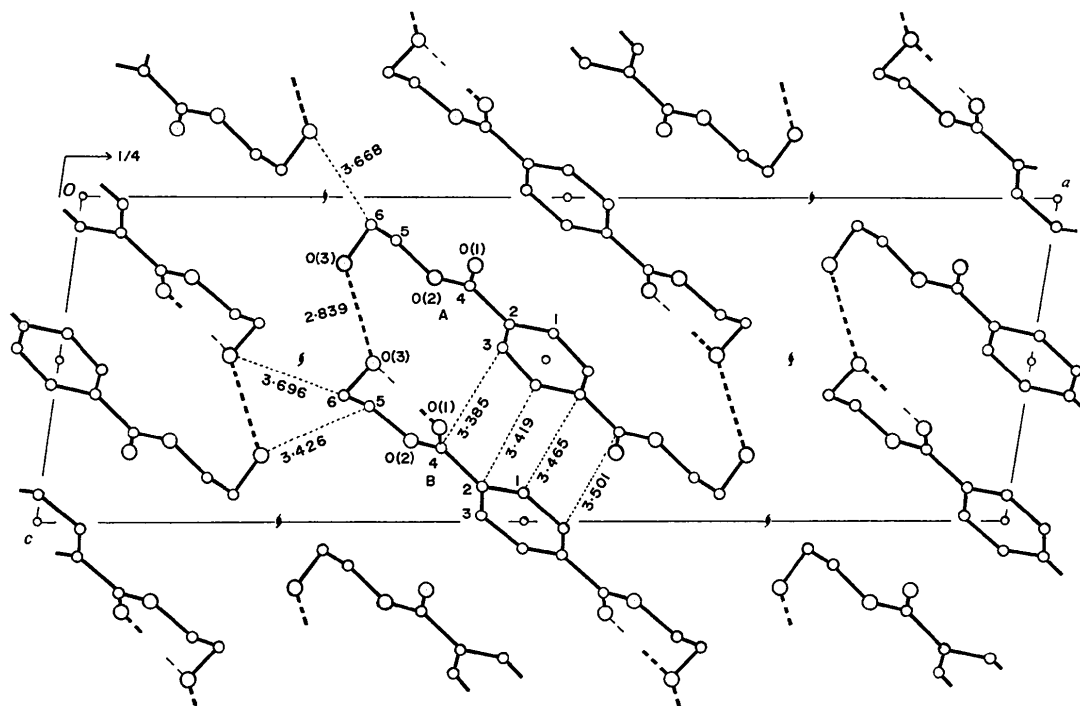
Fig. 1. Projection of the crystal structure viewed along the *b* axis. Broken lines show hydrogen bonds, and dotted lines intermolecular contacts.

In the present compound short contacts are also found between the b-translated molecules; C(*A*1)···C(*A*1') 3·338 (5) Å, C(*B*1)···C(*B*1') 3·417 Å. Corresponding to this packing scheme the melting point and density are higher than those of DETP, 44°C and 1·24 g cm⁻³ (Bailey, 1949).

The bond lengths and angles are shown in Fig. 3. Those of molecules *A* and *B* are broadly similar. The geometry of the ester groups agrees well with that in other aromatic esters: the procaine–bis-*p*-nitrophenyl phosphate complex (Sax, Pletcher & Gustaffson, 1970), 3-carbethoxy-4-oxo-6-methylhomopyrimidazole (COMHP) (Sasvári, Horvai & Simon, 1972) and 4-carbethoxyanilinium bis-*p*-nitrophenylphosphate

Fig. 2. Mode of overlap of the benzene ring planes; (*a*) bis-(2-hydroxyethyl) terephthalate, (*b*) diethyl terephthalate, (*c*) poly(ethylene terephthalate).

(CABNPP) (Pletcher, Sax & Yoo, 1972). The C(5)–C(6) bond lengths of the hydroxyethyl groups are close to those found in ethyl groups; 1·489 Å in COMHP, 1·471 Å in CABNPP.

The benzene rings are planar to within 0·004 Å. The C(4) atoms of molecules *A* and *B* deviate only 0·007 and 0·002 Å respectively from the benzene ring planes.

The internal rotation angles of the side chain are given in Table 5, along with those of the related compounds. The values are based on the definition given in the table. The dihedral angles between the plane through atoms C(2), C(4), O(1) and O(2) and the benzene ring plane correspond to τ(*a–b–g*), which is 4·5 and 8·7° for the molecules *A* and *B*, respectively, and 17·3° in piperazinium terephthalate (Kashino, Sasaki & Haisa, 1973). The only notable difference between the conformations of molecules *A* and *B* is found in the sign of τ(*d–e–f*). Such a difference is also found between procaine complexes (Sax, Pletcher & Gustaffson, 1970; Dexter, 1972). In the present case the difference seems to be caused by the requirement for hydrogen bond formation, whereas in the case of procaine it seems to be caused by the packing requirement. The *trans* conformation of the O–CH₂–CH₂–O group has been deduced on the basis of the infrared absorption at 909 cm⁻¹ (Miyake, 1957). However, the present result shows that the conformation is *gauche* for both kinds of molecules. The corresponding conformation is *gauche* for all the related compounds except PETP and parpanit (Griffith & Robertson, 1972) which has a bulky substituent at C(5). The internal rotation angles
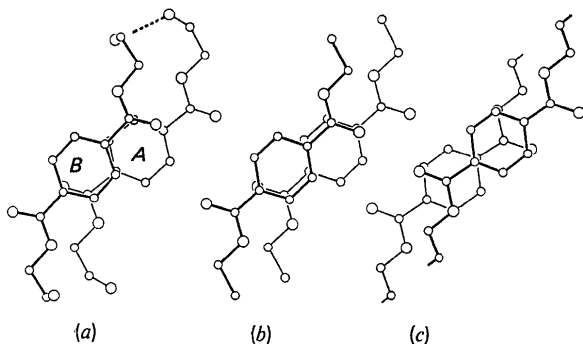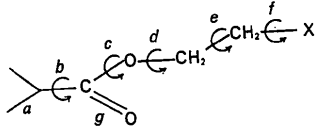
Table 5. *The internal rotation angles* (°) *of some ester groups*

Compound	a–b–c	a–b–g	b–c–d	c–d–e	d–e–f	g–c–d	Reference
BHETP Molecule *A*	174·9	−5·1	182·9	160·7	66·0	2·9	This work
Molecule *B*	171·6	−8·8	179·9	170·0	−73·2	−0·3	
Procaine.HCl	187·3	7·0	178·7	172·7	70·2	1·0	Dexter (1972)
Procaine phosphate	177·0	1·9	176·1	181·3	−65·1	−2·8	Sax, Pletcher & Gustaffson (1970)
PETP	169	1	182	159	180	−9	Daubeny, Bunn & Brown (1954)
DETP	184	3	181	186		3	Bailey (1949)
Parpanit			177·9	189·4	−94·4	0·2	Griffith & Robertson (1972)
CABNPP	171·1	−9·9	181·0	191·4		1·9	Pletcher, Sax & Yoo (1972)
COMHP Molecule *A*	157·2	−21·4	181·3	183·5		0·0	Sasvári, Horvai & Simon (1972)
Molecule *B*	174·9	−4·3	176·4	173·7		−4·4	
Ethyl 3,5-dinitrobenzoate	183·2	0·8	170·0	100·8		−7·6	Hughes & Trotter (1971)
			195·6	179·0		18·0	
Ethyl *p*-azoxybenzoate	178·5	−2·8	180·1	186·3		1·2	Krigbaum & Barber (1971)
	182·2	1·8	177·7	−84·7		−1·6	
Ethyl tyrosinate			189·3	166·3		5·4	Pieret, Durant, Griffé, Germain & Debaerdemaeker (1970)

$\tau(b{-}c{-}d)$ and $\tau(c{-}d{-}e)$ are *trans*, as found in many related compounds. It is of interest that such a *trans–trans–gauche* conformation is frequently found in some compounds: for example a useful high polymer, poly(ethylene oxide) (Tadokoro, Chatani, Yoshihara, Tahara & Murahashi, 1964) and cholinergic molecules relevant to acetylcholinesterase (Chothia & Pauling, 1969).

References

ASHIDA, T. (1973). *The Universal Crystallographic Computing System*, The Computation Centre, Osaka Univ.

BAILEY, M. (1949). *Acta Cryst.* **2**, 120–126.

BATEMAN, J., RICHARDS, R. E., FARROW, G. & WARD, I. M. (1960). *Polymer*, **1**, 63–71.

BYRN, S. R., CURTIN, D. Y. & PAUL, I. C. (1972). *J. Amer. Chem. Soc.* **94**, 890–898.

CHOTHIA, C. & PAULING, P. (1969). *Nature, Lond.* **223**, 919–921.

DAUBENY, R. DE P., BUNN, C. W. & BROWN, C. J. (1954). *Proc. Roy. Soc.* A**226**, 531–542.

DEXTER, D. D. (1972). *Acta Cryst.* B**28**, 77–82.

GRIFFITH, E. A. H. & ROBERTSON, B. E. (1972). *Acta Cryst.* B**28**, 3377–3384.

HUGHES, D. L. & TROTTER, J. (1971). *J. Chem. Soc.* (*A*), pp. 2358–2361.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

KASHINO, S., SASAKI, M. & HAISA, M. (1973). *Bull. Chem. Soc. Japan*, **46**, 1375–1379.

KRIGBAUM, W. R. & BARBER, P. G. (1971). *Acta Cryst.* B**27**, 1884–1891.

MIYAKE, A. (1957). *Bull. Chem. Soc. Japan*, **30**, 361–363.

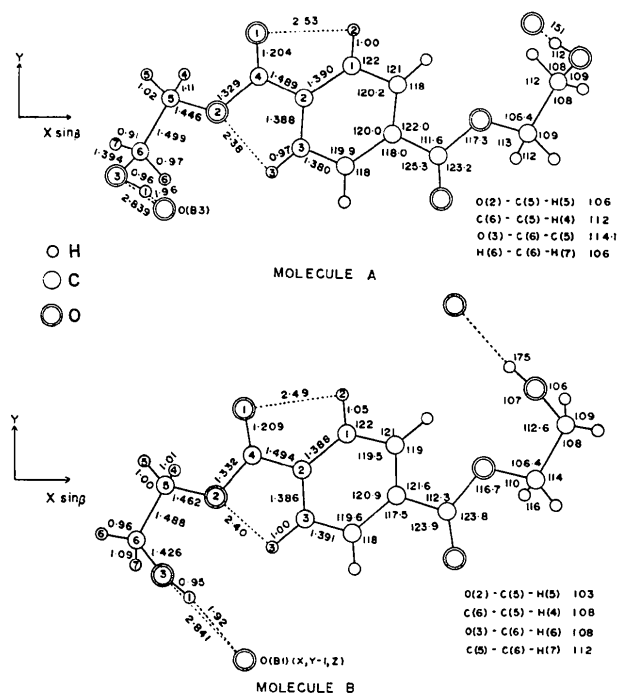PIERET, A. F., DURANT, F., GRIFFÉ, M., GERMAIN, G. & DEBAERDEMAEKER, T. (1970). *Acta Cryst.* B**26**, 2117–2124.

Fig. 3. Bond lengths (Å) and angles (°). The estimated standard deviations are 0·005 Å and 0·3° for non-hydrogen atoms and 0·04 Å and 3° for hydrogen atoms.

PLETCHER, J., SAX, M. & YOO, C. S. (1972). *Acta Cryst.* B**28**, 378–387.

SASVÁRI, K., HORVAI, J. C. & SIMON, K. (1972). *Acta Cryst.* B**28**, 2405–2416.

SAX, M., PLETCHER, J. & GUSTAFFSON, B. (1970). *Acta Cryst.* B**26**, 114–124.

TADOKORO, H., CHATANI, Y., YOSHIHARA, T., TAHARA, S. & MURAHASHI, S. (1964). *Makromol. Chem.* **73**, 109–127.