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Conformational Studies of Oligomethylene Glycol Derivatives and Related Compounds. VI. The Crystal and Molecular Structure of Hexamethylene Glycol Dibenzoate, $C_{20}H_{22}O_4$
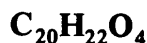
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The diester hexamethylene glycol dibenzoate, $C_{20}H_{22}O_4$, crystallizes in the orthorhombic space group *Pbca* with four molecules per unit cell of dimensions $a = 8.728$ (3), $b = 19.676$ (5), $c = 10.551$ (3) Å. The structure, solved by direct methods, was refined by block-diagonal least squares to a final R_w value of 0.049. The molecule, which has a crystallographic centre of symmetry, is in the all-*trans* conformation. The molecules are packed in a herring-bone manner. Van der Waals interactions maintain the molecules together in the crystal. The conformational resemblance of this molecule to the polymer poly(hexamethylene glycol terephthalate) is discussed.

Introduction

One method of determining polymer structures is to study crystal structures of small related molecules or oligomers. This provides accurate information about the molecular geometry of these model compounds. Bond lengths and angles, specific to the chemical species studied, are used as standards for further conformational analysis and as constraints in the least-squares refinement of polymer structures. Previous research has shown some evidence that the solid-state conformation of the polymer could be close to that of the related model compound or oligomer. However, because of the difficulty of obtaining good oligomer crystals (in the case of biopolymers) or perhaps as a result of some lack of communication between polymer crystallographers and single-crystal crystallographers, this approach has not yet been fully explored. In order to investigate the similarities or differences between the solid-state conformation of the polymer and that of the related model compound we have undertaken a systematic study of oligomethylene glycol derivatives related to the poly(oligomethylene terephthalates): $[O-(CH_2)_p-O-CO-C_6H_4-CO]_n$, with $p = 2$ to 10. For ethylene glycol dibenzoate (Pérez & Brisse, 1976a), trimethylene glycol dibenzoate and trimethylene glycol di-*p*-chlorobenzoate (Pérez & Brisse, 1977, 1976b) the conformations were found to be closely related to those of the polymers poly(ethylene terephthalate) and poly(trimethylene terephthalate) respectively.

As a continuation of our systematic studies of oligomethylene glycol derivatives, we present here the crystal and molecular structure of hexamethylene glycol dibenzoate, which is considered to be a model compound for poly(hexamethylene glycol terephthalate): $[O-(CH_2)_6-O-CO-C_6H_4-CO]_n$.

Experimental

Crystals of hexamethylene glycol dibenzoate, $C_{20}H_{22}O_4$, were obtained by slow evaporation of an

Table 1. *Crystal data*

$C_{20}H_{22}O_4$, $M_r = 326.4$, m.p. 55 °C, $F(000) = 696$
Orthorhombic, *Pbca*, $Z = 4$, $D_o = 1.20$, $D_c = 1.197$ g cm^{-3}
$a = 8.728(3)$, $b = 19.676(5)$, $c = 10.551(3)$ Å, $V = 1811.9$ Å^3
$\mu(\text{Mo } K\alpha) = 0.89$ cm^{-1}, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $t = 20(1)°C$

ethanol solution at room temperature. Weissenberg and precession photographs indicated that the crystals were orthorhombic, space group *Pbca* (systematic absences: $0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h \neq 2n$). The unit-cell dimensions were obtained as part of the crystal alignment on an automatic diffractometer by a least-squares fit to the setting of 12 well centred reflexions. These and other relevant crystallographic data are presented in Table 1.

Intensity data were collected within one octant of the Mo sphere, limited by $2\theta \leq 50°$, on a Syntex $P\bar{1}$ diffractometer with a graphite monochromator and the θ–2θ technique. The data collection was performed at a variable speed [1° (2θ) to 24° (2θ) min^{-1}], depending on the intensity of the reflexion being measured. A scan range of 1.2° (2θ) below $K\alpha_1$ and above $K\alpha_2$ was selected. The background time to scan time ratio was BSR = 0.40. The intensities of three reference reflexions measured every 50 reflexions decreased by about 4% of their initial values over the duration of the data collection. The data reduction was performed with the programs of Ahmed, Hall, Pippy & Huber (1966). Of the 1611 independent reflexions measured, 823 were assigned zero intensity as the net count of each was less than $1.96\sigma(I)$. The standard deviation $\sigma(I)$ was calculated according to $\sigma^2(I) = [(I_T + B/\text{BSR}^2)V_b^2 + (pI_N)^2]/\tau$, where τ is the transmission coefficient, I_T the total count, I_N the net count, B the total background count, V_b the scan rate, and $p(= 0.04)$ is the long-term instability constant. The X-ray scattering factors were obtained from Cromer & Waber (1965) for C and O, and from Stewart, Davidson & Simpson (1965) for H.

Structure determination and refinement

A set of normalized structure factors was calculated with the assumption that the groups of atoms were in random positions and orientation. This was performed with a partial knowledge of the structure deduced from the molecular geometry of ethylene glycol dibenzoate (Pérez & Brisse, 1976a).

The structure was solved with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974), for all E's down to a minimum value of 1.70. Of the four different solutions provided by this computation only one appeared to be self-consistent. The values of various parameters used as criteria for the choice of the best set of phases are listed in Table 2. The resulting E map calculated with this set of phases located all the

nonhydrogen atoms. The value of R computed at this stage was 0.24. Each reflexion was assigned a weight w inversely proportional to the variance derived from the value of $\sigma(I)$, $w = 1/\sigma^2(F)$. The refinement then proceeded smoothly to a final R_w value of 0.049. The standard deviation of an observation of unit weight, $\sigma_F = [\Sigma w(F_o^2 - F_c^2)/(m - n)]^{1/2}$, where m is the number of reflexions and n the number of refined parameters, was 2.01. At the end of the refinement the average shift-to-coordinates ratio was less than 0.6σ. A final electron density map showed no significant residual density, the extreme fluctuations being 0.17 and -0.19 e Å^{-3}.*

Results and discussion

The positional and thermal parameters and their standard deviations are presented in Table 3. The stereoscopic chemical structure of hexamethylene glycol dibenzoate and its thermal ellipsoids are shown in Fig. 1.

Bond distances and angles

The interatomic bond distances and angles are schematically summarized in Fig. 2. Thermal-motion analysis was conducted according to the method detailed by Schomaker & Trueblood (1968). The r.m.s. value of ΔU_{ij} is 0.0087 Å^2, while $\overline{\sigma(U_{ij})}$ is 0.0095 Å^2. It is thus concluded that the thermal motion of the molecule cannot be described in terms of a rigid body. Consequently the bond distances and angles have not been corrected for thermal motion. The standard deviations of these quantities, derived from the calculated e.s.d.'s of the final coordinates, amount to 0.004 Å and 0.3° for bond distances and angles respectively for the nonhydrogen atoms, and to 0.03 Å for C—H distances. The observation noted previously for the structures of oligomethylene glycol dibenzoates (Pérez & Brisse, 1976a,b, 1977) is again found here, *i.e.* some of the distances in the 'glycol' part of the

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32297 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Figures of merit (FOM) of the best set of phases and extreme values*

	Absolute FOM	ψ_0 $(\times 10^3)$	Residual	Combined FOM
Best set of phases	1.1363	0.1993	19.23	2.00
Maximum value	1.1393	0.3094	20.65	
Minimum value	1.1363	0.1993	19.23	

molecule are remarkably shorter than is usual for $C(sp^3)$–$C(sp^3)$ bond distances. Thus, the C(8)–C(9) and C(10)–C(10') distances are only 1·485 (4) and 1·496 (4) Å respectively.

The geometry of the dibenzoate part of the molecule, up to O(2), is in excellent agreement with the average geometry computed from the distances and angles of several dibenzoate groups (Brisse & Pérez, 1976). The $C(sp^2)$–$C(sp^2)$ aromatic distances observed in this work average 1·379 Å, identical to the mean bond length computed from 78 $C(sp^2)$–$C(sp^2)$ distances by Brisse & Sygusch (1974). The average $C(sp^2)$–H bond distance is 0·98 Å. The average bond angle for the six-membered ring is 120°. All the angles involving H atoms in the phenyl group are consistent with sp^2 geometry.

Mean planes and torsion angles

The equations for the aromatic mean plane (plane A) and for the carboxylic group (plane B) are given in Table 4. The carboxylic plane is tilted by only 3·3° from the aromatic ring plane. As noted elsewhere (Brisse & Pérez, 1976), the relative orientation of these planes is distributed around 0°, but cannot be considered as a conformational constant of either the benzoate or the terephthalate groups.

The torsion angles listed in Table 5 do not differ very much from 0 or 180°, so that the molecule has the all-*trans* conformation, within experimental errors. The departure from the all-*trans* conformation is mainly located around the O(2)–C(8) bond, the value of the torsion angle about this bond being 174·2°. The cal-

Table 3. *Fractional coordinates, thermal parameters and their e.s.d.'s*

The thermal parameters are the coefficients of the expression $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + 2U_{12}a^*b^*hk + \cdots)]$. The isotropic thermal parameters are defined by $T = \exp[-8\pi^2 U(\sin^2 \theta/\lambda^2)]$. The coordinates are in fractions of unit-cell edges × 10⁵ for O and C, and × 10⁴ for H. The thermal parameters are given × 10⁴ for O and C, and × 10³ for H. The standard deviations refer to the least significant digit.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	54945 (27)	87794 (12)	80579 (20)	749 (17)	1255 (20)	461 (13)	282 (19)	11 (16)	90 (15)
O(2)	44689 (25)	90796 (12)	99113 (20)	517 (13)	862 (16)	550 (14)	221 (15)	−26 (15)	−8 (13)
C(1)	68441 (34)	85281 (16)	99478 (30)	401 (18)	498 (20)	510 (21)	3 (18)	5 (20)	26 (18)
C(2)	68631 (37)	85308 (17)	112640 (30)	531 (21)	649 (23)	527 (22)	57 (21)	31 (21)	1 (20)
C(3)	80738 (40)	82352 (18)	119132 (32)	620 (24)	862 (26)	584 (24)	142 (24)	−89 (22)	38 (22)
C(4)	92478 (39)	79427 (19)	112575 (34)	592 (24)	755 (25)	787 (28)	157 (25)	−194 (24)	−26 (22)
C(5)	92528 (38)	79460 (18)	99522 (34)	636 (25)	841 (26)	733 (27)	225 (25)	−26 (25)	−110 (24)
C(6)	80589 (38)	82393 (17)	92996 (30)	607 (23)	700 (23)	501 (23)	107 (22)	−12 (21)	15 (20)
C(7)	55599 (37)	88051 (16)	91935 (30)	513 (20)	628 (22)	533 (20)	−4 (21)	33 (22)	40 (19)
C(8)	31776 (38)	93704 (19)	92329 (35)	542 (23)	955 (30)	712 (27)	280 (24)	−105 (23)	−33 (24)
C(9)	20118 (35)	95859 (17)	101761 (33)	507 (22)	637 (23)	701 (26)	113 (21)	−59 (22)	8 (21)
C(10)	6038 (36)	98902 (17)	95403 (30)	503 (23)	607 (23)	658 (25)	40 (21)	−31 (21)	12 (20)

	x	y	z	U		x	y	z	U
H(21)	6037 (30)	8762 (13)	11721 (27)	67 (4)	H(82)	3594 (38)	9779 (18)	8668 (32)	123 (6)
H(31)	8104 (34)	8231 (14)	12830 (29)	92 (5)	H(91)	2547 (35)	9934 (14)	10721 (25)	77 (4)
H(41)	10099 (30)	7725 (13)	11688 (24)	63 (4)	H(92)	1616 (29)	9234 (13)	10618 (26)	70 (4)
H(51)	10085 (37)	7749 (15)	9472 (30)	102 (5)	H(101)	131 (35)	9555 (16)	8954 (27)	87 (5)
H(61)	8032 (34)	8244 (15)	8354 (26)	86 (5)	H(102)	954 (29)	10303 (13)	9021 (25)	59 (4)
H(81)	2766 (32)	9037 (14)	8651 (25)	78 (4)					
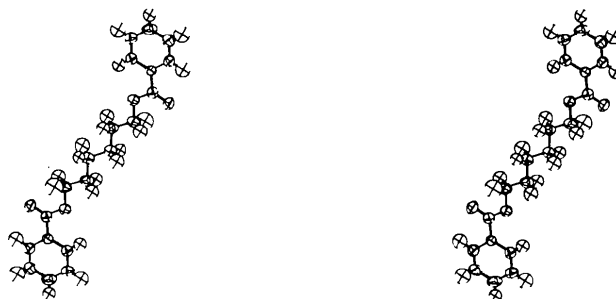
Fig. 1. Stereoscopic view of one molecule of hexamethylene glycol dibenzoate.

culated distance between the centres of the phenyl groups of the molecule is 15·719 Å. The corresponding distance if all the torsion angles of interest were 180° is 15·725 Å. The molecule is only 0·006 Å shorter than the fully extended all-*trans* conformation.

The unit cell of poly(hexamethylene terephthalate) was first examined by Farrow, McIntosh & Ward (1960). The fibre repeat was reported to be 15·40 Å. Recently, Joly, Nemoz Douillard & Vallet (1975) found that the polymer crystallizes in the triclinic $P\bar{1}$ space group with two independent chains within the asymmetric unit. According to these authors the fibre repeat was also 15·40 Å and the chains were assumed to be in the *trans* conformation. The small difference of 0·32 Å between the fibre repeat and the corresponding distance in hexamethylene glycol dibenzoate indicates that in the polymer there is a slight departure from planarity.

Fig. 2. Schematic diagram showing the bond distances and angles in hexamethylene glycol dibenzoate.

Table 5. Torsion angles (°)

C(9)—C(10)—C(10′)—C(9′)*	180·0†
C(8)—C(9)—C(10)—C(10′)	179·6
O(2)—C(8)—C(9)—C(10)	−179·3
C(7)—O(2)—C(8)—C(9)	174·2
C(1)—C(7)—O(2)—C(8)	179·2
O(1)—C(7)—O(2)—C(8)	−1·6

* The primed atoms are centrosymmetrically related to the unprimed atoms having the same number.

† The torsion angle around C(10)—C(10′) is constrained to be 180° since the middle of the C(10)—C(10′) bond is a centre of symmetry for the molecule.

Table 4. Mean planes

The planes are expressed by $lX + mY + nZ - p = 0$, with X,Y,Z and p in Å. The orthogonal system of axes has X, Y and Z parallel to the a, b and c axes respectively.

	Atoms	Deviations from plane		Atoms	Deviations from plane
Plane A			Plane B		
$\chi^2 = 15·4$	C(1)	−0·008 (3) Å	$\chi^2 = 2·4$	O(1)	−0·001 (2) Å
	C(2)	0·004 (3)		O(2)	−0·001 (2)
	C(3)	0·003 (3)		C(1)	−0·001 (3)
	C(4)	−0·007 (4)		C(7)	0·005 (3)
	C(5)	0·002 (3)			
	C(6)	0·006 (3)	Plane C†		
	*H(21)	0·06 (3)	$\chi^2 = 2·7$	C(8)	0·002 (2)
	*H(31)	0·01 (3)		C(9)	−0·002 (2)
	*H(41)	−0·03 (3)		C(10)	0·003 (2)
	*H(51)	0·0i (3)			
	*H(61)	0·00 (3)			

Plane A: 0·482X + 0·876Y − 0·001Z − 17·583 = 0
Plane B: 0·464X + 0·884Y − 0·055Z − 17·035 = 0
Plane C: 0·417X + 0·908Y + 0·043Z − 18·313 = 0

* Not included in the mean-plane calculation.
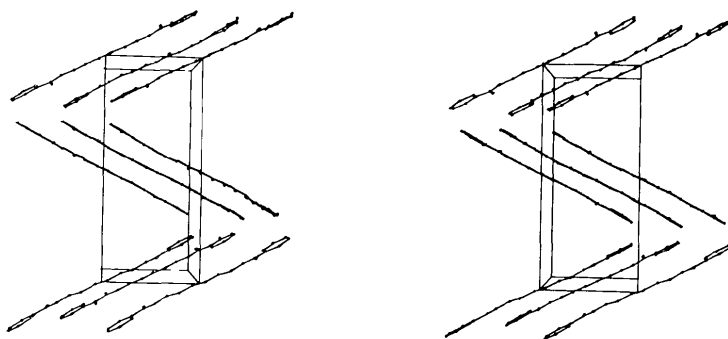† This plane passes through the centre of symmetry of the molecule.

Fig. 3. Packing of the molecules showing their 'herring-bone' arrangement.

Packing of the molecules

As can be observed in Fig. 3, the hexamethylene glycol dibenzoate molecules are packed in the crystal in a herring-bone manner. None of the intermolecular contacts are shorter than 3·30 Å. Consequently the molecules are held in the crystal by van der Waals forces only.

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