Crystal Structure of Cyclic Di(ethylene terephthalate)

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ABSTRACT: The crystal structure of cyclic di(ethylene terephthalate), a cyclic dimer of poly(ethylene terephthalate), was determined by X-ray diffraction. The crystal is monoclinic with cell parameters of $a = 8.546$ (1), $b = 12.675$ (2), $c = 7.984$ (2) Å, and $\beta = 90.70$ (1)°. The space group is $P2_1/c$ and the unit cell contains two centrosymmetrical molecules. The benzene rings were deformed slightly into a boat shape. Ethylene glycol residues have torsion angles of 21.2° and -21.2°, close to a *cis* conformation. The $\text{CH}_2\text{--CH}_2$ and O--CH_2 bond lengths and $\text{O--CH}_2\text{--CH}_2$ bond angles are larger compared to those in two types of cyclic trimers of poly(ethylene terephthalate) and in a cyclic dimer of poly(butylene terephthalate).

KEY WORDS Crystal Structure / Cyclic Oligomer / Cyclic Di(ethylene terephthalate) / Poly(ethylene terephthalate) /

A few % of cyclic oligomers are usually contained in commercial poly(ethylene terephthalate)(PET). The most abundant cyclic trimer was first found by solvent-extraction from PET films.¹ Peebles, Jr. *et al.*,² and Repin and Papanikolau³ isolated a cyclic dimer, *i.e.*, cyclic di(ethylene terephthalate) from a mixture of cyclic oligomers obtained by reacting terephthaloyl chloride with bis(hydroxyethyl) terephthalate. Later, the presence of the cyclic dimer in PET was recognized while separating isolated PET oligomers by chromatography.^{4,5}

The cyclic trimer exists in two crystal forms giving distinct X-ray diffraction patterns and IR absorption spectra.⁶ These two crystal forms have been designated Type A and B and their crystal structures have been determined by Hašek *et al.*,^{7,8} and Kitano *et al.*,⁹ respectively. The cyclic dimer may have a more strained molecular structure than those of the higher homologs. However, the crystal structure has not yet been determined, although unit cell parameters and a space group have been proposed.³ In this study we prepared the dimer and analyzed its crystal structure.

EXPERIMENTAL

Materials

The cyclic dimer was prepared according to the procedure of Repin and Papanikolau.³ The melting point was 225—227°C (uncor.) (lit., 229°C³). The crystals grown from acetone were colorless plates.

X-Ray Diffraction

The unit cell parameters and reflection intensities were measured on a Rigaku AFC four-circle diffractometer using graphite-monochromatized MoK_α radiation. The crystal data are summarized in Table I.

Intensity data were collected up to $2\theta = 55^\circ$ using the $2\theta\text{--}\omega$ scan mode and a scan range of $(1.78 + 0.40 \tan \theta)^\circ$ in ω . Three standard reflections for orientation control were measured every 100 reflections and remained essentially constant through out the run. 940 Reflections with $I > 3\sigma(I)$ were used in the refinement of the structure. Lorentz and polarization corrections were applied taking into account the monochromator crystal.

Table I. Crystals data

Chemical formula	C ₂₀ H ₁₆ O ₈
Molecular weight	384.34
Crystal system	Monoclinic
Space group	P2 ₁ /c
Cell constants	$a = 8.546$ (1) Å $b = 12.675$ (2) Å $c = 7.984$ (2) Å $\beta = 90.70$ (1)°
Volume of the unit cell	$V = 864.8$ (2) Å ³
Density	$D_c = 1.476$ g cm ⁻³
No. of molecules in the unit cell	$Z = 2$
No. of electrons in the unit cell	$F(000) = 400$
Absorption coefficient	$\mu = 1.1$ cm ⁻¹ (for MoK α)
No. of reflections	941

Table II. Fractional atomic coordinates and temperature factors for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} /Å ²
O (1)	0.1161 (4)	0.0780 (3)	0.6594 (5)	3.4 (2)
O (2)	0.0798 (5)	-0.0822 (3)	0.7722 (5)	4.7 (2)
O (3)	0.6583 (4)	-0.0997 (3)	0.1148 (5)	3.5 (2)
O (4)	0.6455 (4)	-0.2637 (3)	0.2209 (5)	4.3 (2)
C (1)	0.2287 (6)	-0.0656 (4)	0.5223 (6)	2.4 (2)
C (2)	0.2949 (6)	0.0035 (4)	0.4075 (7)	2.8 (2)
C (3)	0.4060 (6)	-0.0323 (4)	0.2968 (6)	2.8 (2)
C (4)	0.4531 (6)	-0.1375 (4)	0.3002 (6)	2.6 (2)
C (5)	0.3780 (6)	-0.2081 (4)	0.4062 (7)	3.1 (2)
C (6)	0.2671 (6)	-0.1733 (4)	0.5156 (7)	3.0 (3)
C (7)	0.1325 (6)	-0.0287 (5)	0.6632 (7)	3.1 (3)
C (8)	0.5921 (6)	-0.1761 (5)	0.2077 (7)	3.1 (3)
C (9)	0.0634 (6)	0.1305 (5)	0.8118 (7)	3.9 (3)
C (10)	0.8124 (6)	-0.1213 (5)	0.0472 (7)	4.3 (3)

^a *B*_{eq} is the equivalent isotropic temperature factor calculated from anisotropic temperature coefficients.

The structure was solved by direct-methods using the TEXSAN program¹⁰ which located all the non-hydrogen atoms. Hydrogen atoms were located at ideal positions by calculation. Refinement of the structure was carried out by a full-matrix least-squares method anisotropically with the non-hydrogen atoms and isotropically with the hydrogen atoms. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1.0$ for all of the reflections. The final *R*- and

Figure 1. Molecular structure of cyclic di(ethylene terephthalate) with atom labeling. The thermal ellipsoids are drawn at a 50% probability level.

*R*_w-values were 0.068 and 0.083, respectively.

RESULTS AND DISCUSSION

The crystal was monoclinic and the values of the unit cell parameters are in good agreement with those presented by Repin and Papanikolaou: $a = 8.58 \pm 0.05$, $b = 12.75 \pm 0.1$, $c = 8.01 \pm 0.04$ Å, and $\beta = 90.7 \pm 0.2^\circ$.³ The systematic absences of reflections are also consistent with the space group P2₁/c proposed by them.

Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table II. The

Table III. Bond lengths, bond angles, and torsion angles^a

Bond length (Å)			
O1-C7	1.360 (7)	C1-C7	1.478 (7)
O1-C9	1.463 (6)	C2-C3	1.381 (7)
O2-C7	1.195 (6)	C3-C4	1.393 (7)
O3-C8	1.348 (6)	C4-C5	1.393 (7)
O3-C10	1.456 (6)	C4-C8	1.489 (7)
O4-C8	1.205 (6)	C5-C6	1.369 (7)
C1-C2	1.393 (7)	C9-C10'	1.542 (8)
C1-C6	1.405 (7)		
Bond angle (°)			
C7-O1-C9	117.8 (4)	C4-C5-C6	120.6 (5)
C8-O3-C10	117.1 (5)	C1-C6-C5	120.0 (5)
C2-C1-C6	119.3 (5)	O1-C7-O2	122.7 (5)
C2-C1-C7	122.4 (5)	O1-C7-C1	110.9 (5)
C6-C1-C7	118.0 (5)	O2-C7-C1	126.4 (5)
C1-C2-C3	120.1 (5)	O3-C8-O4	123.3 (5)
C2-C3-C4	120.2 (5)	O3-C8-C4	112.3 (5)
C3-C4-C5	119.4 (5)	O4-C8-C4	124.2 (5)
C3-C4-C8	122.4 (5)	O1-C9-C10'	110.9 (4)
C5-C4-C8	117.9 (5)	O3-C10-C9'	111.2 (4)
Torsion angle (°)			
O1-C7-C1-C2	1.8 (7)	C1-C7-O1-C9	-163.2 (4)
O1-C7-C1-C6	175.1 (4)	C2-C1-C6-C5	5.2 (8)
O1-C9-C10'-O3'	21.2 (7)	C2-C3-C4-C5	5.4 (8)
O2-C7-O1-C9	13.9 (8)	C2-C3-C4-C8	-168.2 (5)
O2-C7-C1-C2	-175.1 (6)	C3-C2-C1-C6	-4.8 (8)
O2-C7-C1-C6	-1.8 (8)	C3-C2-C1-C7	168.4 (5)
O3-C8-C4-C3	-3.8 (7)	C3-C4-C5-C6	-5.0 (8)
O3-C8-C4-C5	-177.4 (5)	C4-C8-O3-C10	167.5 (4)
O4-C8-O3-C10	-8.6 (8)	C5-C6-C1-C7	-168.3 (5)
O4-C8-C4-C3	172.2 (5)	C6-C5-C4-C8	168.8 (5)
O4-C8-C4-C5	-1.4 (8)	C7-O1-C9-C10'	66.6 (6)
C1-C2-C3-C4	-0.4 (8)	C8-O3-C10-C9'	-66.5 (7)
C1-C6-C5-C4	-0.3 (8)		

^a Primed atoms are related to the corresponding unprimed ones by inversion through the molecular center.

molecular structure with atom labeling is shown in Figure 1. Bond lengths, bond angles, and torsion angles are presented in Table III and the displacements of atoms from the mean plane of the benzene ring are in Table IV.

Only two molecules are contained in a unit cell with the space group $P2_1/c$; therefore, the cyclic dimers are forced to situate in specific positions in the cell and they are centrosymmetrical.³ The two benzene rings in the molecule are approximately overlapped and their centers are about 4.1 Å apart; whereas, the distance between the nearest benzene ring

Table IV. Displacement (Å) of the atoms from the least-squares best plane

C1	0.054	C2 ^a	0.002 (5)
C3 ^a	-0.002 (5)	C4	0.055
C5 ^a	0.002 (5)	C6 ^a	-0.002 (5)
C7	0.312	C8	0.311

^a Atoms included in the calculation of the plane.

is 4.56 Å in the PET crystal.¹¹ The benzene rings are slightly deformed into a boat shape; two of the carbon atoms, C1 and C4, are displaced toward another benzene ring from

the plane of the other four carbon atoms by 0.054 Å and 0.055 Å, respectively. The carbonyl carbon atoms, C7 and C8, are bent further inward from the plane of the phenyl ring by 0.312 Å and 0.311 Å, respectively. These facts demonstrate that the molecule is sterical-

ly strained. Such deformation of the benzene rings from a planar structure have also been observed in a cyclic dimer of poly(butylene terephthalate) (PBT);¹² however, the extent of bending is significantly less. Two of the carbonyl groups take on a syn conformation

Table V. Comparison of the bond lengths (Å), bond angles (°), and torsion angles (°) of cyclic oligo(alkylene terephthalate)s

	Dimer (PET)	Trimer(PET)		Dimer(PBT*) ¹²
		Type A ⁸	Type B ⁹	
Bond length (average)				
O-C(=O)	1.354	1.337	1.337	1.325
O-CH ₂	1.460	1.448	1.422	1.436
C=O	1.200	1.204	1.205	1.202
C-C(=O)	1.484	1.492	1.478	1.485
CH ₂ -CH ₂	1.542	1.488	1.480	1.502
C-C (phenyl)	1.389	1.385	1.393	1.379
Bond angle (average)				
CH ₂ -O-C(=O)	117.5	117.3	117.5	116.2
CH-C-C(=O)	122.4	122.1	121.5	121.9
CH-C-C(=O)	118.0	118.5	117.8	119.3
O-C=O	123.0	123.3	121.8	123.4
O-C(=O)-C	111.6	112.1	113.6	112.5
C-C=O	125.3	124.5	123.9	124.1
O-CH ₂ -CH ₂	111.1	108.7	103.6	103.8
C-C-C (phenyl)	119.9	120.0	120.0	120.0
Torsion angle				
O-CH ₂ -CH ₂ -O	±21.2	58.6	66.6	±84.8 ^b
		58.6	80.7	±90.9 ^b
		62.5	-56.4	
CH ₂ -CH ₂ -O-C(=O)	±66.6 ±66.5	89.5	-110.8	±170.8
		148.2	121.7	±169.2
		164.3	137.4	
			156.7	
CH ₂ -O-C(=O)-C	±167.5 ±163.2		150.2	
			-104.4	
		-172.5	-169.2	±176.7
		-177.4	165.8	±178.3
		176.4	171.1	
			153.1	
O-C(=O)-C-CH	±1.8 ±3.8		149.9	
			176.1	
		3.1	-11.2	±14.1
		-20.1	5.1	±5.8
		-0.8	-2.6	
			-17.9	
			-7.3	
	-11.0			

* Poly(butylene terephthalate). ^b O-CH₂-CH₂-CH₂.

toward the benzene rings.

The bond lengths, bond angles, and torsion angles of cyclic oligo(alkylene terephthalate)s are compared in Table V. The conformation of the ethylene glycol moieties are specific in the PET dimer. Thus, the torsion angles of the $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$ are $\pm 21.2^\circ$; whereas, 58.6° , 62.5° , and 58.6° are for Type A of the cyclic trimer of PET⁸ and 66.6° , 80.7° , and -56.4° are for Type B⁹ instead of the *cis* conformation in the dimer, which is *gauche* in the trimer. Those of the $\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})$ are close to *gauche* ($\pm 66.6^\circ$ and $\pm 66.5^\circ$); whereas, they are

Figure 2. Crystal structure viewed along the *a*-axis.

Figure 3. Crystal structure viewed along the *b*-axis.

trans ($\pm 170.8^\circ$ and $\pm 169.2^\circ$) in the cyclic dimer of PBT,¹² and yield a variety of values for both types of cyclic trimer of PET.^{8,9} The molecular structure of the ethylene glycol part of the dimer is significantly different from that of the trimer not only in torsion angles but also in bond lengths and angles (see Table V). The CH_2-CH_2 bond length is $1.542 \text{ \AA}$ which is significantly longer compared to that of other cyclic oligoesters^{8,9} and the linear dimer of PET.¹⁴ Such extraordinarily long bonds are often observed in highly strained compounds. The bridging CH_2-CH_2 bond in [2,2]paracyclophane increases significantly to $1.59 \text{ \AA}$ due to mutual repulsion between the two benzene rings.¹³ The $\text{O}-\text{CH}_2$ bonds are also somewhat longer and the $\text{O}-\text{CH}_2-\text{CH}_2$ bond angles are larger in this dimer than others. This might be to reduce the steric hindrance in the ethylene glycol component. Despite almost having a *cis* conformation, the distance between the oxygen atoms of $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$ is $2.638 \text{ \AA}$, while it is 2.668 to $2.784 \text{ \AA}$ in the cyclic trimer.^{8,9} For

Figure 4. Crystal structure viewed along the *c*-axis.

the bond lengths and angles of other components there is not a marked difference among these cyclic oligomers.

The molecular packings viewed along the three crystal axes are shown in Figures 2 to 4, respectively. The molecules are packed approximately parallel to the (101) plane. The shortest intermolecular contacts are $C2(I) \cdots O4(II) = 3.167(7) \text{ \AA}$ for $C \cdots O$ and $C5(I) \cdots C8(III) = 3.345(7) \text{ \AA}$ for $C \cdots C$.

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Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters for the non-hydrogen atoms, and fractional atomic coordinates and equivalent isotropic thermal parameters for the hydrogen atoms. On request, these materials are available from authors or editorial office of The Society of the Polymer Science, Japan.

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