

## Crystal Structure of Cyclic Dimer of Poly(butylene terephthalate)\*

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**ABSTRACT:** The crystal structure of a cyclic dimer from poly(butylene terephthalate) was determined. The dimer crystallized in a monoclinic space group  $P2_1/c$ , with  $a=11.006(1)$ ,  $b=11.926(1)$ ,  $c=8.489(1)$  Å and  $\beta=95.742(6)^\circ$ ;  $D_c=1.320$ ,  $D_m=1.31$  Mg m $^{-3}$ ,  $Z=2$ . The final  $R$  was 0.052 for 1778 observed data ( $F_o \geq 2\sigma(F_o)$ ). The molecule has crystallographically imposed  $\bar{1}$  molecular symmetry, so that the two bridging tetramethylene chains are oriented *anti* to each other and the aromatic moieties constitute necessarily a pair of parallel rings. Each benzene ring is bent to a small extent into a boat shape with its bow and stern displaced inward toward the other ring, attesting to the presence of intramolecular steric strain. The tetramethylene carbon chain exhibits abnormal torsional angles far from  $60^\circ$  (*gauche*) or  $180^\circ$  (*trans*), the independent torsion angles being  $84.8^\circ$ ,  $-152.6^\circ$ , and  $-90.9^\circ$ , respectively. A significant shortening of the  $C_{sp^3}-C_{sp^3}$  bonds of the tetramethylene part is observed in the molecule as generally found in the *n*-methylene dibenzoate derivatives.

**KEY WORDS** Crystal Structure / Poly(butylene terephthalate) Cyclic Oligomer /

The informations gained by X-ray diffraction on oligomers are of great importance because they provide an insight into not only the conformational aspects of both low-molecular weight analogues and the related high polymers but also the relationships between molecular structure and physical and mechanical properties of related polymers. In particular, poly(butylene terephthalate) is well known to have two conformational modifications which change reversibly on mechanical stress and relaxation but the structural models which have been proposed have some discrepancies among the geometries.<sup>1-4</sup> A comparison between the structures of the polymer already published was also examined in detail.<sup>5-8</sup>

In order to obtain more accurate geometrical information around the glycol part the crystal structure of the title compound has been

undertaken. The present work constitutes a sequel of our previous report on the crystal structure of dimethyl 4,4'-[ethylene bis(oxy-carbonyl)] dibenzoate as a model compound for poly(ethylene terephthalate).<sup>9</sup>

### EXPERIMENTAL

#### *Materials and Method*

The samples of the cyclic dimer were extracted from a piece of poly(butylene terephthalate) "Toray PBT-1100" powder with chloroform and isolated by preparative liquid chromatography over silica gel using chloroform as eluent with the yield of about 1 wt% of polymers. Recrystallization was followed first from chloroform and then from dimethylformamide as colorless plates elongated in the *b* direction.

The unit-cell parameters were refined by

\* 1,6,13,18-Tetraoxadibenzo[abc, mno]cyclotetracosane-7,12,19,24-tetrone.

**Table I.** Crystal data

Chemical formula	C <sub>24</sub> H <sub>24</sub> O <sub>8</sub>
Molecular weight	440.06
Space group	P2 <sub>1</sub> /c
Cell constants	$a = 11.006(1) \text{ \AA}$ $b = 11.926(1)$ $c = 8.489(1)$ $\beta = 95.742(6)^\circ$
Volume of the unit cell	$V = 1108.69 \text{ \AA}^3$
Density	
Calcd.	1.320 Mg m <sup>-3</sup>
Obsd.	1.31 Mg m <sup>-3</sup>
Number of molecules in the unit cell	Z = 2

least-squares fit of 20 reflections measured on a diffractometer. The density was measured by flotation in a carbon tetrachloride-hexane mixture. A crystal with dimensions of  $0.2 \times 0.35 \times 0.3 \text{ mm}^3$  was used for the data collection. The crystal data are summarized in Table I.

#### Data Collection

The measurement was made on a Rigaku automatic four-circle diffractometer up to an angle of  $2\theta = 125^\circ$  with graphite monochromated CuK $\alpha$  radiation, using the  $2\theta$ - $\omega$  scan technique and scan range of  $(1.50 + 0.142 \tan \theta)^\circ$  in  $\omega$ . The scan speed and the background counting time were  $10^\circ/\text{min}$  and 2 s at each terminus of the scans for  $0^\circ < 2\theta \leq 100^\circ$ ,  $5^\circ/\text{min}$  and 4 s for  $100^\circ < 2\theta \leq 110^\circ$ , and  $3^\circ/\text{min}$ , 8 s for  $110^\circ < 2\theta \leq 125^\circ$ . Three standard reflections ((204), (600), and (062)) were measured every 100 measurements with no significant deterioration in intensity. Lorentz and polarization correction were applied, but not that for absorption. Out of 2001 reflections collected, 1778 with  $F_o > 2\sigma(F_o)$  were used in the refinement of the structure.

#### Structure Determination

The structure was directly solved with MULTAN 78 program<sup>10</sup> which located all the non-hydrogen atoms. The hydrogen atoms were located by difference Fourier synthesis.

**Table II.** Atomic parameters and temperature factors for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Beq/ $\text{\AA}^2$
O(1)	0.8217(3)	0.0779(3)	0.3627(4)	7.8
O(2)	0.8949(4)	0.2513(4)	0.3752(6)	11.6
O(3)	0.3212(3)	0.2230(3)	0.7282(4)	7.9
O(4)	0.3628(4)	0.4058(3)	0.7158(5)	11.4
C(1)	0.8178(4)	0.1846(5)	0.4016(6)	7.5
C(2)	0.7075(4)	0.2139(4)	0.4798(5)	6.1
C(3)	0.6337(4)	0.1313(3)	0.5376(6)	6.0
C(4)	0.5317(4)	0.1613(3)	0.6071(5)	6.1
C(5)	0.5010(4)	0.2737(3)	0.6212(5)	6.3
C(6)	0.5763(5)	0.3550(4)	0.5649(6)	8.0
C(7)	0.6763(5)	0.3257(4)	0.4965(6)	7.9
C(8)	0.3901(5)	0.3099(4)	0.6940(6)	7.5
C(9)	0.2094(7)	0.2480(6)	0.7951(9)	12.0
C(10)	0.1655(6)	0.1350(8)	0.8502(8)	13.5
C(11)	0.9231(6)	0.0459(7)	0.2788(9)	12.5
C(12)	0.9153(6)	-0.0811(9)	0.2755(7)	13.5

Beq is the equivalent isotropic temperature factor calculated from the anisotropic temperature coefficients.<sup>13</sup>

**Table III.** Atomic positional parameters and isotropic temperature factors for hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Biso/ $\text{\AA}^2$
H(C3)	0.658(4)	0.049(3)	0.530(5)	5.4
H(C4)	0.481(4)	0.105(3)	0.651(5)	5.0
H(C6)	0.551(4)	0.439(4)	0.571(5)	6.1
H(C7)	0.726(4)	0.381(4)	0.456(5)	7.5
H1(C9)	0.149(5)	0.292(5)	0.733(6)	9.9
H2(C9)	0.230(5)	0.296(5)	0.906(7)	10.4
H1(C10)	0.105(4)	0.134(4)	0.943(5)	13.0
H2(C10)	0.232(4)	0.068(3)	0.871(5)	13.0
H1(C11)	0.974(6)	0.049(5)	0.352(7)	12.7
H2(C11)	0.924(5)	0.091(5)	0.179(6)	10.8
H1(C12)	0.874(5)	-0.123(5)	0.370(7)	13.5
H2(C12)	0.995(6)	-0.128(5)	0.249(7)	13.5

The structure was refined first by block-diagonal and then by full-matrix least-squares refinement anisotropically with non-hydrogen atoms and isotropically with hydrogen atoms. In the refinement, the function minimized was  $\sum \omega (|F_o| - |F_c|)^2$  with  $\omega = [\sigma^2(F_o) + a|F_o| + b|F_o|^2]^{-1}$  for  $F_o \neq 0$  and  $\omega = c$  for  $F_o = 0$ , where  $\sigma(F_o)$  is the standard deviations based on counting statistics. Final refinement ( $a =$

0.03956,  $b=0.00022$  and  $c=0.00123$ ) gave  $R=0.052$  and  $\omega R=0.073$ . No significant peaks were observed in the final difference map. The large thermal ellipsoids associated to the carbon atoms of tetramethylene moieties were indicative of conformational disorder. The atomic scattering factors were taken from *International Tables for X-ray Crystallography*.<sup>11</sup> All calculations were performed with the UNICS programs<sup>12</sup> on a FACOM M-200 computer. The positional parameters and the isotropic thermal factors for the non-hydrogen atoms and those for the hydrogen atoms are listed in Tables II and III, respectively.\*

## RESULTS AND DISCUSSION

An ORTEP<sup>14</sup> stereo drawing of the molecule with atom labeling is shown in Figure 1. Bond distances, bond angles and selected torsion angles are displayed in Table IV and the displacements of atoms from the benzene ring mean plane in Table V. All the geometries have not been corrected for thermal vibration of atoms.

Cyclic dimer of poly(butylene terephthalate) has crystallographically imposed  $\bar{1}$  molecular symmetry, so that the two bridging tetramethylene chains are oriented *anti* to each other

**Table IV.** Bond lengths (Å), angles (°) and selected torsion angles (°) with e.s.d.'s in parentheses<sup>a</sup>

Bond lengths (Å)			
O(1)–C(1)	1.316(6)	O(3)–C(8)	1.333(6)
O(1)–C(11)	1.434(9)	O(3)–C(9)	1.437(8)
O(2)–C(1)	1.201(7)	O(4)–C(8)	1.202(7)
C(1)–C(2)	1.483(7)	C(5)–C(8)	1.486(7)
C(2)–C(3)	1.396(6)	C(3)–C(4)	1.367(7)
C(4)–C(5)	1.391(7)	C(5)–C(6)	1.391(8)
C(6)–C(7)	1.341(8)	C(7)–C(2)	1.388(7)
C(9)–C(10)	1.521(8)	C(11)–C(12)	1.517(8)
C(10)–C(12')	1.468(8)		
Bond angles (°)			
O(1)–C(1)–O(2)	123.5(5)	O(3)–C(8)–O(4)	123.3(5)
O(1)–C(1)–C(2)	112.9(4)	O(3)–C(8)–C(5)	112.0(4)
O(2)–C(1)–C(2)	123.5(5)	O(4)–C(8)–C(5)	124.6(5)
C(1)–C(2)–C(3)	121.5(4)	C(8)–C(5)–C(6)	118.9(5)
C(1)–C(2)–C(7)	119.6(4)	C(8)–C(5)–C(4)	122.2(4)
C(2)–C(3)–C(4)	119.9(4)	C(5)–C(6)–C(7)	120.7(5)
C(3)–C(4)–C(5)	120.4(4)	C(6)–C(7)–C(2)	121.1(5)
C(4)–C(5)–C(6)	119.0(5)	C(7)–C(2)–C(3)	118.9(4)
C(1)–O(1)–C(11)	115.4(5)	C(8)–O(3)–C(9)	117.0(5)
O(1)–C(11)–C(12)	103.2(7)	O(3)–C(9)–C(2)	104.4(6)
C(11)–C(12)–C(10')	118.7(9)	C(9)–C(10)–C(12')	110.6(8)
Torsion angles (°)			
C(2)–C(1)–O(1)–C(11)	176.7(5)	C(5)–C(8)–O(3)–C(9)	–178.3(4)
C(1)–O(1)–C(11)–C(12)	170.8(5)	C(8)–O(3)–C(9)–C(10)	–169.2(5)
O(1)–C(11)–C(12)–C(10')	84.8(10)	O(3)–C(9)–C(10)–C(12')	–90.9(8)
C(11)–C(12)–C(10')–C(9')	–152.6(7)	C(4)–C(5)–C(8)–O(3)	–5.8(9)
C(3)–C(2)–C(1)–O(1)	14.1(7)	C(6)–C(5)–C(8)–O(4)	–4.0(9)
C(7)–C(2)–C(1)–O(2)	13.4(8)		

<sup>a</sup> Primed atoms are related to the corresponding unprimed ones by inversion through the molecular center.

\* The anisotropic thermal parameters of the non-hydrogen atoms and a list of the observed and calculated structure factors will be provided by the authors upon request.

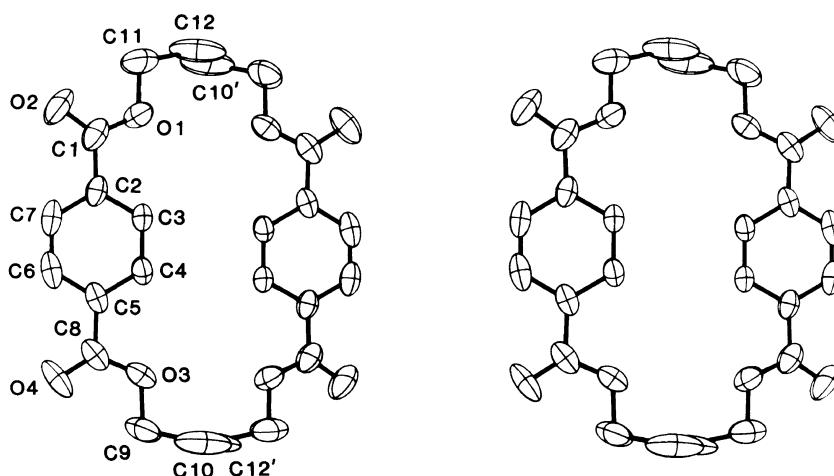


Figure 1. An ORTEP stereo drawing of the molecule with atom labeling. The thermal ellipsoids are drawn at 50% probability level.

Table V. Least-squares best plane and displacement of the atoms from the plane<sup>a</sup>

C(1)	-0.024(7) Å	C(2) <sup>a</sup>	-0.005(7) Å
C(3) <sup>a</sup>	0.004(7)	C(4) <sup>a</sup>	0.001(7) Å
C(5) <sup>a</sup>	-0.005(7)	C(6) <sup>a</sup>	0.004(8)
C(7) <sup>a</sup>	0.004(8)	C(8)	-0.025(7)
C(9)	-0.233(8)	C(10)	-0.107(9)
C(11)	-0.431(8)	C(12)	-0.546(9)
C(10')	-1.869(9)	C(12')	-1.430(9)
O(1)	-0.326(7)	O(2)	0.201(7)
O(3)	-0.162(7)	O(4)	0.033(7)

<sup>a</sup> Atoms included in the calculation of the plane.

and the aromatic moieties constitute necessarily a pair of parallel rings. As shown in Tables IV and V, it may be featured that the molecule is composed of two approximate planes connected by tetramethylene carbon chains; terephthalic acid moiety and carbon atoms of each half of tetramethylene chain are approximately coplaner, but the displacements of the atoms are significant. Each benzene ring is bent to a small extent into a boat shape with its bow and stern [(C(2) and C(5)] displaced inward toward the other ring, attesting to the presence of intramolecular steric strain in the system. Interestingly C(1), C(8), O(1), and O(3) atoms in the carboxylic acid moieties and

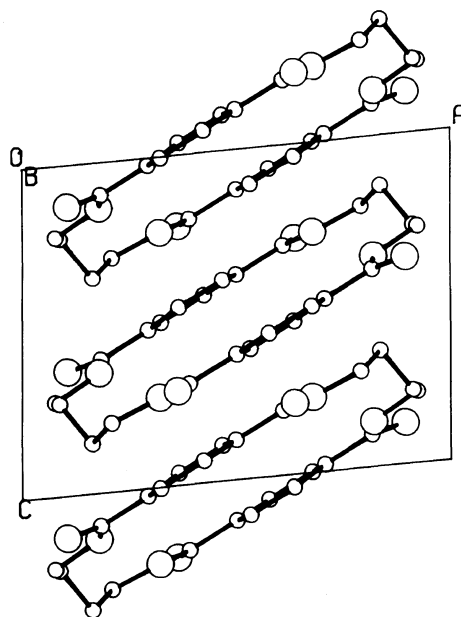


Figure 2. Crystal structure viewed along the *b*-axis.

C(9), C(10), C(11), and C(12) atoms in the tetramethylene carbon lie on one side of the mean plane defined by benzene ring. On the contrary two carbonyl oxygen atoms, O(2) and O(4), which take the *syn* conformation to the benzene ring with each other are displaced outward by 0.201 Å and 0.030 Å, respectively.

The molecular conformations are specified by the torsion angles given in Table IV. The tetramethylene chains exhibit abnormal torsional angles far from  $60^\circ$  (*gauche*) or  $180^\circ$  (*trans*), the independent torsion angles being  $84.8^\circ$ ,  $-152.6^\circ$ , and  $-90.9^\circ$ , respectively. These anomalous features probably explain a great deal of disorder as described before.

Phenyl ring shows normal geometries,  $1.379 \text{ \AA}$  and  $120.0^\circ$  for the mean  $C_{sp2}-C_{sp2}$  bond distance and the mean internal angle for the ring, respectively. The distance is rather short as compared with the value indicated by Sutton [ $1.395(5) \text{ \AA}$ ]<sup>15</sup> but is the same as the value shown by Brisse and Sygusch [ $1.379 \text{ \AA}$ ].<sup>16</sup> The geometry of the carboxylic parts of the molecule compares very well with those of compounds that have already been observed in a wide variety of similar derivatives.<sup>9,17-20</sup> The  $C_{sp3}-C_{sp3}$  bond distances of the tetramethylene part are  $1.517 \text{ \AA}$ ,  $1.468 \text{ \AA}$ , and  $1.521 \text{ \AA}$ , respectively. These sig-

nificant shortening of the distances from the expected value of  $1.537(5) \text{ \AA}$ <sup>15</sup> have been systematically noted for a variety of analogous derivatives:  $1.448 \text{ \AA}$ ,  $1.521 \text{ \AA}$ , and  $1.462 \text{ \AA}$  in 1,4-butanediyl dibenzoate,<sup>21</sup>  $1.521 \text{ \AA}$  and  $1.493 \text{ \AA}$  in 1,4-butanediyl bis(*o*-chlorobenzoate),<sup>22</sup>  $1.523 \text{ \AA}$ ,  $1.512 \text{ \AA}$ , and  $1.483 \text{ \AA}$  in 2,5-hexanediyl dibenzoate,<sup>23</sup>  $1.505 \text{ \AA}$ ,  $1.528 \text{ \AA}$ , and  $1.512 \text{ \AA}$  in 2,5-hexanediyl bis(*p*-chlorobenzoate)<sup>24</sup> and  $1.480 \text{ \AA}$  in trimethylene glycol dibenzoate.<sup>20</sup>

The crystal structure viewed along the *b* and *c* axes are shown in Figures 2 and 3, respectively. The molecules are packed approximately parallel to (403) with phenyl rings being stacked side by side. The shortest intermolecular approaches are as follows:  $O(2) [x, y, z]-C(12)[2-x, 1/2+y, 1/2-z] = 3.245(7) \text{ \AA}$  and  $O(2)[x, y, z]-C(10)[1+x, 1/2-y, 1/2+z] = 3.289(7) \text{ \AA}$ .

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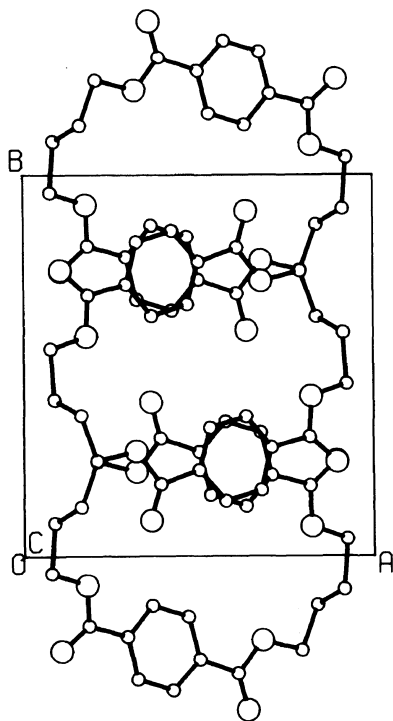


Figure 3. Crystal structure viewed along the *c*-axis.

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