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1,6,11,16-Tetraoxacycloeicosane-2,5,12,15-tetraone

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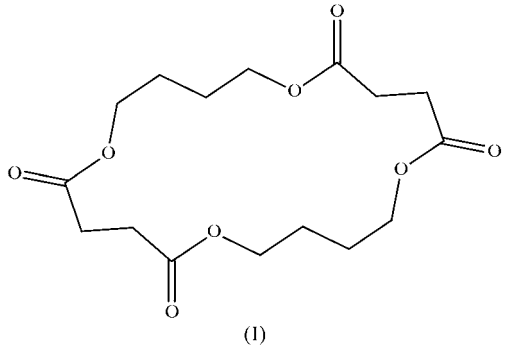
The 20-membered ring of the title compound, $C_{16}H_{24}O_8$, adopts an approximately flat rectangular structure with three- and seven-bond sides and lies across a crystallographic center of inversion. The corners of the ring occur at both ends of one of the planar ester segments. All of the carbonyl O atoms are involved in intermolecular C—H···O hydrogen bonds.

Comment

The products of step-growth polymerization of bifunctional monomers generally contain a small cyclic oligomer fraction. The title compound, (I), is one such cyclic oligomer, which was obtained during polyester condensation polymerization of butane-1,4-diol and succinic acid. The cyclic butylene succinate oligomers were also obtained by lipase-catalyzed degradable transformation of poly(butylene succinate), which



(I)

is a typical biodegradable synthetic polymer (Okajima *et al.*, 2003). In addition, it was found that the produced cyclic oligomers can be repolymerized readily by lipase into a high molecular weight polyester. From the viewpoint of sustainable chemical recycling of polymer materials, it has been recognized in recent years that cyclic oligomers of polyesters are useful starting compounds for repolymerization (Okajima *et al.*, 2003; Takahashi *et al.*, 2004; Osanai *et al.*, 2004; Kaihara *et al.*, 2005). In order to obtain the basic structural features of the cyclic oligomer of poly(butylene succinate), the structure of the title compound has been determined.

The molecule of (I) lies across a crystallographic center of inversion so that the asymmetric unit contains one-half of the molecule (Fig. 1). The 20-membered rings exist in a nearly flat rectangular shape and the shortest transannular contact, O1···C3 at $(1-x, 1-y, 1-z)$, is 4.063 (1) Å. According to Dale's (1973) nomenclature, this ring conformation is called a [3737] form (Table 1), where the numbers in brackets indicate the number of bonds along each edge of the ring. The planar ester segment C7—C8—O2—C1^{i} [symmetry code: (i) $1-x$, $1-y$, $1-z$] provides the three-bond edge of the ring. On the other hand, the seven-bond edge is composed of butylene (C1—C2—C3—C4), ester (C4—O1—C5—C6) and ethylene (C6—C7) segments. Similar ring conformations have been observed in the crystal structures of related 20-membered rings, such as 1,4,11,14-tetraoxacycloeicosane-5,10,15,20-tetraone (Shanzer *et al.*, 1981) and 1,11-dioxacycloeicosane-2,4,12,14-tetraone (Chen *et al.*, 1993). The tight hairpin turn composed of the three-bond planar ester segment with *gauche* conformations at both ends of the ester segment occurs in each of these three 20-membered rings. In addition, such a hairpin structure is commonly observed in other macrocyclic ring compounds that possess ester segments, *e.g.* Cambridge Structural Database (Version 5.26; Allen, 2002) refcodes BEDNAZ, BEDNIH (Shanzer *et al.*, 1981), DILVID (Malinovskii *et al.*, 1985), MAJYAX (Ruddick *et al.*, 1999) and ZORKUM (Zaidi et al., 1995). This conformational feature may be related to the reactivity of macrocyclic monomer compounds and the biodegradability of chain-folded lamellar crystals of polyesters.

The macrocyclic rings of (I) are slightly tilted with respect to the *ac* plane and are stacked along the *b* axis (Fig. 2). The

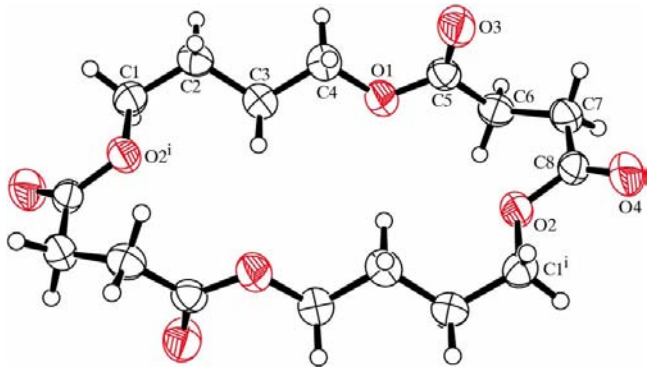


Figure 1
The molecular structure of (I), showing the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x+1$, $-y+1$, $-z+1$.]

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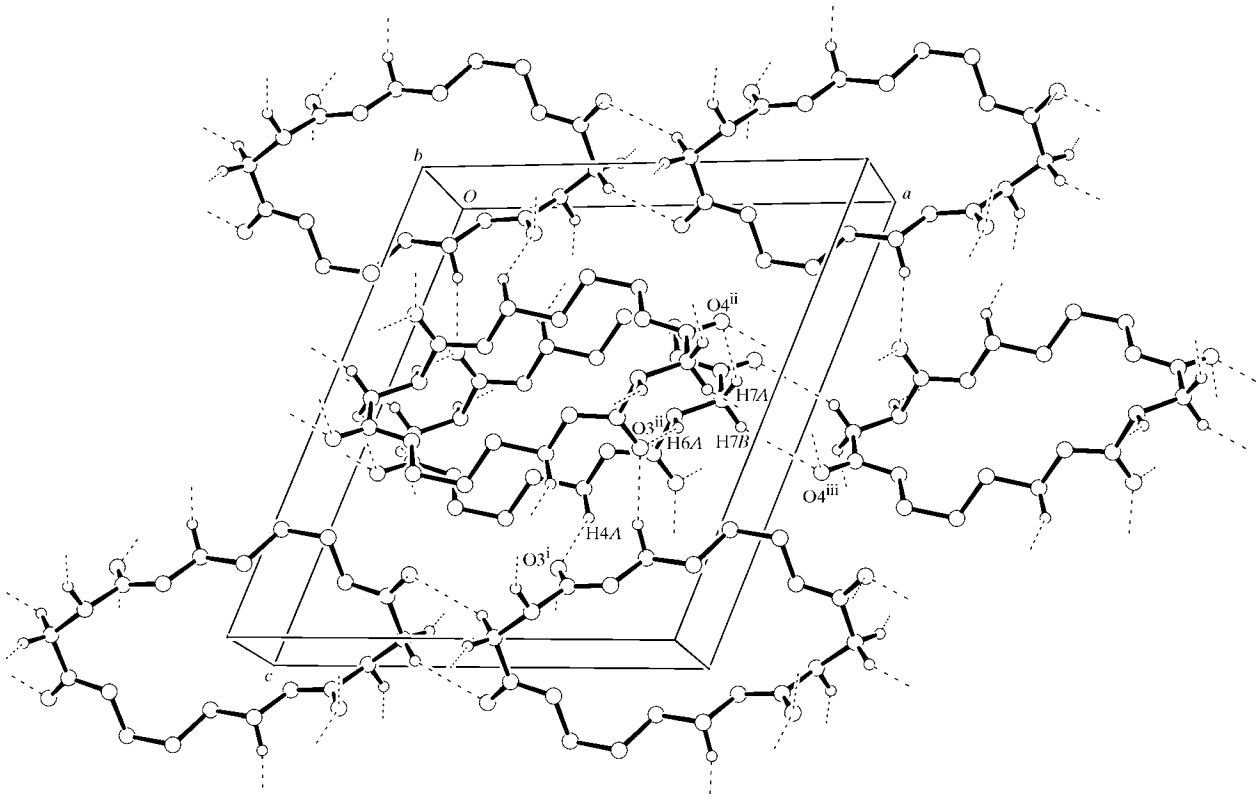

Figure 2
The molecular packing of (I). Broken lines indicate the C—H···O hydrogen-bonding interactions. [Symmetry codes: (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y+1, z$; (iv) $-x+2, -y+1, -z+1$.]

angle between the normal of the least-squares plane of the 20-membered ring and the *b* axis is 26.06 (1)°. The crystal packing involves four weak intermolecular C—H···O(carbonyl) hydrogen bonds (Table 2). The C6—H6*A*···O3(x, 1 + y, z), C7—H7*A*···O4(x, 1 + y, z) and C4—H4*A*···O3($\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) hydrogen bonds connect the molecules parallel to the *b* axis. The H···O distance of the fourth hydrogen bond, C7—H7*B*···O4(2 − x, 1 − y, 1 − z), is slightly longer than that of Jeffrey's (1997) criterion, but is not much longer than the longest of the other three H···O contacts shown in Table 2. Thus, the fourth intermolecular C—H···O interaction is somewhat weaker than the others. The cyclic molecules are linked parallel to the *a* axis by this hydrogen bond.

Experimental

The title compound, (I), was extracted with methanol from as-polymerized samples of poly(butylene succinate). Gel-permiation chromatography revealed that the methanol extract contains the cyclic butylene succinate dimer (74%) and other oligomers (26%). Final purification was achieved by recrystallization from aqueous solution. This recrystallization was repeated twice. Crystals of (I) for X-ray measurements were grown by slow evaporation of an acetone solution at room temperature (m.p. 391.5 K). ^{1}H NMR ($CDCl_3$): δ 4.12 (*m*, 4H), 2.64 (*s*, 4H), 1.71 (*m*, 4H); ^{13}C NMR ($CDCl_3$): δ 171.9, 64.3, 29.5, 25.3; HRMS (FAB) calculated for $C_{16}H_{25}O_8$ $[M+H]^+$ 345.1549, found 345.1561.

Crystal data

$C_{16}H_{24}O_8$
M_r = 344.35
Monoclinic, $P2_1/n$
a = 13.1756 (12) Å
b = 4.7279 (5) Å
c = 14.8400 (14) Å
β = 109.927 (6)°
V = 869.08 (15) Å^3
Z = 2
D_x = 1.316 Mg m^{-3}
Cu $K\alpha$ radiation
μ = 0.89 mm^{-1}
T = 296.1 K
Platelet, colorless
0.52 × 0.24 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.700, T_{max} = 0.914
14440 measured reflections
1589 independent reflections
1508 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 68.2°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.088
S = 1.04
1589 reflections
110 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.1553P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0310 (15)

All H atoms were found in difference maps and were subsequently treated as riding atoms, with C—H distances of 0.97 Å and U_{iso}(H) values of 1.2U_{eq}(C).

Table 1
Selected torsion angles (°).

O2^{i}—C1—C2—C3	67.06 (14)	O1—C5—C6—C7	−147.32 (10)
C1—C2—C3—C4	−173.80 (11)	C5—C6—C7—C8	72.38 (13)
C2—C3—C4—O1	−168.37 (10)	C6—C7—C8—O2	11.03 (14)
C3—C4—O1—C5	−174.91 (10)	C7—C8—O2—C1^{i}	174.47 (9)
C4—O1—C5—C6	−174.57 (9)	C8—O2—C1^{i}—C2^{i}	−179.73 (9)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4A···O3^{ii}	0.97	2.58	3.3957 (17)	142
C6—H6A···O3^{iii}	0.97	2.49	3.3583 (17)	148
C7—H7A···O4^{iii}	0.97	2.60	3.4252 (17)	144
C7—H7B···O4^{iv}	0.97	2.66	3.5308 (16)	149

Symmetry codes: (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y+1, z$; (iv) $-x+2, -y+1, -z+1$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3015). Services for accessing these data are described at the back of the journal.

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