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Structure of Dimethyl 4,4′-[Ethylenebis(oxycarbonyl)]dibenzoate: a Model for Poly(ethylene terephthalate)

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Abstract. $C_{20}H_{18}O_8$, $M_r = 386{\cdot}36$, monoclinic, $C2/c$, $a = 29{\cdot}612\,(1)$, $b = 3{\cdot}945\,(2)$, $c = 20{\cdot}645\,(1)$ Å, $\beta = 132{\cdot}148\,(2)°$, $V = 1788{\cdot}1\,(7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}435$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}903$ mm^{-1}, $F(000) = 808$, $T = 296$ K, final $R = 0{\cdot}046$ for 1570 independent reflections. The molecule has an inversion center on the central CH_2—CH_2 bond. The deviation from planarity of the molecule is mainly due to a rotation around the methylene—O bonds, the torsion angle C(1′)—C(1)—O(1)—C(2) being 161·9 (7)°. The CH_2—CH_2 bond [1·51 (1) Å] is short and the C(1′)—C(1)—O(1) angle [104·2 (6)°] is small; this is related to the torsion around the methylene—O bond. The planes of the inner and outer carboxylic groups are at angles of 8·4 and 0·6° to the phenyl rings. The distance between the centers of two aromatic rings (10·73 Å) is equal to the repeat distance of poly(ethylene terephthalate).

Introduction. Geometrical information based on crystallographic approaches of oligomers has been extensively accumulated for understanding the conformation and the relationships between molecular structure and the physical and mechanical properties of related polymers. In particular, because of their industrial importance the structures of polyester derivatives have been extensively investigated on the basis of those of related monomers (Pérez & Brisse, 1975, 1976*a*,*b*, 1977; Bocelli & Grenier-Loustalot, 1982*a*,*b*, 1983*a*,*b*, 1984).

The title compound is the smallest model compound of poly(ethylene terephthalate) (Daubeny, Bunn & Brown, 1954; Tomashpol'skii & Markova, 1964; Arnott & Wonacott, 1966) which shows considerable deviation from the planar conformation in the glycol part of the chain as was mentioned by Pérez & Brisse (1976*a*) in the study of ethylene glycol dibenzoate. We have determined the crystal structure of the title compound to obtain more accurate geometrical information about the glycol part of the chain.

Experimental. The compound was prepared by the reaction of terephthalic acid monomethyl ester chloride and ethylene glycol in the presence of *N*-methylpyrrolidone. Crystals from methanol–acetone solution by slow evaporation at room temperature as colorless needles. Rigaku AFC5R automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation with a 12 kW rotating-anode generator; crystal size 0·20 × 0·03 × 0·03 mm. Unit-cell dimensions obtained from a least-squares refinement of 24 reflections in the range $41 < 2\theta < 69°$. 2θ–ω scan, scan range $\Delta\omega = (1{\cdot}15 + 0{\cdot}30\tan\theta)°$ up to $2\theta = 120{\cdot}2°$, scan rate 16·0° min^{-1} in ω. $0 \le h \le 32$, $0 \le k \le 4$, $-22 \le l \le 16$. Weak reflections [$I < 10\sigma(I)$] rescanned (max. of two scans) and the counts accumulated to ensure good counting statistics, background counts on each side of reflections, the ratio of peak counting time to background counting time 2:1.

Three monitor reflections measured after every 150 reflections, no significant change in intensities. 1609 reflections measured, 1570 unique with $I > 3\sigma(I)$ regarded as observed, $R_{\mathrm{int}} = 0{\cdot}037$. Corrections for Lorentz–polarization, secondary extinction (coefficient: $0{\cdot}92 \times 10^{-6}$), but not for absorption. The structure was solved by direct methods (*MITHRIL*; Gilmore, 1983) in space group $C2$. As the molecule could be shown to have an inversion center on the C(1)—C(1′) bond, the center of the molecule was located at (1/4, 1/4, 0) in the standard setting of $C2/c$. Full-matrix least-squares anisotropic procedure for non-H atoms. H atoms included in the structure-factor calculation in idealized positions ($d_{\mathrm{C—H}} = 0{\cdot}95$ Å), with B 20% larger than the B_{eq} of the bonded atoms.

Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o^2)$ is the standard deviation based on counting statistics. Final refinement gave $R = 0{\cdot}046$, $wR = 0{\cdot}057$, $S = 1{\cdot}22$. $\Delta/\sigma = 0{\cdot}00$, $\Delta\rho_{\max} = 0{\cdot}18$, $\Delta\rho_{\min} = -0{\cdot}22$ e Å^{-3}. Neutral-atom scattering factors and $\Delta f'$, $\Delta f''$ from *International Tables for X-ray Crystallography* (1974, Vol. IV). Most of the

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calculations were performed with the VAX-based programs of the MSC structure analysis package, *TEXRAY* (Molecular Structure Corporation, 1985).

Discussion. Since there are four molecules per unit cell, the center of the CH_2—CH_2 bond of the molecule has to be on a crystallographic center of symmetry. An *ORTEP* drawing (Johnson, 1974) of a complete molecule with the numbering scheme is shown in Fig. 1. The positional parameters and equivalent isotropic thermal parameters are listed in Table 1* and bond lengths, angles and selected torsion angles are presented in Table 2.

The most interesting structural feature of the molecule is the geometry around the central ethylenic part where the CH_2—CH_2 bond length is 1·51 (1) Å. This significant shortening of the C(sp^3)—C(sp^3) distance from the expected value of 1·537 (5) Å (Sutton, 1965), was systematically found in other analogous derivatives: 1·499 Å in ethylene glycol dibenzoate (Pérez & Brisse, 1976*a*), 1·493 Å in ethylene glycol di(*p*-chlorobenzoate) (Pérez & Brisse, 1975), 1·480 Å in trimethylene glycol dibenzoate (Pérez & Brisse, 1977), 1·504 Å in trimethylene glycol di(*p*-chlorobenzoate) (Pérez & Brisse, 1976*b*), 1·448 Å and 1·462 Å in 1,4-butanediyl dibenzoate (Bocelli & Grenier-Loustalot, 1982*a*) and 1·505 Å in diphenyl succinate (Brisse, Molhant & Pérez, 1979).

The bond angle, C(1′)—C(1)—O(1), 104·2 (6)°, is much narrower than expected in relation to the torsion around the methylene C(1)—O(1) bond. Similar narrowings of the —CH_2—CH_2—O— bond angle, which were generally accompanied by ethylenic bond shortening, were observed in those analogous derivatives.

The deviation from planarity of the molecule is mainly due to a rotation around the methylene—O(1) bonds, and the torsion angle C(1′)—C(1)—O(1)—C(2) is 161·9 (7)°. This departure from a *trans* conformation is larger than that of ethylene glycol dibenzoate in which the corresponding torsion angle is 172·8° (Pérez & Brisse, 1976*a*). The C(2) atom deviates significantly (by 0·07 Å) from the phenyl-ring plane to the same side as the ethylene group. The perpendicular distance between the two phenyl-ring planes is 1·38 Å. The bond lengths and angles of the two carboxylic groups are similar to those of dimethyl terephthalate (Brisse & Pérez, 1976) and a number of analogous derivatives. However, the dihedral angles between the carboxylic

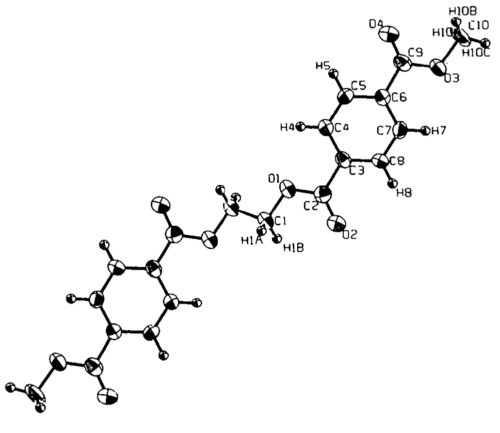

Fig. 1. Molecular structure and atomic numbering. Thermal ellipsoids are drawn at the 50% probability level, H atoms given arbitrary thermal parameters for clarity.

Table 1. *Atomic positional and thermal parameters with their e.s.d.'s in parentheses*

B_{eq} is the equivalent isotropic temperature factor calculated from the anisotropic temperature coefficients (Hamilton, 1959).

	x	*y*	*z*	B_{eq}(Å^2)
O(1)	0·2037 (2)	0·451 (1)	0·0151 (3)	4·0 (2)
O(2)	0·1038 (2)	0·357 (2)	−0·0952 (3)	5·1 (2)
O(3)	0·0582 (2)	1·001 (1)	0·1701 (3)	4·2 (2)
O(4)	0·1553 (2)	1·158 (2)	0·2715 (3)	5·4 (3)
C(1)	0·2164 (3)	0·290 (2)	−0·0338 (4)	3·8 (3)
C(2)	0·1453 (3)	0·464 (2)	−0·0228 (5)	3·3 (3)
C(3)	0·1371 (3)	0·622 (2)	0·0339 (4)	2·8 (3)
C(4)	0·1856 (3)	0·766 (2)	0·1129 (4)	3·4 (3)
C(5)	0·1776 (3)	0·894 (2)	0·1667 (4)	3·1 (3)
C(6)	0·1206 (3)	0·887 (2)	0·1412 (4)	2·6 (3)
C(7)	0·0724 (3)	0·743 (2)	0·0619 (4)	3·1 (3)
C(8)	0·0801 (3)	0·612 (2)	0·0081 (4)	3·4 (3)
C(9)	0·1149 (3)	1·029 (2)	0·2024 (5)	3·5 (3)
C(10)	0·0464 (3)	1·130 (3)	0·2235 (5)	5·7 (4)

Table 2. *Bond lengths* (Å), *angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

A prime denotes an atom at $\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$.

O(1)—C(2)	1·337 (8)	C(3)—C(4)	1·379 (8)
O(1)—C(1)	1·442 (8)	C(3)—C(8)	1·39 (1)
O(2)—C(2)	1·208 (7)	C(4)—C(5)	1·38 (1)
O(3)—C(9)	1·333 (8)	C(5)—C(6)	1·389 (9)
O(3)—C(10)	1·453 (8)	C(6)—C(7)	1·379 (8)
O(4)—C(9)	1·197 (7)	C(6)—C(9)	1·49 (1)
C(1)—C(1′)	1·51 (1)	C(7)—C(8)	1·38 (1)
C(2)—C(3)	1·48 (1)		

C(2)—O(1)—C(1)	116·8 (5)	C(4)—C(5)—C(6)	120·6 (6)
C(9)—O(3)—C(10)	117·1 (6)	C(7)—C(6)—C(5)	119·1 (6)
O(1)—C(1)—C(1′)	104·2 (6)	C(7)—C(6)—C(9)	122·9 (6)
O(2)—C(2)—O(1)	123·6 (7)	C(5)—C(6)—C(9)	118·0 (6)
O(2)—C(2)—C(3)	123·6 (7)	C(6)—C(7)—C(8)	120·8 (6)
O(1)—C(2)—C(3)	112·8 (6)	C(7)—C(8)—C(3)	119·7 (6)
C(4)—C(3)—C(8)	120·1 (6)	O(4)—C(9)—C(3)	123·1 (7)
C(4)—C(3)—C(2)	120·8 (6)	O(4)—C(9)—C(6)	125·4 (7)
C(8)—C(3)—C(2)	119·0 (7)	O(3)—C(9)—C(6)	111·5 (7)
C(3)—C(4)—C(5)	119·7 (6)		

O(1)—C(2)—C(3)—C(4)	6 (1)	C(1′)—C(1)—O(1)—C(2)	161·9 (7)
O(3)—C(9)—C(6)—C(7)	−1 (1)	C(6)—C(9)—O(3)—C(10)	180 (2)
C(1)—O(1)—C(2)—C(3)	177·7 (6)	O(1′)—C(1′)—C(1)—O(1)	180

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* Lists of structure factors, anisotropic thermal parameters and atomic coordinates for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53223 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

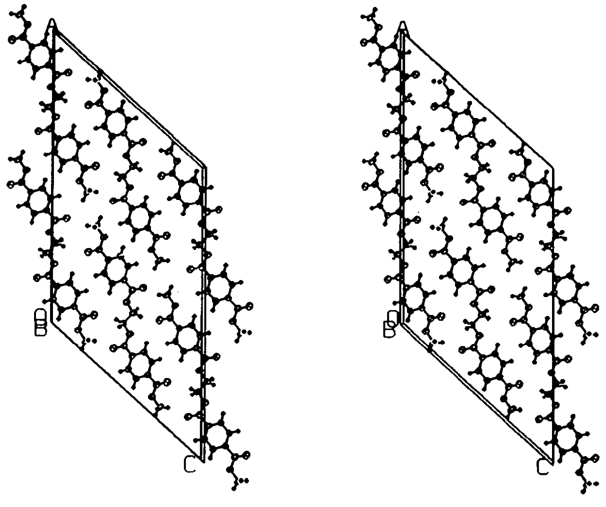

Fig. 2. Stereoview of the crystal packing of the molecules viewed along **b**.

moieties and phenyl ring are not the same. The plane of the inner carboxylic group is at angle of 8·38° to the phenyl ring but that of the outer carboxylic moiety is at an angle of 0·6°. The former is larger than the angles of 3° in ethylene glycol dibenzoate and 7·5° in its di(*p*-chlorobenzoate) derivative, but not as large as 12° in poly(ethylene terephthalate) (Daubeny, Bunn & Brown, 1954).

It is noteworthy that the distance of 10·73 Å between the centers of the two aromatic rings is approximately equal to that in ethylene glycol dibenzoate (10·75 Å) and the repeat distances of 10·75 Å reported by Daubeny, Bunn & Brown (1954) and 10·77 Å by Tomashpol'skii & Markova (1964) in poly(ethylene terephthalate).

The molecular arrangement in the crystal viewed along **b** is illustrated in Fig. 2. The molecules are packed in a herringbone manner held together by van der Waals forces.

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Structure Cristalline du Solvate Spironolactone–Acétonitrile (2:1)

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Abstract. 7α-Acetylthio-3-oxo-17α-pregn-4-ene-21,17β-carbolactone acetonitrile solvate, $2C_{24}H_{32}O_4S.C_2H_3N$, $M_r = 874{\cdot}38$, monoclinic, $P2_1$, $a = 11{\cdot}858\,(4)$, $b = 19{\cdot}665\,(3)$, $c = 11{\cdot}346\,(3)$ Å, $\beta = 118{\cdot}17\,(3)°$, $V = 2332\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}24$ Mg m^{-3}, $\lambda(\text{Mo } K\overline{\alpha}) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}16$ mm^{-1}, $F(000) = 940$, $T = 294\,(1)$ K, final $R = 0{\cdot}036$ for 3196 unique reflections. Bond lengths and angles are consistent with values found in analogous steroids. The two independent spironolactone molecules have the same *A*, *B* and *C* rings but different *D* and *E* rings. One *D* ring is intermediate between a