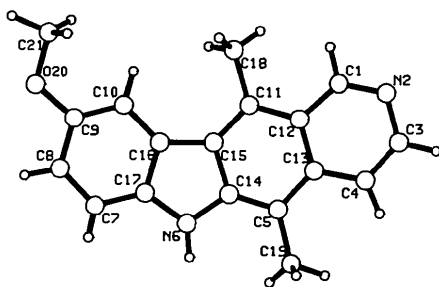
Fig. 1. The molecular structure of 5-*n*-butyl-11-demethylellipticine.

Fig. 2. The molecular structure of 9-methoxyellipticine.

these parameters. The largest difference between (I) and (II) occurs in the exocyclic bond to C(5), which is some 4σ longer in (I). The methoxy group attached at atom C(9) in (II) has produced no discernible effect on the bonding geometry of the ellipticine ring system, even though it may be presumed to have had some effect on its electronic properties. The exocyclic angles around

C(9) in (II) are markedly asymmetric, angle C(8)–C(9)–O(20) being some 9° smaller than C(10)–C(9)–O(20); this is presumably due to steric repulsions from the proton on C(10). The dihedral angle C(10)–C(9)–O(20)–C(21) is $9.0(3)^\circ$. The ellipticine ring system in both compounds is planar within experimental error, as is the parent ellipticine itself. The *n*-butyl side chain in (I) adopts a staggered conformation, with the dihedral angles around bonds C(18)–C(19) and C(19)–C(20) $174.5(9)$ and $178.7(9)^\circ$, respectively.

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Stereochemical Studies of Oligomers. III.* The Structure of 2,3-Butanediyl Dibenzoate, $C_{18}H_{18}O_4$

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Abstract. $M_r = 298.3$, monoclinic, $P2_1/c$, $a = 106.4(2)^\circ$, $V = 1540.2 \text{ \AA}^3$, $Z = 4$, $D_x = 1.29 \text{ Mg m}^{-3}$, $11.760(2)$, $b = 18.104(2)$, $c = 7.541(1) \text{ \AA}$, $\beta = 106.4(2)^\circ$, $\lambda = 1.5418 \text{ \AA}$, $\mu = 7.01 \text{ cm}^{-1}$, $F(000) = 632$, $T = 298 \text{ K}$, $R_w = 0.038$ for 2281 independent measured reflections. The two aromatic rings

* Part II: Bocelli & Grenier-Loustalot (1982b).

are not coplanar and form a dihedral angle of $39.61(4)^\circ$; the two carboxylic moieties are tilted with respect to their rings [$9.06(4)$ and $20.96(5)^\circ$]. The ethylenic part of the chain presents a conformation which is relatively far from all-*trans*. The length of the molecule [$10.77(2)$ Å] is practically equal to that observed in the mono- and polyethylene analogues.

Introduction. Very often the knowledge of the crystal structure of oligomers has allowed important progress in founding a correct polymer structure with much reliability. This type of approach was usefully employed in the structure determination of polynucleotides, polysaccharides, polypeptides and proteins. Moreover, the increasing commercial applications of poly(ethylene terephthalate) derivatives as fibers or as thermoplastic resins greatly develops the studies on the structure determination of crystalline polymers and, consequently, of related oligomers.

The present paper reports the structure analysis of one of these oligo-derivatives.

Experimental. Crystals synthesized (Grenier-Loustalot, 1983) and recrystallized at room temperature from a methanolic solution, colorless prismatic crystal, $0.30 \times 0.25 \times 0.55$ mm, Siemens AED single-crystal diffractometer, routines *PH* and *CEN* (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) employed to locate and to center 29 reflections ($12.5 < \theta < 43.9^\circ$) and to refine unit-cell parameters by least-squares fit; selection of the scan rate and the attenuator insertion by a fast 'flash' (1 s), scan range from Δ_0 below θ to Δ_1 above ($\Delta_0 = 0.55^\circ$, $\Delta_1 = \{0.55 + [(\lambda\alpha_1 - \lambda\alpha_2)/\lambda] \tan\theta\}^\circ$) with a speed range of $6\text{--}24$ s deg^{-1} , profile analysis to define peak and background values evaluated following

the Lehmann & Larsen notation (1974), data collection $2 < \theta < 60^\circ$, Ni-filtered Cu *K* α radiation, 2281 reflections after scaling and merging equivalents, 1234 having $I > 2\sigma(I)$ used in the structure analysis, corrections for Lorentz and polarization effects, no absorption correction; direct methods with *SHELX* (Sheldrick, 1976), positions of all heavy atoms shown on an *E* map computed for the best set of phases, anisotropic full matrix, hydrogen (from ΔF synthesis) isotropic, $w = [\sigma^2(F_o^2) + 0.003 F_o^2]^{-1}$, based on counting statistics, no significant features (< 0.2 e Å $^{-3}$) at the end of the refinement, scattering factors those of *SHELX*, final $R_w = 0.038$ ($R = 0.070$).

All calculations performed on the CDC CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna) with financial support of the University of Parma.

Discussion. The positional parameters with their standard deviations are listed in Table 1.* A projection of the molecule with arbitrary numbering scheme is illustrated in Fig. 1.

Bond distances, bond angles and selected torsion angles are reported in Table 2.

As is clearly seen in Fig. 2 the two aromatic rings are not coplanar but form a dihedral angle of $39.61(4)^\circ$. The two carboxylic moieties form angles of $9.06(4)$ and $20.96(5)^\circ$ with the respective mean phenyl ring planes. This is not surprising behavior for these molecular fragments and has already been observed in a great number of similar derivatives (Pérez & Brisse, 1975, 1976*a,b*, 1977*a,b*; Bocelli & Grenier-Loustalot, 1982*a,b*). For all these compounds the value of the dihedral angle ranges between 0.3 and 7.5° . It may be

* Lists of structure factors, anisotropic thermal parameters, coordinates and bond distances of H atoms, the analysis of the planar parts of the molecule and a list of the contacts < 3.5 Å have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38358 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic B_{eq} (Å 2)

| | x | y | z | B_{eq}^* |
|-------|-----------|----------|----------|-------------------|
| O(1) | 8241 (1) | 4080 (1) | 2675 (2) | 4.46 |
| O(2) | 10179 (1) | 4210 (1) | 2998 (2) | 6.42 |
| O(3) | 4830 (1) | 5683 (1) | 1849 (2) | 6.92 |
| O(4) | 6796 (1) | 5828 (1) | 2681 (2) | 4.61 |
| C(1) | 9378 (2) | 2999 (1) | 2979 (2) | 3.62 |
| C(2) | 10420 (2) | 2653 (1) | 2916 (3) | 4.49 |
| C(3) | 10484 (2) | 1893 (1) | 2928 (3) | 5.05 |
| C(4) | 9529 (2) | 1474 (1) | 3019 (3) | 4.84 |
| C(5) | 8501 (2) | 1815 (1) | 3096 (3) | 4.43 |
| C(6) | 8418 (2) | 2577 (1) | 3057 (2) | 3.91 |
| C(7) | 9339 (2) | 3820 (1) | 2908 (3) | 4.22 |
| C(8) | 8075 (2) | 4878 (1) | 2396 (3) | 6.42 |
| C(9) | 7943 (2) | 5059 (1) | 392 (3) | 6.92 |
| C(10) | 6975 (2) | 5036 (1) | 2991 (3) | 4.61 |
| C(11) | 7109 (3) | 4874 (1) | 5008 (3) | 3.62 |
| C(12) | 5683 (2) | 6078 (1) | 2155 (3) | 4.49 |
| C(13) | 5633 (2) | 6896 (1) | 2027 (2) | 5.05 |
| C(14) | 6575 (2) | 7333 (1) | 2942 (3) | 4.84 |
| C(15) | 6481 (2) | 8089 (1) | 2824 (3) | 4.43 |
| C(16) | 5451 (2) | 8417 (1) | 1787 (3) | 3.91 |
| C(17) | 4519 (2) | 7981 (1) | 856 (3) | 4.22 |
| C(18) | 4597 (2) | 7222 (1) | 971 (3) | 4.36 |

* According to Hamilton (1959).

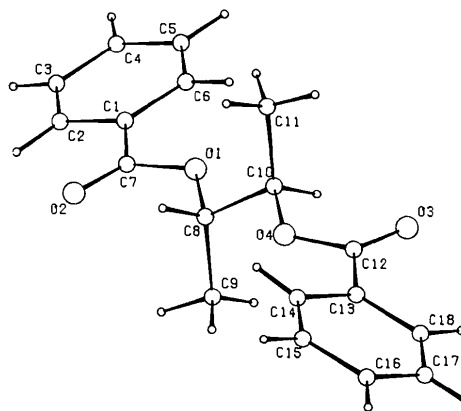


Fig. 1. Projection of the compound.

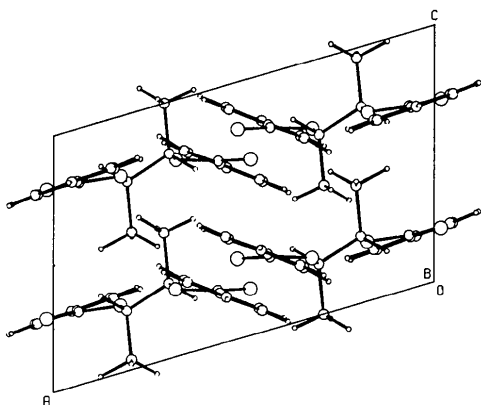


Fig. 2. Packing of the molecules.

Table 2. Bond distances (Å), bond angles (°) and selected torsion angles (°)

| | | | | | |
|-----------------------|------------|------------------------|------------|-------------|-----------|
| O(1)—C(7) | 1.339 (3) | C(1)—C(7) | 1.488 (3) | C(12)—C(13) | 1.484 (3) |
| O(1)—C(8) | 1.465 (3) | C(2)—C(3) | 1.378 (3) | C(13)—C(14) | 1.378 (3) |
| O(2)—C(7) | 1.201 (3) | C(3)—C(4) | 1.373 (3) | C(13)—C(18) | 1.385 (4) |
| O(3)—C(12) | 1.200 (3) | C(4)—C(5) | 1.373 (3) | C(14)—C(15) | 1.374 (3) |
| O(4)—C(10) | 1.458 (3) | C(5)—C(6) | 1.383 (3) | C(15)—C(16) | 1.377 (4) |
| O(4)—C(12) | 1.335 (3) | C(8)—C(9) | 1.511 (3) | C(16)—C(17) | 1.372 (3) |
| C(1)—C(2) | 1.389 (3) | C(8)—C(10) | 1.511 (4) | C(17)—C(18) | 1.378 (3) |
| C(1)—C(6) | 1.378 (3) | C(10)—C(11) | 1.513 (3) | | |
| C(7)—O(1)—C(8) | 116.8 (2) | C(9)—C(8)—C(10) | 113.6 (2) | | |
| C(10)—O(4)—C(12) | 117.8 (2) | O(4)—C(10)—C(8) | 103.6 (2) | | |
| C(6)—C(1)—C(7) | 122.6 (3) | C(8)—C(10)—C(11) | 114.0 (3) | | |
| C(2)—C(1)—C(7) | 117.9 (3) | O(4)—C(10)—C(11) | 108.7 (2) | | |
| C(2)—C(1)—C(6) | 119.5 (2) | O(3)—C(12)—O(4) | 123.5 (2) | | |
| C(1)—C(2)—C(3) | 119.8 (3) | O(4)—C(12)—C(13) | 112.0 (3) | | |
| C(2)—C(3)—C(4) | 120.5 (3) | O(3)—C(12)—C(13) | 124.5 (3) | | |
| C(3)—C(4)—C(5) | 119.7 (2) | C(12)—C(13)—C(18) | 118.3 (2) | | |
| C(4)—C(5)—C(6) | 120.4 (3) | C(12)—C(13)—C(14) | 121.9 (2) | | |
| C(1)—C(6)—C(5) | 120.0 (3) | C(14)—C(13)—C(18) | 119.7 (2) | | |
| O(2)—C(7)—C(11) | 124.7 (3) | C(13)—C(14)—C(15) | 120.1 (3) | | |
| O(1)—C(7)—C(11) | 112.0 (3) | C(14)—C(15)—C(16) | 120.5 (2) | | |
| O(1)—C(7)—O(2) | 123.3 (2) | C(15)—C(16)—C(17) | 119.3 (2) | | |
| O(1)—C(8)—C(10) | 103.6 (2) | C(16)—C(17)—C(18) | 120.8 (3) | | |
| O(1)—C(8)—C(9) | 109.2 (2) | C(13)—C(18)—C(17) | 119.5 (3) | | |
| C(2)—C(1)—C(7)—O(1) | 169.8 (2) | C(9)—C(8)—C(10)—O(4) | -60.6 (3) | | |
| C(2)—C(1)—C(7)—O(2) | -8.3 (4) | C(9)—C(8)—C(10)—C(11) | -178.6 (2) | | |
| C(6)—C(1)—C(7)—O(1) | -8.5 (4) | C(8)—C(10)—O(4)—C(12) | 146.4 (2) | | |
| C(6)—C(1)—C(7)—O(2) | 173.3 (3) | C(11)—C(10)—O(4)—C(12) | -92.1 (3) | | |
| C(1)—C(7)—O(1)—C(8) | -174.0 (2) | C(10)—O(4)—C(12)—O(3) | -3.4 (4) | | |
| O(2)—C(7)—O(1)—C(8) | 4.2 (4) | C(10)—O(4)—C(12)—C(13) | 175.7 (2) | | |
| C(7)—O(1)—C(8)—C(9) | 82.0 (3) | O(4)—C(12)—C(13)—C(14) | -20.9 (4) | | |
| C(7)—O(1)—C(8)—C(10) | -156.6 (2) | O(4)—C(12)—C(13)—C(18) | 160.0 (2) | | |
| O(1)—C(8)—C(10)—O(4) | -179.0 (2) | O(3)—C(12)—C(13)—C(14) | 158.2 (2) | | |
| O(1)—C(8)—C(10)—C(11) | 63.0 (3) | O(3)—C(12)—C(13)—C(18) | -21.0 (4) | | |

important to observe that an angle of 12° between the —C(=O)O— group and the plane of the benzene ring was reported for poly(ethylene terephthalate) (Daubeny, Bunn & Brown, 1954).

The conformation of the ethylenic part of the chain is relatively far from all-*trans*, some torsion angles of the chain differing noticeably from 180° (see Table 2). This conformation is different from the *trans-gauche* observed in ethylene bis(*p*-chlorobenzoate) (Pérez & Brisse, 1975) or the *trans-trans* of ethylene dibenzoate (Pérez & Brisse, 1976a). Therefore the presence of two methyl groups in the molecule remarkably changes the chain conformation.

The two methyls, like the two carbonylic oxygens, are *trans* with respect to the chain, and the two C(9)—C(8) and C(11)—C(10) bond directions, being practically parallel, form angles of $36.7(1)$ and $35.9(1)^\circ$ with the mean O(1), C(8), C(10), O(4) plane.

From the data reported in Table 2 it may be observed that the symmetric bond distances and angles of the molecule present only very small differences (0.009 \AA and 1.0° at most).

The two aromatic rings show bond distances and angles as expected [mean values: C—C = $1.381(4)$, $1.377(2) \text{ \AA}$; C—H = $0.98(2)$, $0.95(2) \text{ \AA}$; C—C—C = $119.9(2)$, $119.9(2)^\circ$; C—C—H = $119.8(7)$, $119.9(6)^\circ$].

The geometry of the carboxylic parts of the molecule compares very well with those of already quoted compounds.

The $\text{Csp}^3\text{—Csp}^3$ ethylenic distance [C(8)—C(10) = $1.511(4) \text{ \AA}$] is longer than the values observed for ethylene bis(*p*-chlorobenzoate) [$1.493(2) \text{ \AA}$] (Pérez & Brisse, 1975) and for ethylene dibenzoate [$1.499(3) \text{ \AA}$] (Pérez & Brisse, 1976a) but still show a shortening with respect to the theoretical value reported by Sutton (1965) [$1.537(5) \text{ \AA}$].

The O(1)—C(8)—C(10) and O(4)—C(10)—C(8) angles [$103.6(2)$, $103.6(2)^\circ$] show a reduction compared with the values of the two related compounds reported by Pérez & Brisse (1975, 1976a) [$107.3(2)^\circ$; $104.7(2)$ and $105.2(2)^\circ$].

Finally, it is most interesting to observe that the length of the molecule [distance between the center of the aromatic rings = $10.77(2) \text{ \AA}$] is practically equal to that of ethylene dibenzoate (10.75 \AA) and poly(ethylene terephthalate) (10.9 \AA).

The packing of the molecules is illustrated in Fig. 2. The crystal cohesion is determined by van der Waals contacts of $\text{O}\cdots\text{H}$ and $\text{C}\cdots\text{H}$ type.

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Stereochemical Studies of Oligomers. V. * 2,4-Pentanediyil Dibenzoate, C₁₉H₂₀O₄

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Abstract. $M_r = 312.4$, $P2_12_12_1$, $a = 10.976$ (2), $b = 11.706$ (2), $c = 13.013$ (2) Å, $V = 1672.0$ (5) Å³, $Z = 4$, $D_x = 1.24$ g cm⁻³, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 6.66$ cm⁻¹, $F(000) = 664$, $T = 298$ K, $R = 0.034$ for 894 observed reflections. The conformation of the chain produces a rotation of one aromatic ring with respect to the other and the molecule assumes an *endo* conformation. The introduction of pendant methyl groups on the aliphatic chain radically changes the molecular conformation compared with those found in the analogous unmethylated oligomer and in its related polymer.

Introduction. The crystal analysis results of oligomers in which the conformation of the aliphatic chain seems greatly influenced by pendant methyl groups has already been reported (Bocelli & Grenier-Loustalot, 1982b, 1983). From these studies and from those obtained spectroscopically rose the necessity to have more data to clarify the role of the pendant methyls in the conformational change and to try to form a rationalization of these variations. Consequently we have synthesized a new series of this type of oligomer and the results of the crystal analysis of the first of these is reported in this paper.

Experimental. Crystals grown from methanol solution, colorless prism, $0.21 \times 0.33 \times 0.49$ mm, accurate cell constants determined by least squares from 20 reflections automatically centered on a Siemens diffractometer, reflection centering performed by *CTDIF* routine (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979); 1854 reflections ($2 < \theta < 70^\circ$) collected with Ni-filtered Cu $K\alpha$ radiation, 895 considered as observed

[$I > 2\sigma(I)$] used for subsequent analysis, scan speed ($6\text{--}24$ s deg⁻¹) determined from the intensity of a 'flash' (1 s), scans taken from Δ_0 below θ to Δ_1 above ($\Delta_0 = 0.55^\circ$; $\Delta_1 = \{0.55 + [(\lambda\alpha_1 - \lambda\alpha_2)/\bar{\lambda}]\tan\theta\}^\circ$), integrated intensities obtained by a modification of the Lehmann & Larsen (1974) procedure using a program written by Belletti *et al.* (1979), 1 standard reflection monitored every 50 measurements, statistical fluctuations in intensity corrected during data processing with Lp corrections, absorption effects neglected; direct methods with *SHELX* (Sheldrick, 1976), $E's > 1.2$ used, starting set of $E's$ with assigned phases for origin, enantiomorph and multisolution phases chosen manually, position of all heavy atoms found on an E map with best consistency, full-matrix least-squares refinement with anisotropic thermal parameters, all hydrogen atoms found from a difference synthesis and refined isotropically, $R = 0.0338$ ($R_w = 0.0336$); on a final difference synthesis no peaks greater than 0.13 e Å⁻³, $w = [\sigma^2(F_o^2) + 0.027F_o^2]^{-1}$, reflection 200 omitted in the last cycles, scattering factors of *SHELX* used.

All calculations performed on the CDC CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna) with financial support of the University of Parma.

Discussion. The positional parameters are listed in Table 1† and a projection of the molecule with arbitrary numbering is given in Fig. 1. Table 2 lists bond lengths and angles and selected torsion angles.

† Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms with their bond distances, and contacts < 3.5 Å have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38359 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Part IV: Bocelli & Grenier-Loustalot (1982a).