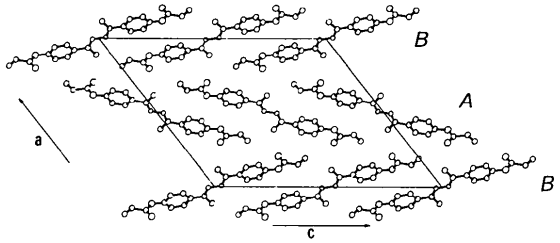

Fig. 2. Crystal packing of the title compound viewed along [010].

The crystal packing is shown in Fig. 2. It may be described by an ...*ABAB*... sequence of molecular layers piled along **b** × **c**. Each layer contains only crystallographically related molecules. Within each layer the molecules are packed with their long axes parallel to each other and tilted by +75° (layer *A*) or −75° (layer *B*) with respect to **b** × **c**.

References

Arcovito, G., Bonamico, M., Domenicano, A. & Vaciago, A. (1969). *J. Chem. Soc. B*, pp. 733–741.

Burke-Laing, M. & Laing, M. (1976). *Acta Cryst.* B**32**, 3216–3224.

Enraf–Nonius (1981). *Structure Determination Package.* Delft, Holland.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Roviello, A. & Sirigu, A. (1975). *J. Polym. Sci. Polym. Lett. Ed.* **13**, 455–463.

Roviello, A. & Sirigu, A. (1976). *Mol. Cryst. Liq. Cryst.* **33**, 19–34.

Acta Cryst. (1985). C**41**, 485–487

Stereochemical Studies of Oligomers. XV.* Structure of 2-Methyl-1,4-butanediyl Dibenzoate, $C_{19}H_{20}O_4$

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Abstract. $M_r = 312{\cdot}4$, triclinic, $P\bar{1}$, $a = 13{\cdot}211\ (3)$, $b = 8{\cdot}059\ (2)$, $c = 8{\cdot}704\ (2)$ Å, $\alpha = 114{\cdot}57\ (4)$, $\beta = 97{\cdot}98\ (3)$, $\gamma = 91{\cdot}57\ (3)°$, $V = 830{\cdot}9\ (5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}25$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 6{\cdot}70$ cm^{-1}, $F(000) = 332$, room temperature, $R = 0{\cdot}062$ for 2056 observed reflections. The conformation of the chain is *trans–trans–gauche* without any variation with respect to that of the unmethylated derivative. The planar carboxylic groups are tilted by 2·3 (1) and 2·5 (1)° with respect to their phenyl rings which have normal bond lengths and angles.

Introduction. In preceding papers of this series the influence of methyl groups, attached to the aliphatic chain, on the conformation of this type of derivative was extensively examined (Bocelli & Grenier-Loustalot, 1982*a*,*b*, 1983*a*,*b*,*c*,*d*, 1984*b*,*c*, 1985). In particular, the structure analyses of derivatives with ethanediyl chains clearly showed that the presence of one methyl group moves the conformation away from a *trans* arrangement (Bocelli & Grenier-Loustalot, 1983*a*,*b*,*c*,*d*, 1984*b*). This result seems instead to be contradicted by the analysis of derivatives with propanediyl chains (Bocelli & Grenier-Loustalot, 1985). Furthermore the conformations of derivatives with a butanediyl chain and with 1,4-dimethyl groups also seem to be influenced by the presence of chlorine atoms on the rings (Bocelli & Grenier-Loustalot, 1984*c*).

It may be interesting to know which type of conformational changes occur when the methyls are not on the extremities of the chain and this is the goal of the present analysis.

Experimental. White crystals recrystallized from methanol, prism, 0·14 × 0·11 × 0·04 mm, Siemens AED single-crystal diffractometer equipped with a General Automation Jumbo 220 computer, Ni-filtered Cu *Kα* radiation, cell parameters from angular values of 24

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* Part XIV: Bocelli & Grenier-Loustalot (1985).

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reflections ($13{\cdot}1 \leq \theta \leq 34{\cdot}9°$) accurately measured on the diffractometer, data collected at room temperature with a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure, one check reflection every 50 measurements without significant variation, no correction for absorption, 3066 collected reflections ($3 \leq \theta \leq 70°$; $-16 \leq h \leq 15$, $-8 \leq k \leq 8$, $0 \leq l \leq 9$), 2847 unique ($R_{\rm int} = 0{\cdot}029$), 2066 observed at 2σ level, direct methods with *MULTAN*74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974), anisotropic block-matrix with *SHELX*76 (Sheldrick, 1976), $\sum(\Delta F)^2$ minimized, H atoms (from ΔF map) isotropic, final $R = 0{\cdot}062$, $R_w = 0{\cdot}074$, $w = 1{\cdot}0/(\sigma^2F + 0{\cdot}0874F^2)$, ten reflections omitted in last cycle, 75 and 214 parameters refined comprising parameters of a ring and of the rest of the molecule and a scale factor, no peaks $>0{\cdot}18$ e Å^{-3} in last ΔF map, $(\Delta/\sigma)_{\rm max}$ 0·86, $S = 1{\cdot}67$.

Atomic scattering factors from *SHELX*76. Calculations for *MULTAN*74 performed on the CDC Cyber 76 of the CINECA, Casalecchio (Bologna), those for *SHELX*76 on a Gould SEL 32/77 computer.

Discussion. Final atomic parameters are in Table 1* with Fig. 1 showing the atom numbering. Bond distances, angles and selected torsion angles are in Table 2. The mean bond distances and angles of the aromatic rings are normal [1·374 (5), 1·382 (2) Å; 120·0 (3), 120·0 (3)°].

The carboxylic groups are planar [maximum out-of-plane deviations 0·009 (3) Å for C(7) and 0·005 (3) Å for C(13)] and form dihedral angles of 2·3 (1) and 2·5 (1)° with respect to their phenyl planes. In these groups the angles opposite to the C=O bonds are, as expected, smaller than the adjacent ones.

The C_{sp^3}—C_{sp^3} distances of the aliphatic chain are all relatively shorter than the value reported by Sutton (1965) [1·537 (5) Å] but not so markedly as previously found in some of the preceding papers of this series (Bocelli & Grenier-Loustalot, 1984*a*,*b*, 1985).

The methyl group is axial with respect to the C(8)—C(9)—C(10)—C(12) sequence, 142·4 (2)° being the angle between the C(10)—C(11) bond line and the normal to the C(8)···C(12) mean plane.

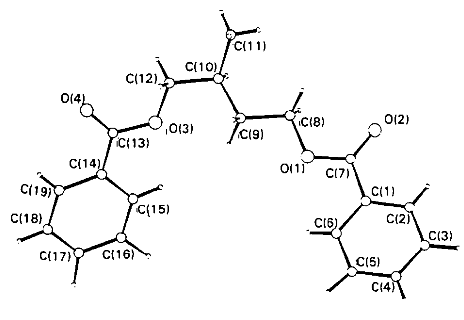

Fig. 1. Projection of the molecule along **b**.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with* B_{eq} *values*

	x	y	z	$B_{\rm eq}$*(Å^2)
O(1)	735 (1)	7490 (2)	6764 (2)	5·7
O(2)	−845 (1)	7341 (4)	7333 (2)	7·6
O(3)	4303 (1)	6519 (2)	9044 (2)	5·5
O(4)	5913 (1)	7835 (2)	9960 (2)	6·9
C(1)	−628 (2)	7412 (3)	4691 (3)	5·1
C(2)	−1664 (2)	7396 (4)	4163 (3)	6·2
C(3)	−2022 (2)	7447 (4)	2623 (4)	7·1
C(4)	−1351 (3)	7488 (4)	1598 (4)	7·7
C(5)	−316 (3)	7484 (6)	2076 (4)	8·2
C(6)	49 (2)	7461 (5)	3640 (4)	6·9
C(7)	−279 (2)	7392 (3)	6391 (3)	5·3
C(8)	1141 (2)	7577 (4)	8446 (3)	5·6
C(9)	2301 (2)	7852 (4)	8662 (3)	5·1
C(10)	2828 (2)	7809 (3)	10309 (3)	5·0
C(11)	2538 (2)	9311 (5)	11908 (4)	6·5
C(12)	3980 (2)	8013 (4)	10463 (3)	5·3
C(13)	5301 (2)	6606 (3)	8928 (3)	5·3
C(14)	5559 (1)	5071 (3)	7410 (3)	5·2
C(15)	4832 (2)	3669 (3)	6281 (3)	5·7
C(16)	5102 (2)	2265 (3)	4874 (3)	6·7
C(17)	6095 (2)	2224 (4)	4564 (4)	7·2
C(18)	6822 (2)	3616 (4)	5656 (4)	7·3
C(19)	6557 (2)	5037 (4)	7083 (3)	6·4

* According to Hamilton (1959).

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

O(1)—C(7)	1·326 (3)	C(5)—C(6)	1·388 (6)
O(1)—C(8)	1·460 (3)	C(8)—C(9)	1·517 (4)
O(2)—C(7)	1·196 (4)	C(9)—C(10)	1·518 (4)
O(3)—C(12)	1·447 (3)	C(10)—C(11)	1·524 (4)
O(3)—C(13)	1·338 (3)	C(10)—C(12)	1·508 (4)
O(4)—C(13)	1·207 (3)	C(13)—C(14)	1·477 (3)
C(1)—C(2)	1·380 (4)	C(14)—C(15)	1·386 (3)
C(1)—C(6)	1·376 (5)	C(14)—C(19)	1·386 (3)
C(1)—C(7)	1·494 (4)	C(15)—C(16)	1·378 (3)
C(2)—C(3)	1·376 (5)	C(16)—C(17)	1·374 (4)
C(3)—C(4)	1·351 (5)	C(17)—C(18)	1·373 (4)
C(4)—C(5)	1·373 (6)	C(18)—C(19)	1·392 (4)
C(7)—O(1)—C(8)	115·8 (2)	C(9)—C(10)—C(12)	111·3 (2)
C(12)—O(3)—C(13)	116·5 (2)	C(9)—C(10)—C(11)	113·0 (3)
C(6)—C(1)—C(7)	122·3 (3)	C(11)—C(10)—C(12)	107·6 (2)
C(2)—C(1)—C(7)	118·9 (3)	O(3)—C(12)—C(10)	109·8 (2)
C(2)—C(1)—C(6)	118·9 (3)	O(3)—C(13)—O(4)	122·6 (3)
C(1)—C(2)—C(3)	121·1 (3)	O(4)—C(13)—C(14)	124·4 (3)
C(2)—C(3)—C(4)	119·6 (3)	O(3)—C(13)—C(14)	113·0 (2)
C(3)—C(4)—C(5)	120·8 (3)	C(13)—C(14)—C(19)	119·2 (3)
C(4)—C(5)—C(6)	119·7 (4)	C(13)—C(14)—C(15)	122·2 (2)
C(1)—C(6)—C(5)	119·9 (3)	C(15)—C(14)—C(19)	118·6 (3)
O(2)—C(7)—C(1)	124·1 (3)	C(14)—C(15)—C(16)	120·5 (3)
O(1)—C(7)—C(1)	112·4 (3)	C(15)—C(16)—C(17)	120·8 (3)
O(1)—C(7)—O(2)	123·5 (3)	C(16)—C(17)—C(18)	119·5 (3)
O(1)—C(8)—C(9)	106·8 (2)	C(17)—C(18)—C(19)	120·1 (3)
C(8)—C(9)—C(10)	112·3 (2)	C(14)—C(19)—C(18)	120·5 (3)
C(7)—O(1)—C(8)—C(9)	−175·0 (2)	C(13)—O(3)—C(12)—C(10)	174·3 (2)
O(1)—C(8)—C(9)—C(10)	−175·3 (2)	O(3)—C(12)—C(10)—C(9)	−60·7 (3)
C(8)—C(9)—C(10)—C(12)	177·8 (3)	O(3)—C(12)—C(10)—C(11)	175·0 (3)
C(8)—C(9)—C(10)—C(11)	−60·9 (4)		

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* Lists of structure factors, anisotropic thermal parameters and H coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39886 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The conformation of the aliphatic chain is *trans–trans–gauche* so the presence of one methyl group at the chain does not cause conformational variations with respect to the 1,4-butanediyl dibenzoate (Bocelli & Grenier-Loustalot, 1982*a*). It is noticeably important that the conformation of the analogous derivative with two methyls was *gauche–trans–gauche* (Bocelli & Grenier-Loustalot, 1982*b*).

Intermolecular contacts are in the range of van der Waals interactions.

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References

BELLETTI, D., UGOZZOLI, F., CANTONI, A. & PASQUINELLI, G. (1979). *Gestione on Line di Diffrattometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo* 220. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma. Internal Reports 1–3/79.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1982*a*). *Acta Cryst.* B**38**, 2072–2075.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1982*b*). *Acta Cryst.* B**38**, 3135–3139.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1983*a*). *Acta Cryst.* C**39**, 633–636.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1983*b*). *Acta Cryst.* C**39**, 636–638.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1983*c*). *Acta Cryst.* C**39**, 1659–1661.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1983*d*). *Acta Cryst.* C**39**, 1661–1663.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1984*a*). *Acta Cryst.* C**40**, 679–683.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1984*b*). *Acta Cryst.* C**40**, 1394–1397.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1984*c*). *Acta Cryst.* C**40**, 1400–1402.

BOCELLI, G. & GRENIER-LOUSTALOT, M. F. (1985). *Acta Cryst.* C**41**, 249–252.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–589.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J.-P. (1974). *MULTAN74. A System of Comptuer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions, Suppl.* 1956–59. Spec. Publ. No. 18. London: The Chemical Society.

Acta Cryst. (1985). C**41**, 487–490

Structure and Absolute Configuration of Euphoscopin A *p*-Bromobenzoate, $C_{38}H_{43}BrO_9$, and Euphornin Acetal *p*-Bromobenzoate, $C_{37}H_{45}BrO_7$

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Abstract. $C_{38}H_{43}BrO_9$ (I): $M_r = 723{\cdot}7$, orthorhombic, $P2_12_12_1$, $a = 16{\cdot}271\,(2)$, $b = 23{\cdot}577\,(3)$, $c = 9{\cdot}786\,(1)$ Å, $V = 3754{\cdot}1\,(6)$ Å^3, $Z = 4$, $D_m = 1{\cdot}28\,(2)$, $D_x = 1{\cdot}28$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 2{\cdot}07$ mm^{-1}, $F(000) = 1512$, $T = 298\,(1)$ K, $R = 0{\cdot}046$ for 2948 unique reflections. $C_{37}H_{45}BrO_7$ (II): $M_r = 681{\cdot}7$, monoclinic, $P2_1$, $a = 17{\cdot}104\,(3)$, $b = 13{\cdot}837\,(2)$, $c = 7{\cdot}611\,(1)$ Å, $\beta = 99{\cdot}14\,(2)°$, $V = 1778{\cdot}4\,(5)$ Å^3, $Z = 2$, $D_m = 1{\cdot}22\,(2)$, $D_x = 1{\cdot}27$ Mg m^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70926$ Å, $\mu = 1{\cdot}19$ mm^{-1}, $F(000) = 716$, $T = 300\,(1)$ K, $R = 0{\cdot}036$ for 1793 unique reflections. It is confirmed that the polyoxygenated novel diterpenes euphoscopin A and euphornin have the jatrophone skeleton with the *trans* ring junction. In the two molecules three of the seven asymmetric carbon atoms have opposite absolute configurations. The molecules are held together by van der Waals forces.

Introduction. Euphoscopins are new toxic substances isolated from the plant *Euphorbia helioscopia* L. (Yamamura, Kosemura, Ohba, Ito & Saito, 1981). Euphornin was isolated from the plant *Euphorbia maddeni* B. by Sahai, Rastogi, Jakupovic & Bohlmann (1981) and from the plant *Euphorbia helioscopia* L. (Shizuri, Kosemura, Ohtsuka, Terada, Yamamura, Ohba, Ito & Saito, 1984). The cytotoxicity of euphoscopin A is stronger than that of euphornin. Their NMR and mass spectra suggest that they have the same jatrophone skeleton with different absolute con-

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