

- DUBLER, E., HÄNGGI, G. & SCHMALLE, H. W. (1987). *Acta Cryst.* **C43**, 1872–1875.
- HESSE, A. & BACH, D. (1982). *Harnsteine, Klinische Chemie in Einzeldarstellungen*, Vol. 5, pp. 48–62. Stuttgart: Georg Thieme.
- HURST, D. T. (1980). *An Introduction to the Chemistry and Biochemistry of Pyrimidines, Purines and Pteridines*, pp. 179–203. New York: John Wiley.
- JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- LICHTENBERG, D., BERGMANN, F. & NEIMAN, Z. (1972). *Isr. J. Chem.* **10**, 805–817.
- MUNNS, A. R. I. & TOLLIN, P. (1970). *Acta Cryst.* **B26**, 1101–1113.
- PULLMAN, B. & PULLMAN, A. (1971). *Adv. Heterocycl. Chem.* **13**, 77–159.
- ROSENSTEIN, R. D., OBERDING, M., HYDE, J. R., ZUBIETA, J., KARLIN, K. D. & SEEMAN, N. C. (1982). *Cryst. Struct. Commun.* **11**, 1507–1513.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1985). *SHELXS86. Crystallographic Computing*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- SLETTEN, J. & JENSEN, L. H. (1969). *Acta Cryst.* **B25**, 1608–1614.
- TAYLOR, R. & KENNARD, O. (1982a). *J. Mol. Struct.* **78**, 1–28.
- TAYLOR, R. & KENNARD, O. (1982b). *J. Am. Chem. Soc.* **104**, 5063–5070.
- THEWALT, U., BUGG, C. E. & MARSH, R. E. (1970). *Acta Cryst.* **B26**, 1089–1101.

Acta Cryst. (1988). **C44**, 736–737

Methyl *rel*-(2*R*,3*S*,5*R*,6*S*)-7-Oxabicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate

BY FRANZ H. KOHNKE* AND J. FRASER STODDART

Department of Chemistry, The University, Sheffield S3 7HF, England

AND ALEXANDRA M. Z. SLAWIN AND DAVID J. WILLIAMS

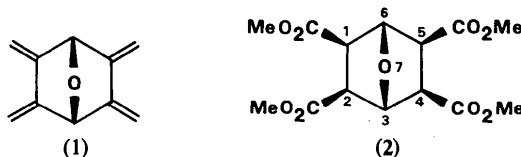
Department of Chemistry, Imperial College, London SW7 2AY, England

(Received 22 October 1987; accepted 4 January 1988)

Abstract. $C_{14}H_{18}O_9$, $M_r = 330.3$, orthorhombic, $F2dd$, $a = 5.065$ (1), $b = 13.632$ (3), $c = 43.636$ (9) Å, $V = 3013$ Å³, $Z = 8$ (the molecule possesses a twofold axis), $D_x = 1.45$ Mg m⁻³, $Cu K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 0.10$ mm⁻¹, $F(000) = 1392$, room temperature, $R = 0.048$ for 572 observed reflections with $|F_o| > 3\sigma(|F_o|)$. The all-*exo* configuration of the ester group proposed on the basis of NMR spectroscopic studies for the title compound is confirmed.

Introduction. In the course of the synthesis (Kohnke, Slawin, Stoddart & Williams, 1987) of a new class of rigid macropolycyclic molecules with belt-like shapes that relies upon the Diels–Alder reaction, the bisdiene (1) (Vogel & Florey, 1974) was identified as one of the key starting materials. It can be prepared (Mahaim, Carrupt, Hagenbuch, Florey & Vogel, 1980) in four steps from the *exo*-furan–maleic anhydride adduct which is subjected, in the first instance, to catalytic carbonylation (James & Stille, 1976) in methanolic solution to afford a tetraester. On basis of the ¹H and ¹³C NMR spectroscopic data, this compound has been assigned (Mahaim *et al.*, 1980) the all-*exo* configuration (2). During our own preparation of a sample of the bisdiene (1), good-quality single crystals were obtained (Kohnke *et al.*, 1987). Here we report the results of an

X-ray crystallographic investigation carried out on the tetraester (2).



Experimental. Single crystals (found: C 51.1, H 5.5%. $C_{14}H_{18}O_9$ requires C 50.9, H 5.5%) of (2), suitable for X-ray crystallography, were grown at room temperature from $CHCl_3$ and had m.p. 430–431 K. Crystal size 0.20 × 0.30 × 0.40 mm. Refined unit-cell parameters obtained from setting angles of 19 reflections with $8 \leq \theta \leq 33^\circ$. Nicolet *R3m* diffractometer. 574 independent reflections ($\theta \leq 58^\circ$) measured, $Cu K\alpha$ radiation (graphite monochromator), ω scan. 572 [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range $h 0/5$, $k 0/14$, $l 0/46$; two check reflections measured every 50 reflections, net count constant; Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods; non-hydrogen atoms refined anisotropically; positions of H atoms calculated (C–H = 0.96 Å); H atoms assigned isotropic thermal parameters, $U(H) = 1.2 U_{eq}(C)$, and allowed to ride on parent C atoms; methyl groups refined as rigid bodies. An empirical extinction correction was applied [$g = 0.007$ (1)]. Refinement using F

* Permanent address: Dipartimento di Chimica Organica e Biologica dell'Università di Messina, Contrada Papardo, Salita Sperone, 98100 Messina, Italy.

magnitudes by block-cascade full-matrix least squares; $R = 0.048$; $wR = 0.052$ [$w^{-1} = \sigma^2(F) + 0.00036F^2$]. $(\Delta/\sigma)_{\max} = 0.014$; residual electron density in difference map within -0.22 and $0.25 \text{ e } \text{Å}^{-3}$; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^3$)

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O(1)	3755	5000	0	43 (1)
C(1)	1879 (11)	5689 (3)	-119 (1)	40 (1)
C(2)	193 (10)	5944 (3)	163 (1)	36 (1)
C(3)	195 (10)	4941 (3)	342 (1)	37 (1)
C(4)	1309 (12)	6826 (3)	335 (1)	42 (1)
O(4)	3095 (8)	7324 (2)	253 (1)	58 (1)
O(5)	-125 (9)	6984 (2)	591 (1)	55 (1)
C(5)	740 (17)	7789 (3)	780 (1)	71 (2)
C(6)	1322 (11)	4946 (3)	660 (1)	42 (1)
O(6)	338 (10)	4543 (2)	876 (1)	61 (1)
O(7)	3638 (9)	5414 (2)	680 (1)	53 (1)
C(7)	4723 (13)	5541 (4)	983 (1)	63 (2)

Table 2. Bond lengths (Å) and bond angles ($^\circ$)

O(1)—C(1)	1.433 (5)	O(1)—C(1')	1.433 (5)
C(1)—C(2)	1.537 (6)	C(1)—C(3')	1.555 (6)
C(2)—C(3)	1.573 (5)	C(2)—C(4)	1.527 (5)
C(3)—C(6)	1.503 (6)	C(3)—C(1')	1.554 (6)
C(4)—O(4)	1.186 (6)	C(4)—O(5)	1.349 (6)
O(5)—C(5)	1.441 (6)	C(6)—O(6)	1.199 (5)
C(6)—O(7)	1.338 (7)	O(7)—C(7)	1.444 (6)
C(1)—O(1)—C(1')	96.9 (4)	O(1)—C(1)—C(2)	103.2 (3)
O(1)—C(1)—C(3')	103.2 (3)	C(2)—C(1)—C(3')	108.7 (4)
C(1)—C(2)—C(3)	101.5 (3)	C(1)—C(2)—C(4)	111.4 (4)
C(3)—C(2)—C(4)	116.1 (3)	C(2)—C(3)—C(6)	117.1 (3)
C(2)—C(3)—C(1')	99.8 (3)	C(6)—C(3)—C(1')	112.0 (4)
C(2)—C(4)—O(4)	125.8 (4)	C(2)—C(4)—O(5)	109.5 (4)
O(4)—C(4)—O(5)	124.7 (4)	C(4)—O(5)—C(5)	115.6 (4)
C(3)—C(6)—O(6)	124.6 (5)	C(3)—C(6)—O(7)	113.1 (4)
O(6)—C(6)—O(7)	122.2 (4)	C(6)—O(7)—C(7)	116.6 (4)

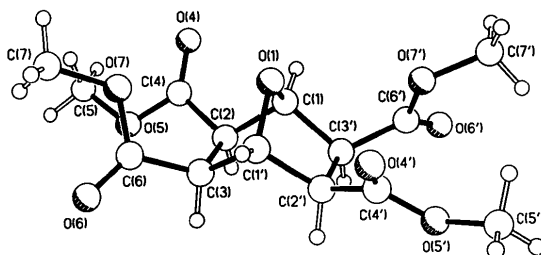


Fig. 1. Ball-and-stick representation of the structure of (2) showing the atomic numbering scheme.

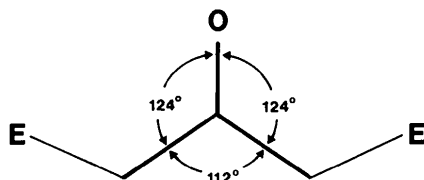


Fig. 2. Diagrammatic representation of the structure of (2) showing dihedral angles ($E \equiv \text{CO}_2\text{Me}$ groups).

Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

Discussion. The structure of (2) with atom numbering is shown in Fig. 1. Table 1* lists the fractional atomic coordinates of the non-hydrogen atoms and Table 2 the bond lengths and angles.

The tetraester (2) possesses crystallographic C_2 symmetry about an axis passing through O(1) and bisecting the C(1)—C(1') vector. All four ester groups have the *exo* configuration as proposed previously (Mahaim *et al.*, 1980) on the basis of ^1H and ^{13}C NMR spectroscopies. Their carbonyl functions on vicinal carbon atoms are oriented in approximately opposite directions with respect to each other, thus minimizing intramolecular dipole-dipole interactions. The C(1)—C(2)—C(4)—O(4) and C(1')—C(3)—C(6)—O(6) torsion angles are $6.6 (6)$ and $109.6 (5)^\circ$, respectively. The dihedral angle between the C(1)—O(1)—C(1') and the C(1)—C(2)—C(3)—C(1') mean planes is $124 (1)^\circ$ and that between the C(1)—C(2)—C(3)—C(1') and the C(1')—C(2')—C(3')—C(1) mean planes is $112 (1)^\circ$ (Fig. 2).

Clearly, catalytic carbonylation in methanolic solution of the olefinic double bond in the *exo*-furan-maleic anhydride adduct proceeds stereospecifically *syn* with *exo* diastereoselectivity to give the tetraester (2) in accordance with expectation. For example, catalytic carbonylation of norbornene in methanolic solution affords (James & Stille, 1976) only the diester with the two contiguous ester functions oriented *exo* and, of course, *syn* on the norbornane skeleton.

We thank the Science and Engineering Research Council and the University of Messina for financial support.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44644 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JAMES, D. E. & STILLE, J. K. (1976). *J. Am. Chem. Soc.* **98**, 1810–1823.
- KOHNKE, F. H., SLAWIN, A. M. Z., STODDART, J. F. & WILLIAMS, D. J. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 892–894.
- MAHAIM, C., CARRUPT, P.-A., HAGENBUCH, J.-P., FLOREY, A. & VOGEL, P. (1980). *Helv. Chim. Acta*, **63**, 1149–1157.
- SHELDRIK, G. M. (1983). *SHELXTL*, revision 4.0, January 1983. *An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Federal Republic of Germany.
- VOGEL, P. & FLOREY, A. (1974). *Helv. Chim. Acta*, **57**, 200–204.