126 (1)°, respectively, and that between the C(1)–C(2)–C(3)–C(4) and the C(1)–C(4)–C(4a)–C(9a) mean planes is 112 (1)°. Comparison with the reported (Pinkerton, Schwarzenbach, Birbaum, Carrupt, Schwager & Vogel, 1984) calculated geometry of 7-oxanorbornadiene, which coincidently matches that found (Kohnke, Stoddart, Slawin & Williams, 1988) for methyl rel-(2R,3S,5R,6S)-7-oxabicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate, shows (Fig. 2) that there is a bending (2°) of the C(1)–O(1)–C(4) plane towards the aromatic ring. This deformation is compatible with the C(2)–C(3) bond [1·308 (3) Å] being significantly shorter than the C(4a)–C(9a) bond [1·401 (2) Å]. In addition to this deformation, there is a slight fold (2°) of the C(1)–C(4)–C(4a)–C(9a) plane out of that of the aromatic ring (Fig. 2). These deviations, though small, are also present in the structure reported by Hart et al. (1983) for the other polymorph, i.e. throughout, the integrity of the internal molecular geometry is retained.

Investigation of the arrangement of the molecules in the unit cells of both polymorphs reveals (Fig. 3) dramatic differences in their packing. Whereas, in the present structure (Fig. 3a), the packing appears to be well ordered and represents an efficient filling of space, that in the other polymorph (Fig. 3b) seems comparatively disorganized. Despite this observation, the calculated density for the latter is higher (1·406 Mg m^{-3}) than that for the former (1·386 Mg m^{-3}).

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Methyl rel-(1R,2R,3S,4S,5S,6S,7R,8R)-1,4:5,8-Diepoxy-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxylate

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Abstract. $C_{22}H_{22}O_{10}$, $M_r = 446·4$, monoclinic, $P2_1/n$, $a = 8·909$ (4), $b = 10·230$ (3), $c = 11·788$ (5) Å, $\beta = 102·10$ (3)°, $V = 1050$ Å^3, $Z = 2$ (the molecule possesses a centre of symmetry), $D_x = 1·41$ Mg m^{-3}, Cu Kα radiation, $\lambda = 1·54178$ Å, $\mu = 0·913$ mm^{-1}, $F(000) = 468$, room temperature, $R = 0·036$ for 1350 observed reflections with $|F_o| > 3\sigma(|F_o|)$. X-ray crystallography has shown that catalytic carbonylation of the anti isomer of 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene in methanol affords stereoselectively the title compound in which all four ester groups have the exo configuration.

Introduction. We have characterized (Kohnke, Stoddart, Slawin & Williams, 1988a) the all-exo isomer (1) of methyl 7-oxabicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate by X-ray crystallography, following the assignment (Mahaim, Carrupt, Hagenbuch, Florey & Vogel, 1980) of its relative configuration by NMR spectroscopy. In order to extend our investigations (Kohnke, Slawin, Stoddart & Williams, 1987) in search of new molecular materials and novel molecular receptors, we explored

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the possibility of converting the *anti* isomer (2) of 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene (Hart, Raju, Meador & Ward, 1983; Kohnke, Stoddart, Slawin & Williams, 1988*b*) into the tetraester (3) with the all-*exo* configuration by catalytic carbonylation of (2) in methanolic solution. Here, we report the isolation of a product from such a reaction carried out on (2) and then establish by a single-crystal X-ray structural analysis that indeed this product is the all-*exo* tetraester (3).

(1)   (2)

(3)
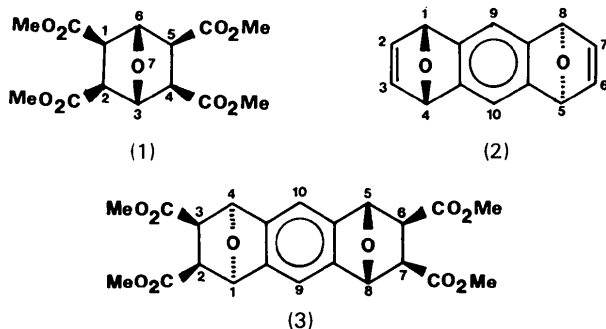
Experimental. Compound (2) was subjected (James & Stille, 1976) to carbonylation in methanol using a Pd/C–CuCl$_2$ catalyst–cocatalyst system at 3·5 atm carbon monoxide at room temperature for 3 d. The reaction afforded the title compound (3) in 5% yield after silica-gel chromatography using chloroform–ether as eluant. Single crystals of (3), suitable for X-ray crystallography, were grown at room temperature from methanol/dichloromethane and had m.p. 579–580 K. Crystal size 0·27 × 0·30 × 0·50 mm. Refined unit-cell parameters obtained from setting angles of 16 reflections with $11 \le \theta \le 29°$. Nicolet R3*m* diffractometer. 1416 independent reflections ($\theta \le 58°$) measured, Cu Kα radiation (graphite monochromator), ω scan, 1350 $[|F_o| > 3\sigma(|F_o|)]$ considered observed, index range h −9/9, k 0/11, l 0/12; 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 [$g = 0·037$ (3)]. Refinement using F magnitudes by block-cascade full-matrix least squares; $R = 0·036$; $wR = 0·046$ [$w^{-1} = \sigma^2(F) + 0·00022F^2$]. $(\Delta/\sigma)_{max} = 0·225$; residual electron density in difference map within −0·15 and 0·18 e Å^{-3}; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

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)	7791 (1)	1935 (1)	8071 (1)	48 (1)
C(1)	7525 (2)	545 (2)	8101 (2)	45 (1)
C(2)	6085 (2)	502 (2)	8627 (1)	43 (1)
C(3)	6446 (2)	1627 (2)	9551 (1)	42 (1)
C(4)	7987 (2)	2148 (2)	9302 (1)	44 (1)
C(4a)	9190 (2)	1137 (2)	9795 (1)	41 (1)
C(9)	9681 (2)	−1076 (2)	9194 (1)	43 (1)
C(9a)	8877 (2)	91 (2)	9020 (1)	42 (1)
C(10)	4619 (2)	717 (2)	7715 (2)	46 (1)
O(10)	4545 (2)	818 (2)	6690 (1)	66 (1)
O(11)	3408 (1)	769 (1)	8214 (1)	56 (1)
C(12)	1959 (2)	1148 (3)	7477 (2)	70 (1)
C(13)	5230 (2)	2681 (2)	9416 (1)	43 (1)
O(13)	5014 (2)	3494 (1)	8667 (1)	63 (1)
O(14)	4425 (2)	2604 (1)	10250 (1)	52 (1)
C(15)	3158 (2)	3514 (2)	10163 (2)	64 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

O(1)–C(1)	1·444 (2)	O(1)–C(4)	1·441 (2)
C(1)–C(2)	1·538 (3)	C(1)–C(9a)	1·514 (2)
C(2)–C(3)	1·571 (2)	C(2)–C(10)	1·523 (2)
C(3)–C(4)	1·557 (3)	C(3)–C(13)	1·514 (2)
C(4)–C(4a)	1·515 (2)	C(4a)–C(9a)	1·397 (2)
C(4a)–C(9′)	1·390 (2)	C(9)–C(9a)	1·385 (2)
C(9)–C(4a′)	1·390 (2)	C(10)–O(10)	1·201 (2)
C10)–O(11)	1·334 (2)	O(11)–C(12)	1·450 (2)
C(13)–O(13)	1·199 (2)	C(13)–O(14)	1·335 (2)
O(14)–C(15)	1·450 (3)		

C(1)–O(1)–C(4)	96·3 (1)	O(1)–C(1)–C(2)	101·1 (1)
O(1)–C(1)–C(9a)	102·1 (1)	C(2)–C(1)–C(9a)	108·0 (1)
C(1)–C(2)–C(3)	101·0 (1)	C(1)–C(2)–C(10)	112·1 (1)
C(3)–C(2)–C(10)	113·8 (1)	C(2)–C(3)–C(4)	100·4 (1)
C(2)–C(3)–C(13)	114·3 (1)	C(4)–C(3)–C(13)	112·1 (1)
O(1)–C(4)–C(3)	102·3 (1)	O(1)–C(4)–C(4a)	102·1 (1)
C(3)–C(4)–C(4a)	106·0 (1)	C(4)–C(4a)–C(9a)	104·1 (1)
C(4)–C(4a)–C(9′)	133·3 (2)	C(9a)–C(4a)–C(9′)	122·4 (2)
C(9a)–C(9)–C(4a′)	115·1 (1)	C(1)–C(9a)–C(4a)	104·7 (1)
C(1)–C(9a)–C(9)	132·8 (2)	C(4a)–C(9a)–C(9)	122·5 (1)
C(2)–C(10)–O(10)	125·5 (2)	C(2)–C(10)–O(11)	110·3 (1)
O(10)–C(10)–O(11)	124·2 (2)	C(10)–O(11)–C(12)	116·6 (1)
C(3)–C(13)–O(13)	124·9 (2)	C(3)–C(13)–O(14)	111·3 (1)
O(13)–C(13)–O(14)	123·8 (2)	C(13)–O(14)–C(15)	116·1 (1)
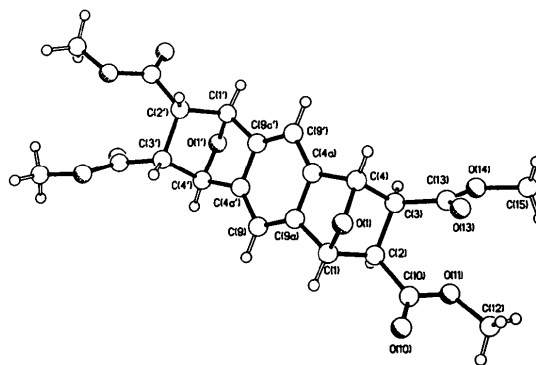
Fig. 1. Ball-and-stick representation of the structure of (3) showing the atomic numbering scheme.

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C_{22}H_{22}O_{10}

Discussion. The structure of (3) 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 (3) possesses crystallographic C_i symmetry. All four ester groups are found to have the *exo* configuration in (3) as already observed (Kohnke *et al.*, 1988a) for the tetraester (1) derived by an analogous synthetic route. In contrast with (1), adjacent pairs of carbonyl functions are directed towards the *exo* face. However, they are not aligned in a parallel manner. The C(1)—C(2)—C(10)—O(10) and C(4)—C(3)—C(13)—O(13) torsion angles are 5·1 (2) and 40·2 (2)°, respectively. The dihedral angles between the C(1)—O(1)—C(4) and the C(1)—C(4)—C(4a)—C(9a) and C(1)—C(2)—C(3)—C(4) mean planes are 128 (1) and 121 (1)°, respectively, and that between the C(1)—C(2)—C(3)—C(4) and the C(1)—C(4)—C(4a)—C(9a) mean planes is 111 (1)°. The C(1)—O(1)—C(4) plane is canted further away from the mean plane of the aromatic ring. This observation is consistent with the increase of the C(2)—C(3) bond length [1·571 (2) Å] in (3) relative to the C(4a)—C(9a) bond [1·397 (2) Å] whereas, in tetraester (1), the situation was the converse. As in the case of the *anti* isomer (2) of 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene (Hart *et al.*, 1983; Kohnke *et al.*, 1988b), there is (Fig. 2) a slight but significant fold (4°) of the C(1)—C(4)—C(4a)—C(9a) plane out of that of the aromatic ring.

* 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 44646 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
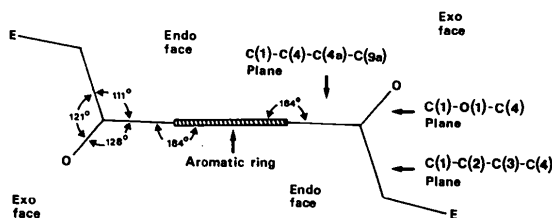

Fig. 2. Diagrammatic representation of the structure of (3) defining space around the molecule, mean planes in the molecule, and showing dihedral angles.

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rel-(1R,4S,5R,8S)-1,4:5,8-Diepoxy-1,4,5,8-tetrahydroanthracene

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Abstract. $C_{14}H_{10}O_2$, $M_r = 210\cdot2$, monoclinic, $P2_1/n$, $a = 8\cdot046$ (1), $b = 14\cdot573$ (3), $c = 8\cdot718$ (1) Å, $\beta = 95\cdot47$ (1)°, $V = 1018$ Å³, $Z = 4$, $D_x = 1\cdot370$ Mg m⁻³, Cu $K\alpha$ radiation, $\lambda = 1\cdot54178$ Å, $\mu = 0\cdot696$ mm⁻¹, $F(000) = 440$, room temperature, $R = 0\cdot040$ for 1304 observed reflections with $|F_o| > 3\sigma(|F_o|)$. Symmetry-related pairs of molecules of the title compound pack so that an olefinic hydrogen atom in one molecule interacts electrostatically with the π system on the *endo* face of another molecule.

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