rel-(1R,4S,5S,8R)-1,4:5,8-Diepoxy-1,4,5,8-tetrahydroanthracene: An Example of Polymorphism

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Abstract. $C_{14}H_{10}O_2$, $M_r = 210 \cdot 2$, monoclinic, $P2_1/c$, $a = 6 \cdot 120$ (2), $b = 6 \cdot 996$ (2), $c = 12 \cdot 122$ (3) Å, $\beta = 104 \cdot 14$ (2)°, $V = 503$ Å^3, $Z = 2$ (the molecule possesses a centre of symmetry), $D_x = 1 \cdot 386$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1 \cdot 54178$ Å, $\mu = 0 \cdot 704$ mm^{-1}, $F(000) = 220$, room temperature, $R = 0 \cdot 042$ for 654 observed reflections with $|F_o| > 3\sigma(|F_o|)$. The title compound is geometrically identical to a structure already reported in the literature [Hart, Raju, Meador & Ward (1983). *J. Org. Chem.* **48**, 4357–4360] but is shown to be an alternative polymorphic form differing both in unit-cell parameters and crystal packing from that previously observed.

Introduction. During our recent synthesis (Kohnke, Slawin, Stoddart & Williams, 1987) of macropolycyclic molecules with rigid toroidal shapes, we identified the *syn* isomer (1) of 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene as a suitable bisdienophilic precursor for use in a sequence of Diels–Alder reactions with 2,3,5,6-tetramethylene-7-oxabicyclo[2.2.1]heptane. The *syn* isomer (1) is obtained (Hart, Raju, Meador & Ward, 1983) in admixture with the *anti* isomer (2) from a reaction of furan with the bisaryne generated *in situ* from 1,2,4,5-tetrabromobenzene with butyllithium. The *syn* and *anti* isomers (1) and (2), which can be easily separated either by silica gel chromatography or by fractional crystallization from acetone–methanol, have been reported by Hart *et al.* (1983) to have m.p. 464–466 K and m.p. 518 K, respectively. When we repeated the synthesis and separation, we obtained two isomers with m.p. 466 K and m.p. 528–530 K. Although the lower-melting product matches the literature value for the *syn* isomer (1), the higher-melting product differed significantly from the value reported for the *anti* isomer (2). As both isomers give identical ¹H and ¹³C NMR spectra and in view of the

ambiguity in the melting points of the supposedly *anti* isomer, a single-crystal analysis was carried out. Preliminary crystallographic investigations showed the compound to have a unit cell and space group both of which are different from those reported by Hart *et al.* (1983) for the *anti* isomer (2). A full structural analysis of the higher-melting product was therefore carried out. We report the results here.

(1)　　　　(2)
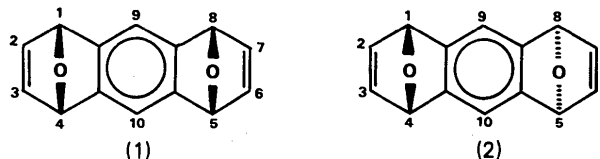
Experimental. Single crystals (found: C 79·5, H, 4·9%. $C_{14}H_{10}O_2$ requires C 80·0, H 4·8%) of (2), suitable for X-ray crystallography, were grown at room temperature from ethyl acetate–light petroleum and had m.p. 528–530 K. Crystal size 0·20 × 0·37 × 0·43 mm. Refined unit-cell parameters obtained from setting angles of 15 reflections with $9 \le \theta \le 31°$. Nicolet $R3m$ diffractometer. 683 independent reflections ($\theta \le 58°$) measured, Cu $K\alpha$ radiation (graphite monochromator), ω scan. 654 [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range $h -6/6$, $k\ 0/7$, $l\ 0/13$; two check reflections measured every 50 reflections, net count constant; Lorentz and polarization corrections, no absorption. Structure solved by direct methods; non-hydrogen atoms refined anisotropically; positions of H atoms on C(1) and C(4) located from ΔF map and refined isotropically; positions of all other H atoms calculated (C–H = 0·96 Å), assigned isotropic thermal parameters, $U(H) = 1 \cdot 2\ U_{eq}(C)$, and allowed to ride on parent C atoms. An empirical extinction correction was applied [$g = 0 \cdot 16$ (2)]. Refinement using F magnitudes by block-cascade full-matrix least squares; $R = 0 \cdot 042$; $wR = 0 \cdot 059$ [$w^{-1} = \sigma^2(F) + 0 \cdot 00022F^2$]. $(\Delta/\sigma)_{max} = 0 \cdot 025$; residual electron density in difference map within $-0 \cdot 15$ and $0 \cdot 15$ e Å^{-3}; atomic scattering factors and dispersion corrections from *International Tables*

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for X-ray Crystallography (1974). 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.

In addition to possessing crystallographic C_i symmetry, the diepoxytetrahydroanthracene (2) has C_{2h} molecular symmetry consistent with the *anti* con-

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* 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 44645 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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)	3135 (3)	1329 (2)	1091 (1)	81 (1)
C(1)	836 (4)	1469 (3)	1218 (2)	61 (1)
C(2)	1297 (4)	2082 (3)	2459 (2)	63 (1)
C(3)	3081 (4)	3179 (3)	2644 (2)	64 (1)
C(4)	3787 (4)	3230 (4)	1517 (2)	69 (1)
C(4a)	1991 (3)	4401 (3)	684 (2)	48 (1)
C(9a)	67 (3)	3244 (3)	492 (1)	47 (1)
C(9)	−1964 (3)	3813 (3)	−197 (2)	52 (1)

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

O(1)—C(1)	1·456 (3)	O(1)—C(4)	1·447 (3)
C(1)—C(2)	1·522 (3)	C(1)—C(9a)	1·529 (3)
C(2)—C(3)	1·308 (3)	C(3)—C(4)	1·531 (3)
C(4)—C(4a)	1·535 (3)	C(4a)—C(9a)	1·401 (2)
C(4a)—C(9')	1·381 (3)	C(9a)—C(9)	1·376 (2)
C(9)—C(4a')	1·381 (3)		

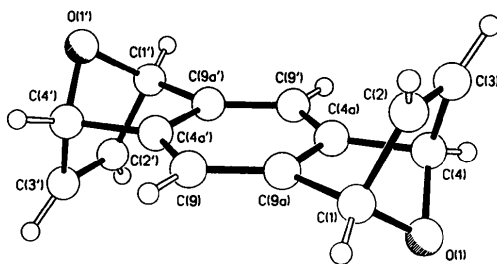| C(1)—O(1)—C(4)	95·1 (2)	O(1)—C(1)—C(2)	99·9 (2)
O(1)—C(1)—C(9a)	99·4 (2)	C(2)—C(1)—C(9a)	107·3 (2)
C(1)—C(2)—C(3)	106·3 (2)	C(2)—C(3)—C(4)	105·4 (2)
O(1)—C(4)—C(3)	100·6 (2)	O(1)—C(4)—C(4a)	99·5 (1)
C(3)—C(4)—C(4a)	106·7 (2)	C(4)—C(4a)—C(9a)	103·9 (2)
C(4)—C(4a)—C(9')	134·1 (2)	C(9a)—C(4a)—C(9')	122·0 (1)
C(1)—C(9a)—C(4a)	104·2 (1)	C(1)—C(9a)—C(9)	133·6 (2)
C(4a)—C(9a)—C(9)	122·2 (2)	C(9a)—C(9)—C(4a')	115·8 (2)

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

figuration observed for the bridging oxygen atoms O(1) and O(1'). Obviously, the *anti* isomer (2) can crystallize in polymorphic forms. The bond lengths and angles in our polymorph do not differ significantly from those reported previously (Hart *et al.*, 1983) for (2). The dihedral angles (Fig. 2) between the C(1)—O(1)—C(4) and the C(1)—C(4)—C(4a)—C(9a) and the C(1)—C(2)—C(3)—C(4) mean planes are 122 (1) and
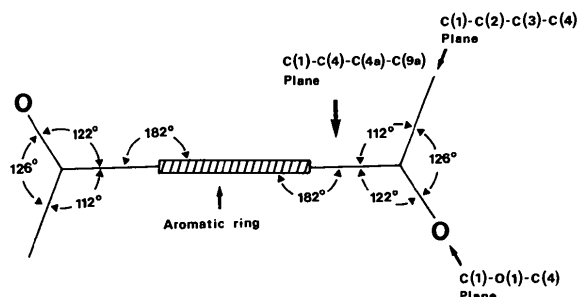

Fig. 2. Diagrammatic representation of the structure of (2) defining mean planes in the molecule and showing dihedral angles.
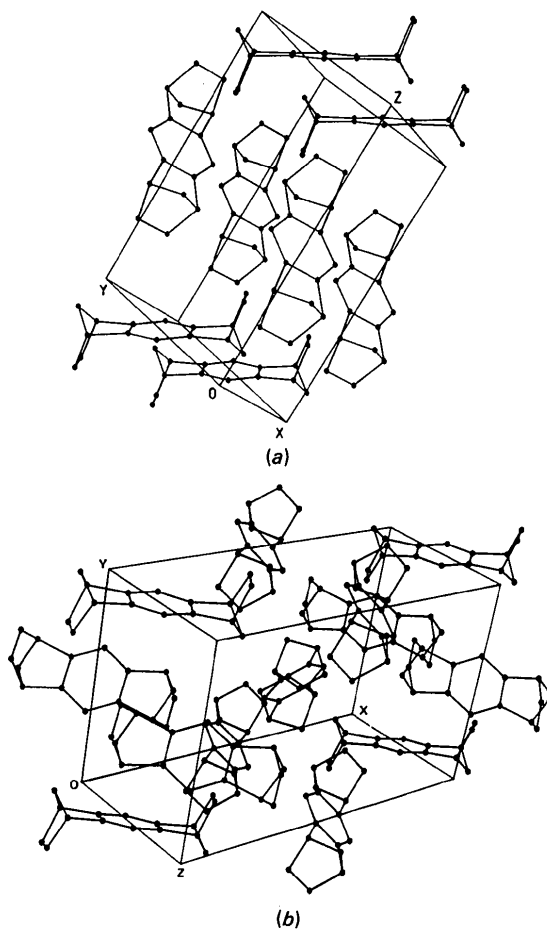

(a)

(b)

Fig. 3. (a) Packing diagram of the title compound (2). (b) Packing diagram of a polymorph (Hart *et al.*, 1983) of (2).

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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