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rel-(1*R*,4*S*,5*R*,8*S*)-1,4:5,8-Diepoxy-1,4,5,8-tetrahydro-9,10-dimethylphenanthrene

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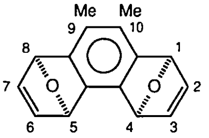
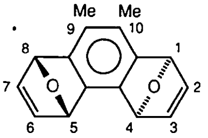
Abstract. $C_{16}H_{14}O_2$, $M_r = 238.3$, monoclinic, $P2_1/n$, $a = 8.134\,(2)$, $b = 8.877\,(3)$, $c = 16.681\,(4)$ Å, $\beta = 90.77\,(2)°$, $V = 1204$ Å^3, $Z = 4$, $D_x = 1.31$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 0.65$ mm^{-1}, $F(000) = 504$, room temperature, $R = 0.049$ for 1478 observed reflections with $|F_o| > 3\sigma(|F_o|)$. Enantiomerically related pairs of molecules of the title compound pack in the crystal so that an olefinic H atom in each interacts electrostatically with an O atom in the endoxide bridge of the other.

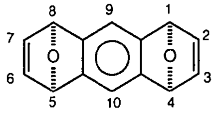
Introduction. Our interest (Stoddart, 1988*a*,*b*, 1989; Ellwood, Mathias, Stoddart & Kohnke, 1988; Kohnke & Stoddart, 1989; Kohnke, Mathias & Stoddart, 1989*a*,*b*) in the use of a repetitive sequence of trebly diastereoselective Diels–Alder reactions to synthesise polyacene and cyclacene derivatives has led us to identify *syn*-1,4:5,8-diepoxy-1,4,5,8-tetrahydro-9,10-dimethylphenanthrene (1) and its *anti* isomer (±)-(2) as useful bisdienophilic building blocks. Previously, it has been claimed (Hart, Shamouilian & Takehira, 1981; Hart & Shamouilian, 1981) that the lithiation of 4,5-dibromo-3,6-diiodo-*o*-xylene with two molar equivalents of *n*-butyllithium, followed by trapping of the bisaryne equivalent generated *in situ* with two equivalents of furan affords only one diastereoisomeric 2:1 adduct. On repeating this reaction, we obtained two diastereoisomers which could be separated by column chromatography on silica gel using chloroform containing 1% propan-2-ol as the eluant, but could not assign to them unambiguously their relative configurations by NMR (^{1}H or ^{13}C) spectroscopic analysis. Here, we report the full crystallographic analysis of the chromatographically more mobile isomer, which is shown to be a racemic mixture (±)-(2) in which the endoxide bridges have the *anti* configuration.



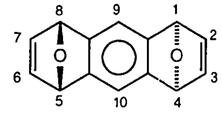
(1)



(±)-(2)



(3)



(4)

Experimental. Treatment of 4,5-dibromo-3,6-diodo-*o*-xylene with 2.2 molar equivalents of *n*-butyllithium at 250 K, followed by trapping of the bisaryne equivalent *in situ* with 2.0 molar equivalents of furan, afforded an equimolar mixture of the diastereoisomeric bisdienophiles (1) and (2). Compound (2) was obtained as a crystalline sample following fractional crystallization from toluene. Single crystals (found: C, 80.3; H, 5.90%. $C_{16}H_{14}O_2$ requires C, 80.6; H, 5.90%) of the *anti* isomer (2), suitable for X-ray crystallography, were grown at room temperature by vapour diffusion of pentane into a deuteriochloroform solution of (2) and had m.p. 437–439 K. Crystal size 0.33 × 0.50 × 0.67 mm. Refined unit-cell parameters obtained from setting angles of 18 reflections with $10.6 \le 2\theta \le 32.2°$. Nicolet *R*3*m* diffractometer. 1877 measured, 1620 independent ($R_{\rm int} = 0.038$) reflections ($2\theta \le 116°$), Cu $K\alpha$ radiation (graphite monochromator), ω scan. 1478 [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range h −8/8, k 0/9, l 0/18: two check reflections measured every 50 reflections, no significant change in net counts; Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods. The non-H atoms were refined anisotropically. All the H

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atoms were located from a ΔF map. The geometries of those on C(2), C(3), C(8) and C(9) were idealized, C—H = 0.96 Å, assigned isotropic thermal parameters, $U(\text{H}) = 1.2\ U_{\text{eq}}(\text{C})$, and allowed to ride on their parent C atoms. Those on C(1), C(4), C(7) and C(10) were refined isotropically subject to a C—H distance constraint. The methyl groups were refined as idealized rigid bodies. Refinement using F magnitudes by block-cascade full-matrix least squares; $R = 0.049$; $wR = 0.059$ [$w^{-1} = \sigma^2(F) + 0.00043F^2$]. $S = 2.68$; 186 refined parameters; $(\Delta/\sigma)_{\text{max}} = 0.037$; residual electron density in final difference map within 0.16 and -0.21 e Å^{-3}; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1985).

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

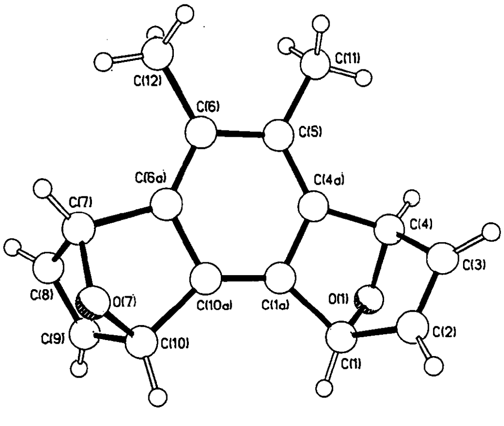

Fig. 1. Ball-and-stick representation of the structure of (2) showing the atomic numbering scheme.

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}
O(1)	5003 (2)	1589 (2)	3824 (1)	53 (1)*
C(1)	6394 (3)	824 (3)	4184 (1)	47 (1)*
C(1a)	6995 (3)	2064 (2)	4754 (1)	37 (1)*
C(2)	7572 (3)	815 (3)	3481 (1)	58 (1)*
C(3)	7285 (3)	2075 (3)	3082 (1)	58 (1)*
C(4)	5931 (3)	2884 (3)	3539 (1)	46 (1)*
C(4a)	6710 (2)	3417 (2)	4329 (1)	36 (1)*
C(5)	7129 (2)	4818 (2)	4615 (1)	36 (1)*
C(6)	7909 (2)	4902 (2)	5394 (1)	36 (1)*
C(6a)	8134 (2)	3579 (2)	5805 (1)	36 (1)*
C(7)	8801 (3)	3224 (2)	6651 (1)	46 (1)*
O(7)	9554 (2)	1768 (2)	6505 (1)	59 (1)*
C(8)	7321 (3)	2740 (3)	7133 (1)	54 (1)*
C(9)	6879 (3)	1407 (3)	6850 (1)	58 (1)*
C(10)	8086 (3)	1061 (2)	6184 (1)	51 (1)*
C(10a)	7687 (2)	2148 (2)	5498 (1)	37 (1)*
C(11)	6773 (3)	6227 (3)	4140 (1)	53 (1)*
C(12)	8448 (3)	6394 (2)	5737 (1)	47 (1)*

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

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(1)	1.443 (3)	O(1)—C(4)	1.458 (3)
C(1)—C(1a)	1.530 (3)	C(1)—C(2)	1.525 (3)
C(1a)—C(4a)	1.412 (3)	C(1a)—C(10a)	1.357 (3)
C(2)—C(3)	1.320 (4)	C(3)—C(4)	1.527 (3)
C(4)—C(4a)	1.529 (3)	C(4a)—C(5)	1.374 (3)
C(5)—C(6)	1.439 (3)	C(5)—C(11)	1.507 (3)
C(6)—C(6a)	1.371 (3)	C(6)—C(i2)	1.506 (3)
C(6a)—C(7)	1.538 (3)	C(6a)—C(10a)	1.416 (3)
C(7)—O(7)	1.452 (3)	C(7)—C(8)	1.519 (3)
O(7)—C(10)	1.446 (3)	C(8)—C(9)	1.322 (3)
C(9)—C(10)	1.525 (3)	C(10)—C(10a)	1.529 (3)
C(1)—O(1)—C(4)	95.8 (2)	O(1)—C(1)—C(1a)	99.3 (2)
O(1)—C(1)—C(2)	100.4 (2)	C(1a)—C(1)—C(2)	106.5 (2)
C(1)—C(1a)—C(4a)	104.5 (2)	C(1)—C(1a)—C(10a)	137.1 (2)
C(4a)—C(1a)—C(10a)	118.4 (2)	C(1)—C(2)—C(3)	105.9 (2)
C(2)—C(3)—C(4)	105.7 (2)	O(1)—C(4)—C(3)	99.9 (2)
O(1)—C(4)—C(4a)	100.0 (2)	C(3)—C(4)—C(4a)	106.4 (2)
C(1a)—C(4a)—C(4)	103.5 (2)	C(1a)—C(4a)—C(5)	123.9 (2)
C(4)—C(4a)—C(5)	132.7 (2)	C(4a)—C(5)—C(6)	117.7 (2)
C(4a)—C(5)—C(11)	121.6 (2)	C(6)—C(5)—C(11)	120.7 (2)
C(5)—C(6)—C(6a)	117.5 (2)	C(5)—C(6)—C(12)	120.8 (2)
C(6a)—C(6)—C(12)	121.8 (2)	C(6)—C(6a)—C(7)	132.7 (2)
C(6)—C(6a)—C(10a)	123.7 (2)	C(7)—C(6a)—C(10a)	103.6 (2)
C(6a)—C(7)—O(7)	100.0 (2)	C(6a)—C(7)—C(8)	105.7 (2)
O(7)—C(7)—C(8)	100.1 (2)	C(7)—O(7)—C(10)	95.8 (2)
C(7)—C(8)—C(9)	106.1 (2)	C(8)—C(9)—C(10)	105.5 (2)
O(7)—C(10)—C(9)	100.3 (2)	O(7)—C(10)—C(10a)	99.8 (2)
C(9)—C(10)—C(10a)	106.6 (2)	C(1a)—C(10a)—C(6a)	118.8 (2)
C(1a)—C(10a)—C(10)	137.0 (2)	C(6a)—C(10a)—C(10)	104.1 (2)

The molecule has the *anti* configuration (2) possessing non-crystallographic C_2 symmetry. However in the crystal, with space group $P2_1/n$ there are equal numbers of (+) and (−) molecules. Clearly, if (±)-(2) can be resolved, then this bisdienophilic building block could be used in repetitive trebly diastereoselective Diels–Alder reactions for imparting chirality to a homogeneous series of oligomeric adducts. The combination of the steric interaction between the *ortho* methyl substituents and the *anti* disposition of the bicyclic rings produces a slight twisting of the aromatic ring. This distortion can be seen in the deviations from planarity of the atoms comprising this ring which range between 0.005 (5) Å for C(4a) to 0.14 (1) Å for C(6). More noticeable are the non-zero torsional angles (1) for C(11)—C(5)—C(6)—C(12) of −2.4 (3)° and (2) for C(1)—C(1a)—C(10a)—C(10) of −7.0 (5)°, and (3) about the ring diagonal C(4)—C(4a)···C(6a)—C(7)

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* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54560 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0065]

of 13.7 (6)°. The dihedral angles between C(1)—O(1)—C(4) and the C(1)—C(2)—C(3)—C(4) and the C(1)—C(1a)—C(4a)—C(4) mean planes are 126 (1)° and 122 (1)°, respectively, and that between C(1)—C(2)—C(3)—C(4) and the C(1)—C(1a)—C(4a)—C(4) mean planes is 112 (1)°. The equivalent dihedral angles in the other bicyclic ring system are identical. Moreover, these values are the same as those we have observed (Kohnke, Stoddart, Slawin & Williams, 1988*a*) for *anti*-1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene (4). However, it is interesting to note that there is a significant difference in bond lengths around the aromatic ring of (±)-(2). Whilst the C(1a)—C(4a), C(5)—C(6) and C(6a)—C(10a) bonds are 1.412 (3), 1.439 (3) and 1.416 (3) Å long, respectively, the alternating C(4a)—C(5), C(6)—C(6a), and C(1a)—C(10a) bonds are 1.374 (3), 1.371 (3) and 1.357 (3) Å long, respectively, *i.e.* there is a pronounced alternation of the bond orders around the aromatic ring. This is in striking contrast to the bonding observed (Kohnke, Stoddart, Slawin & Williams, 1988*a*,*b*) for the *anti*-1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene (4) and its *syn* isomer (3) where the analogous bonds show no significant variations.

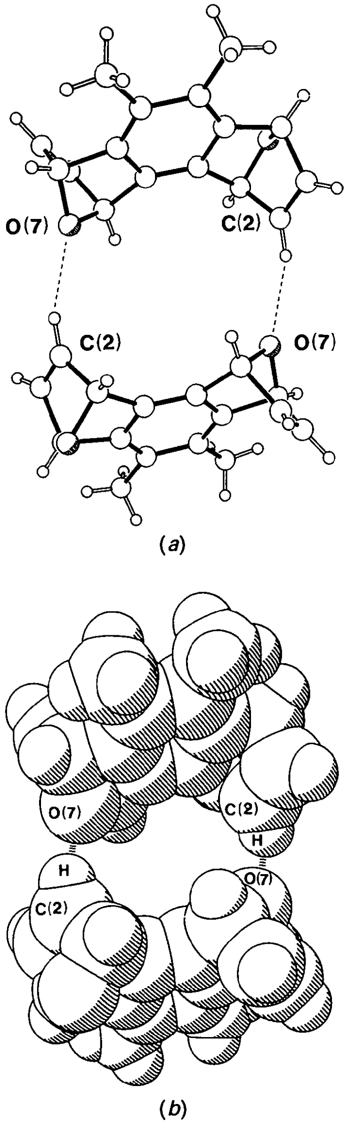

Fig. 2. (a) Ball-and-stick and (*b*) space-filling representation of the packing of a centrosymmetrically related enantiomeric pair of molecules (±)-(2).

Inspection of the packing in (2) shows that (±)-pairs of molecules, related by one of the crystallographic centres of symmetry are oriented such that one of the methyl substituents [C(11)] in one molecule lies directly over the π face of the aromatic ring in the other at a distance of 3.69 (2) Å from the ring centroid and *vice versa*. One of the methyl H atoms is directed towards the opposite aromatic ring plane and at a distance of 2.88 (1) Å. More interesting is the arrangement (Figs. 2*a*,*b*) of the molecules about a different crystallographic symmetry centre which reveals pairs of weak C—H···O interactions between one of the olefinic H atoms [attached to C(2)] and the bridging oxygen atom O(7); C(2)···O(7) is 3.28 (2) Å. In isolation this interaction is weak but two such interactions, creating a pseudomacrocyclic superstructure, are probably significant in determining this packing arrangement.

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