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# *rel*-(1*S*,2*S*,3*S*,3a*R*,4*R*,7*S*,7a*R*)-1,2,3,4,5,6,7,7a-Octahydro-1,3a-etheno-4,7-methano-3a*H*-indene-2,3-dicarboxylic Anhydride, $C_{14}H_{14}O_3$

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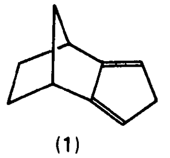
(*Received* 26 *January* 1984; *accepted* 10 *April* 1984)

**Abstract.** $M_r = 230{\cdot}26$, monoclinic, $P2_1/n$, $a = 6{\cdot}387\,(2)$, $b = 10{\cdot}216\,(3)$, $c = 16{\cdot}897\,(7)$ Å, $\beta = 100{\cdot}27\,(3)°$, $V = 1084{\cdot}9\,(6)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}41$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}06$ cm$^{-1}$, $F(000) = 488$, room temperature, $R = 0{\cdot}055$ for 1357 unique reflections with intensities greater than $3\sigma(I)$. The six-membered ring of the norbornane system is in a skew-boat conformation owing to the fusion of two five-membered rings and a methylene bridge. There are two short intramolecular contacts, H(10)-*endo*···H(5) = 2·20 (4) and H(8)-*endo*···H(2) = 2·17 (5) Å; H(8)-*endo* may also interact with the C(2) $\pi$ system.

**Introduction.** Isodicyclopentadiene (1) is prepared by dehydration of the tricyclic alcohol (4) over alumina at 573 K (Alder, Flock & Janssen, 1956). Loss of water does not yield (1) directly, but the reaction passes through (3) and (2) by two consecutive 1,5-sigmatropic hydrogen shifts. Since isomers (2) and (3) have not been detected in this reaction system, the rearrangements must be rapid. In the reaction of (1) with inactive dienophiles at elevated temperatures (453 K) only cycloadducts of (2) are obtained (Subramanyam, Bartlett, Iglesias, Watson & Galloy, 1982; Paquette, Williams, Carr, Charumilind & Blount, 1982). Isomer (1) shows *endo* Diels–Alder stereoselectivity toward certain dienophiles, but isomer (2) has a norbornene-type double bond and shows *exo* selectivity. Isomer (3) can be prepared by the careful quenching of (5) with water in tetrahydrofuran or ether (Bartlett & Wu, 1983). Although (3) isomerizes to (1) on heating to 353 K, it can be purified from a mixture by the selective reaction of (1) with maleic anhydride at 273 K. The Diels–Alder reactivities of the three isomers are in the order (2) > (1) > (3).

The slow reaction of (3) with maleic anhydride at 273 K yielded the title compound (6) as the only adduct. The structure of (6) confirms the structure of (3) and the *exo*-face selectivity.



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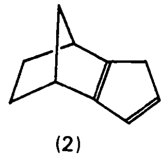

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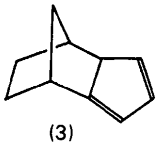

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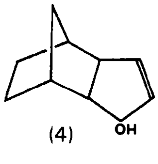

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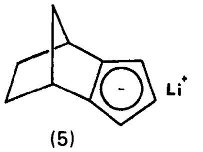

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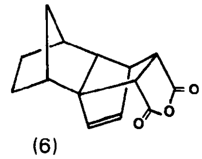

(6)

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Table 1. *Atomic positional parameters* (×$10^4$) *and* $U_{eq}$ *values* (Å$^2$ × $10^3$)

| | $x$ | $y$ | $z$ | $U_{eq}$* |
|---|---|---|---|---|
| C(1) | 2250 (3) | 2259 (2) | 3764 (1) | 27 |
| C(2) | 2635 (3) | 783 (2) | 3799 (1) | 30 |
| C(3) | 776 (4) | 177 (2) | 3794 (2) | 37 |
| C(4) | −901 (3) | 1214 (2) | 3708 (1) | 35 |
| C(5) | 233 (4) | 2410 (2) | 4140 (2) | 32 |
| C(6) | 1179 (4) | 2821 (2) | 5012 (2) | 39 |
| C(7) | 2930 (4) | 1913 (3) | 5440 (2) | 43 |
| C(8) | 4892 (4) | 2228 (3) | 5032 (1) | 42 |
| C(9) | 3910 (4) | 3110 (2) | 4319 (1) | 35 |
| C(10) | 2514 (4) | 3974 (2) | 4760 (2) | 42 |
| C(11) | 1180 (3) | 2521 (2) | 2869 (1) | 31 |
| C(12) | −973 (3) | 1790 (2) | 2828 (2) | 35 |
| C(13) | 2202 (4) | 1877 (2) | 2244 (1) | 37 |
| O(13) | 3838 (3) | 2107 (2) | 2026 (1) | 55 |
| C(14) | −907 (4) | 739 (3) | 2212 (2) | 44 |
| O(14) | −2139 (3) | −108 (2) | 1989 (1) | 62 |
| O(15) | 931 (3) | 851 (2) | 1885 (1) | 47 |

* $U_{eq} = \frac{1}{3}\sum U_{ij} a^*a^*(\mathbf{a}_i.\mathbf{a}_j)$.

Table 2. *Interatomic distances* (Å) *and valence angles* (°)

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·528 (3) | C(6)–C(10) | 1·557 (4) |
| C(1)–C(5) | 1·542 (3) | C(7)–C(8) | 1·567 (4) |
| C(1)–C(9) | 1·551 (3) | C(8)–C(9) | 1·545 (3) |
| C(1)–C(11) | 1·569 (3) | C(9)–C(10) | 1·538 (4) |
| C(2)–C(3) | 1·338 (3) | C(11) C(12) | 1·555 (3) |
| C(3)–C(4) | 1·495 (3) | C(11)–C(13) | 1·490 (3) |
| C(4)–C(5) | 1·537 (3) | C(12)–C(14) | 1·502 (4) |
| C(4)–C(12) | 1·592 (3) | C(13)–O(13) | 1·191 (3) |
| C(5)–C(6) | 1·548 (3) | C(13)–O(15) | 1·397 (3) |
| C(6)–C(7) | 1·532 (3) | C(14)–O(14) | 1·184 (3) |
| | | C(14)–O(15) | 1·387 (3) |
| | | | |
| C(2)–C(1)–C(5) | 102·9 (2) | C(7)–C(8)–C(9) | 102·6 (2) |
| C(2)–C(1)–C(9) | 116·2 (2) | C(1)–C(9)–C(8) | 106·4 (2) |
| C(2)–C(1)–C(11) | 104·2 (2) | C(1)–C(9)–C(10) | 102·8 (2) |
| C(5)–C(1)–C(9) | 103·1 (2) | C(8)–C(9)–C(10) | 98·4 (2) |
| C(5)–C(1)–C(11) | 97·4 (2) | C(6)–C(10)–C(9) | 95·3 (2) |
| C(9)–C(1)–C(11) | 128·4 (2) | C(1)–C(11)–C(12) | 101·0 (2) |
| C(1)–C(2)–C(3) | 108·7 (2) | C(1)–C(11)–C(13) | 116·0 (2) |
| C(2)–C(3)–C(4) | 107·0 (2) | C(12)–C(11)–C(13) | 104·6 (2) |
| C(3)–C(4)–C(5) | 104·4 (2) | C(4)–C(12)–C(11) | 105·0 (2) |
| C(3)–C(4)–C(12) | 104·7 (2) | C(4)–C(12)–C(14) | 112·5 (2) |
| C(5)–C(4)–C(12) | 94·7 (2) | C(11)–C(12)–C(14) | 103·9 (2) |
| C(1)–C(5)–C(4) | 94·7 (2) | C(11)–C(13)–O(13) | 130·7 (2) |
| C(1)–C(5)–C(6) | 101·9 (2) | C(11)–C(13)–O(15) | 110·1 (2) |
| C(4)–C(5)–C(6) | 137·7 (2) | O(13)–C(13)–O(15) | 119·2 (2) |
| C(5)–C(6)–C(7) | 114·4 (2) | C(12)–C(14)–O(14) | 130·0 (2) |
| C(5)–C(6)–C(10) | 94·9 (2) | C(12)–C(14)–O(15) | 110·3 (2) |
| C(7)–C(6)–C(10) | 101·4 (2) | O(14)–C(14)–O(15) | 119·7 (2) |
| C(6)–C(7)–C(8) | 104·0 (2) | C(13)–O(15)–C(14) | 110·9 (2) |

**Experimental.** Crystal of dimensions 0·50 × 0·40 × 0·30 mm, Syntex $P2_1$ four-circle diffractometer. Lattice parameters by least-squares refinement of angular data for 15 medium-angle reflections. Space group consistent with systematic absences $h+l = 2n+1$ for $h0l$. $\theta$:$2\theta$ scan technique ($1·05 \leq 2\theta \leq 49·4°$), variable scan speed (3·91 to 29·30° min$^{-1}$), intensities of 1717 independent reflections measured ($0 \leq h \leq 7$, $0 \leq k \leq 11$, $-19 \leq l \leq 19$), 1357 with $I > 3\sigma(I)$. 1 monitored reflection showed no change in intensity greater than $3\sigma(I)$. Lorentz and polarization but no absorption corrections. All non-hydrogen atoms located in $E$ map phased by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H-atom positions calculated, checked with difference Fourier map, but not refined. Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$ (derived from counting statistics). At convergence $R = 0·055$, $R_w = 0·059$, $S = 3·92$ (154 parameters), $(\Delta/\sigma)_{av} = 0·11$ and $(\Delta/\sigma)_{max} = 0·81$; largest peak in final difference synthesis 0·25 e Å$^{-3}$. Final calculations performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic scattering factors for C and O from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965). Atomic positional parameters and $U_{eq}$ values are listed in Table 1 while Table 2 gives bond lengths and valence angles.*

**Discussion.** Fig. 1 is an *ORTEP* (Johnson, 1971) drawing of the title compound. The six-membered ring of the norbornane system is normally restricted to the boat conformation owing to the bridging methylene group; however, the strain imposed by the ring fusions at C(1) and C(5) leads to a twist-boat conformation. The internal torsion angles of the six-membered ring are −9·3, −63·0, +85·4, −22·1, −52·3, +72·2 (e.s.d. 0·6°) compared with the values of 0, ± 54, 0, ± 54 for an ideal boat (Bucourt, 1974). The skew-boat conformation leads to a twist of the methylene bridge which is reflected in nonequivalent H(10)-*exo*···H(8)-*exo* and H(10)-*exo*···H(7)-*exo* distances of 2·49 (4) and 2·80 (4) Å.

Intramolecular contacts between H(5), H(11) and H(12) range from 2·37 to 2·45 Å. There are nine intermolecular hydrogen atom contacts within the range 2·42 to 2·59 Å. Intramolecular distances H(10)-*endo*···H(5) and H(8)-*endo*···H(2) of 2·20 (4) and 2·17 (5) Å are shorter than normal van der Waals

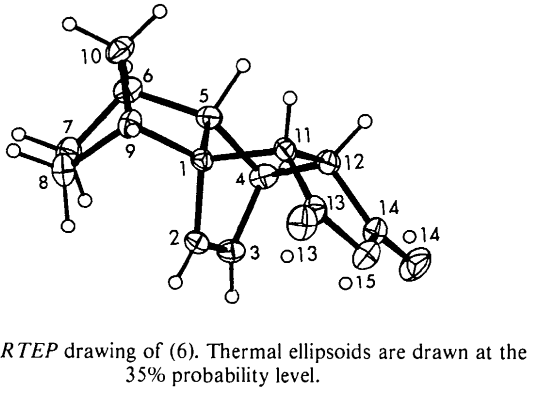

Fig. 1. *ORTEP* drawing of (6). Thermal ellipsoids are drawn at the 35% probability level.

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* Lists of structure factors, thermal parameters and hydrogen-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39394 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

contacts. H(8)-*endo* lies only 2·41 (5) Å above C(2) and probably experiences some interaction with the C(2) $\pi$ system. The C(2)–C(3) $\pi$ system and the $\pi$ system of the anhydride may spatially overlap since the C(2)···C(13) and C(3)···O(14) separations are only 2·824 (4) and 2·757 (4) Å. If a homoconjugative interaction exists it does not affect the C(2)–C(3) separation of 1·339 (3) Å which is the same as found in other norbornene and sesquinorbornene systems (Watson, Galloy, Bartlett & Roof, 1981).

A least-squares plane fitted to C(9)C(1)C(5)C(6) *B* shows deviations of 0·11 (1) Å from planarity while planes fitted to C(6)C(7)C(8)C(9) *A*, C(11)C(12)-C(13)O(13)C(14)O(14)O(15) *D*, C(1)C(2)C(3)C(4) *E* and C(1)C(4)C(11)C(12) *F* show maximum deviations of 0·051 (6), 0·043 (6), 0·005 (6), and 0·013 (8) Å. The interplanar angles *A–B*, *B–C*, *A–C*, *D–E* and *E–F* are 115·8 (6), 121·9 (4), 121·9 (3), 119·5 (4) and 110·0 (4)°.

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# Tri-[*b*,*e*,*h*]-(4,5-dimethoxybenzo)cyclonona-2,5,8-trien-1-one,* $C_{27}H_{28}O_7$

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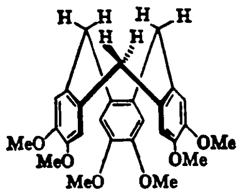
(*Received* 9 *January* 1984; *accepted* 11 *April* 1984)

**Abstract.** $M_r = 464·52$, orthorhombic, $P2_12_12_1$, $a = 16·735$ (2), $b = 18·763$ (3), $c = 7·805$ (1) Å, $V = 2450·5$ (6) Å$^3$, $Z = 4$, $D_m$(flotation, KI + water) = 1·253, $D_x = 1·259$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 0·7$ cm$^{-1}$, $F(000) = 984$, $T = 295$ K, final $R = 0·054$ for 1244 reflections. The molecule contains a nine-membered ring with a twist conformation, fused to three planar six-membered rings; the whole molecule has roughly $C_2$ symmetry, with maximum deviation in torsion angles of 16·8° from an exactly symmetrical geometry, and dihedral-angle differences of up to 18·3°. Bond lengths and angles are normal.

**Introduction.** Cyclotriveratrylene (I) possesses an interesting ring system consisting of a cyclononatriene ring to which three benzo rings are fused; the molecule is believed to have a 'crown' conformation, with the benzo rings forming the three sides of a trigonal pyramid (Lindsey, 1963, 1965; Erdtman, Haglid & Ryhage, 1964; Goldup, Morrison & Smith, 1965; Miller & Gesner, 1965).

For the ketone (II) derived from cyclotriveratrylene, spectroscopic data (UV, IR and NMR) suggest a twist conformation similar to that of cyclohexanone, which is flexible in solution (Anand, Cookson, Halton & Stevens, 1966). Crystals of (II) were made available for X-ray study about twenty years ago, but the problem seemed too difficult to be solved by the techniques of that era; the structure has now been determined by direct methods.



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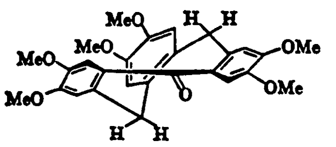

(II)

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* Alternative IUPAC name: 10,15-dihydro-2,3,7,8,12,13-hexamethoxy-5*H*-tribenzo[*a*,*d*,*g*]cyclononen-5-one.

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