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Structures of the Diels–Alder Reaction Products of Thymoquinone and 1-Vinylcyclohexene. II. 7-Isopropyl-4-methyltricyclo[8.4.0.0²,⁷]tetradeca-4,9-diene-3,6-dione, C₁₈H₂₄O₂

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Abstract

The title molecule has an all-*cis* ring-fusion tricyclic structure, with the angular isopropyl group opposite to the two cyclohexene ring substituents. The cyclohexenedione and the cyclohexene rings are both in a slightly distorted sofa conformation, whereas the cyclohexane ring adopts an almost ideal chair con-
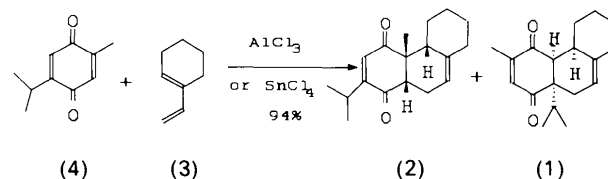
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formation. The molecule has an overall distorted hemispherical conformation.

Comment

The Diels–Alder reactions of thymoquinone (4) and 1-vinylcyclohexene (3) lead to several different products, depending mainly upon the reaction conditions used; the thermal reaction products have been analyzed in part I (Iulek, Zuckerman-Schpector, Brocksom & Silva, 1993). Lewis acid-catalyzed reaction conditions (AlCl₃ or SnCl₄) produce, in excellent yield, a 1:1 ratio of two principal products. Product (1) has been isolated, purified and crystallized thus allowing the definition of the relative stereochemistry of the three contiguous stereogenic centres by a single-crystal X-ray diffraction study. Compounds (1) and (2) are precursors in the reaction pathway aiming at the synthesis of naturally occurring cembrane diterpenes which possess interesting biological activities (Tius, 1988); therefore, the knowledge of the molecular conformation helps in the prediction of the steric course of subsequent reactions.

The cyclohexenedione ring conformation is close to that of a sofa with C(7) 0.617 (5) Å out of the plane defined by C(2)–C(6); O(1) is 0.223 (3) Å in the same direction as C(7) and O(2) is 0.239 (5) Å out of the plane in the opposite direction. The cyclohexene ring is in a slightly distorted sofa conformation with C(7) 0.569 (5) Å out of the plane defined by C(2)—C(1)—C(10)—C(9)—C(8). The cyclohexane ring is in an almost ideal chair conformation, with C(1) 0.690 (4) Å above and C(12) 0.646 (6) Å below the plane defined by the other four atoms. The Cremer & Pople (1975) ring-puckering parameters are: cyclohexenedione, $q_2 = 0.362\,(5)$, $q_3 = -0.274\,(5)$, $Q =$
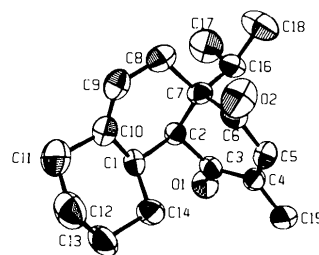

Fig. 1. The molecular structure of (1) with the atom labelling; 50% probability thermal ellipsoids are shown.

0.454 (5) Å, $\theta = 127.1$ (7), $\varphi = 137.6$ (8)°; cyclohexene, $q_2 = 0.310$ (5), $q_3 = -0.274$ (5), $Q = 0.414$ (5) Å, $\theta = 131.4$ (7), $\varphi = 285$ (1)°; cyclohexane, $q_2 = 0.042$ (6), $q_3 = 0.568$ (6), $Q = 0.570$ (6) Å, $\theta = 4.2$ (6), $\varphi = 306$ (8)°.

Experimental

Crystal data

$C_{18}H_{24}O_2$
$M_r = 272.39$
Monoclinic
$P2_1/c$
$a = 14.629$ (1) Å
$b = 9.791$ (2) Å
$c = 11.139$ (1) Å
$\beta = 107.53$ (1)°
$V = 1521.3$ (6) Å^3
$Z = 4$
$D_x = 1.19$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10-17°$
$\mu = 0.70$ mm^{-1}
$T = 293$ K
Irregular
$0.45 \times 0.40 \times 0.25$ mm
Colourless
Crystal source: MeOH-H$_2$O (9:1)

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (DIFABS; Walker & Stuart, 1983)
$T_{min} = 0.84$, $T_{max} = 1.16$
2392 measured reflections
2169 independent reflections

1280 observed reflections
$[I > 3\sigma(I)]$
$R_{int} = 0.016$
$\theta_{max} = 25°$
$h = -17 \rightarrow 16$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 13$
2 standard reflections frequency: 30 min intensity variation: ±1.9%

Refinement

Refinement on F
$R = 0.059$
$wR = 0.062$
$S = 2.34$
1193 reflections
182 parameters
$w = [\sigma^2(|F_o|) + 0.0003|F_o|^2]^{-1}$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from SHELX76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	0.2717 (2)	0.0879 (3)	0.4176 (3)	4.9 (1)
O(2)	0.2784 (3)	-0.0726 (4)	-0.0312 (3)	7.1 (2)
C(1)	0.1727 (3)	-0.1634 (4)	0.2430 (4)	3.6 (2)
C(2)	0.2761 (3)	-0.1008 (4)	0.2845 (4)	3.1 (1)
C(3)	0.2697 (3)	0.0491 (5)	0.3126 (5)	3.6 (2)
C(4)	0.2603 (3)	0.1508 (5)	0.2106 (5)	3.6 (2)
C(5)	0.2686 (3)	0.1086 (5)	0.0994 (5)	4.2 (2)
C(6)	0.2901 (4)	-0.0338 (5)	0.0750 (5)	4.2 (2)
C(7)	0.3336 (3)	-0.1224 (5)	0.1894 (4)	3.6 (2)
C(8)	0.3322 (4)	-0.2736 (5)	0.1509 (5)	4.9 (2)
C(9)	0.2359 (4)	-0.3382 (5)	0.1249 (5)	4.6 (2)
C(10)	0.1664 (4)	-0.2921 (5)	0.1665 (5)	4.2 (2)
C(11)	0.0706 (5)	-0.3646 (6)	0.1397 (6)	6.5 (2)
C(12)	-0.0124 (4)	-0.2698 (7)	0.0782 (6)	6.7 (2)
C(13)	-0.0064 (3)	-0.1398 (6)	0.1540 (6)	5.7 (2)
C(14)	0.0890 (3)	-0.0670 (5)	0.1743 (5)	4.5 (2)
C(15)	0.2378 (4)	0.2945 (5)	0.2350 (5)	5.4 (2)
C(16)	0.4406 (3)	-0.0721 (5)	0.2511 (5)	4.8 (2)
C(17)	0.4938 (4)	-0.1448 (6)	0.3704 (6)	7.6 (3)
C(18)	0.4979 (4)	-0.0857 (7)	0.1570 (6)	7.8 (3)

Table 2. *Geometric parameters* (Å, °)

O(1)—C(3)	1.222 (6)	O(2)—C(10)	1.205 (6)
C(1)—C(2)	1.567 (7)	C(1)—C(10)	1.508 (6)
C(1)—C(14)	1.553 (7)	C(2)—C(3)	1.509 (6)
C(2)—C(7)	1.553 (7)	C(3)—C(4)	1.486 (7)
C(4)—C(5)	1.345 (7)	C(4)—C(15)	1.488 (7)
C(5)—C(6)	1.472 (7)	C(6)—C(7)	1.514 (7)
C(7)—C(8)	1.540 (7)	C(7)—C(16)	1.586 (7)
C(8)—C(9)	1.491 (8)	C(9)—C(10)	1.318 (8)
C(10)—C(11)	1.518 (9)	C(11)—C(12)	1.518 (9)
C(12)—C(13)	1.515 (9)	C(13)—C(14)	1.522 (7)
C(16)—C(17)	1.502 (9)	C(16)—C(18)	1.532 (8)
C(2)—C(1)—C(10)	112.5 (4)	C(2)—C(7)—C(8)	110.9 (4)
C(2)—C(1)—C(14)	117.1 (4)	C(2)—C(7)—C(16)	109.2 (4)
C(10)—C(1)—C(14)	108.9 (4)	C(6)—C(7)—C(8)	110.5 (4)
C(1)—C(2)—C(3)	109.1 (4)	C(6)—C(7)—C(16)	107.2 (4)
C(1)—C(2)—C(7)	114.7 (4)	C(8)—C(7)—C(16)	110.3 (4)
C(3)—C(2)—C(7)	110.7 (4)	C(7)—C(8)—C(9)	113.2 (4)
O(1)—C(3)—C(2)	121.0 (4)	C(8)—C(9)—C(10)	124.8 (5)
O(1)—C(3)—C(4)	119.6 (4)	C(1)—C(10)—C(9)	124.2 (5)
C(2)—C(3)—C(4)	119.4 (4)	C(1)—C(10)—C(11)	113.4 (4)
C(3)—C(4)—C(5)	119.0 (4)	C(9)—C(10)—C(11)	122.4 (5)
C(3)—C(4)—C(15)	117.9 (4)	C(10)—C(11)—C(12)	111.6 (5)
C(5)—C(4)—C(15)	123.0 (5)	C(11)—C(12)—C(13)	111.0 (5)
C(4)—C(5)—C(6)	123.0 (5)	C(12)—C(13)—C(14)	111.9 (5)
O(2)—C(6)—C(5)	120.3 (5)	C(1)—C(14)—C(13)	109.9 (4)
O(2)—C(6)—C(7)	123.0 (5)	C(7)—C(16)—C(17)	114.6 (4)
C(5)—C(6)—C(7)	116.5 (4)	C(7)—C(16)—C(18)	110.4 (4)
C(2)—C(7)—C(6)	108.6 (4)	C(17)—C(16)—C(18)	108.6 (5)

Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by direct methods. H atoms were found in difference synthesis and included as fixed contributors with an overall isotropic temperature parameter of 0.098 (4) Å. Programs used were: SHELXS86 (Sheldrick, 1986), SHELX76 (Sheldrick, 1976) and ORTEP (Johnson, 1965). The refinement was by full-matrix least-squares methods. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de São Carlos.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71331 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1049]

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