ular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($\text{\AA}^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl(1)	0.68223 (7)	0.57826 (6)	0.61354 (9)	0.0269
O(1)	0.6914 (3)	0.4674 (2)	0.5873 (3)	0.0601
O(2)	0.6491 (2)	0.6338 (2)	0.4868 (3)	0.0386
O(3)	0.6034 (2)	0.5973 (2)	0.7248 (3)	0.0365
O(4)	0.7892 (2)	0.6183 (2)	0.6569 (3)	0.0382
N(1)	0.5670 (3)	0.5413 (3)	0.2445 (4)	0.0306
N(5)	0.2974 (3)	0.7947 (3)	0.0770 (4)	0.0292
C(2)	0.5437 (3)	0.6254 (3)	0.1446 (5)	0.0354
C(3)	0.4311 (3)	0.6679 (3)	0.1616 (5)	0.0343
C(4)	0.4103 (3)	0.7561 (3)	0.0657 (4)	0.0307
H(1A)	0.505 (3)	0.498 (3)	0.267 (4)	0.03 (1)
H(1B)	0.583 (3)	0.564 (3)	0.315 (5)	0.04 (1)
H(1C)	0.616 (4)	0.493 (4)	0.210 (5)	0.06 (1)
H(2A)	0.594 (3)	0.673 (3)	0.151 (4)	0.024 (10)
H(2B)	0.550 (3)	0.601 (3)	0.057 (4)	0.04 (1)
H(3A)	0.378 (4)	0.612 (3)	0.138 (4)	0.05 (1)
H(3B)	0.425 (4)	0.690 (4)	0.236 (5)	0.06 (2)
H(4A)	0.423 (2)	0.738 (3)	−0.024 (4)	0.022 (10)
H(4B)	0.452 (3)	0.807 (3)	0.085 (4)	0.04 (1)
H(5A)	0.237 (3)	0.741 (4)	0.056 (5)	0.06 (1)
H(5B)	0.284 (3)	0.816 (3)	0.152 (5)	0.03 (1)
H(5C)	0.290 (3)	0.849 (3)	0.020 (4)	0.04 (1)

Table 2. *Geometric parameters* ($\text{\AA}$, °)

Cl(1)—O(1)	1.456 (3)	N(1)—C(2)	1.480 (5)
Cl(1)—O(2)	1.478 (3)	N(5)—C(4)	1.483 (5)
Cl(1)—O(3)	1.472 (3)	C(2)—C(3)	1.503 (6)
Cl(1)—O(4)	1.478 (3)	C(3)—C(4)	1.491 (6)
O(1)—Cl(1)—O(2)	110.6 (2)	O(3)—Cl(1)—O(4)	108.9 (2)
O(1)—Cl(1)—O(3)	110.1 (2)	N(1)—C(2)—C(3)	112.0 (3)
O(1)—C(1)—O(4)	108.8 (2)	C(2)—C(3)—C(4)	111.6 (3)
O(2)—C(1)—O(3)	110.1 (2)	N(5)—C(4)—C(3)	111.8 (3)
O(2)—C(1)—O(4)	108.3 (2)		

Table 3. *Hydrogen-bonding geometry* ($\text{\AA}$, °)

D	H	A	D—H	H···A	D···A	D—H···A
N(1)	H(1A)	O(3^i)	0.97 (4)	1.82 (4)	2.775 (5)	168 (3)
N(1)	H(1B)	O(2)	0.76 (4)	2.06 (5)	2.819 (5)	170 (4)
N(1)	H(1C)	O(4^{ii})	0.93 (5)	1.92 (5)	2.845 (5)	172 (4)
N(5)	H(5A)	O(2^{iii})	1.04 (5)	1.80 (5)	2.833 (5)	171 (4)
N(5)	H(5B)	O(4^{iv})	0.79 (4)	2.04 (5)	2.811 (5)	165 (4)
N(5)	H(5C)	O(1^v)	0.90 (5)	1.86 (5)	2.739 (5)	166 (4)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $\tfrac{3}{2} - x, 1 - y, z - \tfrac{3}{2}$; (iii) $x - \tfrac{1}{2}, y, \tfrac{1}{2} - z$; (iv) $x - \tfrac{1}{2}, \tfrac{3}{2} - y, 1 - z$; (v) $1 - x, \tfrac{1}{2} + y, \tfrac{1}{2} - z$.

Buff plate-like crystals of the title compound were formed as a by-product when the sodium salt of 3-(2-pyrrolmethylidene-amino)propylamine (0.0033 mol) in 100 ml of methanol was reacted with manganese(II) perchlorate (0.0011 mol) also in methanol (50 ml). The resultant red–brown precipitate from this reaction was collected and dried. A sample was then redissolved in methanol and the resultant solution layered with *n*-hexane. This resulted in crystal formation after approximately 2 weeks of standing at ambient temperature.

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Structures of the Diels–Alder Reaction Products of Thymoquinone and 1-Vinylcyclohexene. I. 2-Isopropyl-5-methyl-tricyclo[8.4.0.0²,⁷]tetradeca-4,9-diene-3,6-dione

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Abstract

The title molecule has an all-*cis* ring-fusion tricyclic structure, with the angular isopropyl group next to the two cyclohexene ring substituents. The cyclohexenedione ring is in a sofa conformation, the middle cyclohexene ring adopts a half-chair conformation and the cyclohexane ring adopts an almost-ideal chair conformation. The molecule adopts an overall distorted-hemispherical conformation.

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Comment

The Diels–Alder reaction of thymoquinone (4) and 1-vinylcyclohexene (3) leads to several different products, depending mainly upon the reaction conditions. Thermal reaction conditions produce two principal products in excellent yield, with slightly different ratios depending upon the solvent used in the reaction. The minor product (1) has been isolated, purified and crystallized thus allowing definition of the relative stereochemistry of the three contiguous stereogenic centers by a single-crystal X-ray diffraction study. As compounds (1) and (2) are precursors in the reaction pathway, which is aimed at the synthesis of naturally occurring cembrane diterpenes presenting interesting biological activities (Tius, 1988), knowledge of the molecular conformation helps in the prediction of the steric course of subsequent reactions.
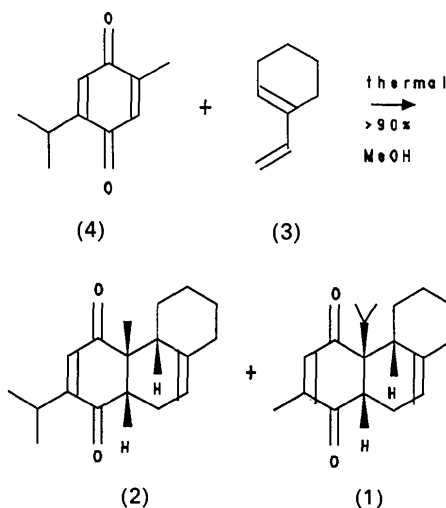
The cyclohexenedione ring conformation is close to that of a sofa with C(7) 0.593 (4) Å out of the plane defined by the other five atoms. O(1) lies on the same plane whereas O(2) is 0.362 (3) Å out of it. The cyclohexene ring is in an essentially half-chair
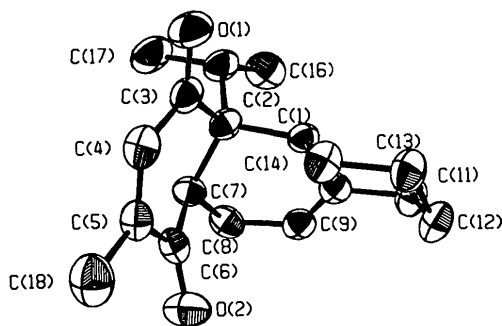
conformation and the cyclohexane ring has an almost-ideal chair conformation with C(1) 0.682 (4) Å above and C(12) 0.666 (5) Å below the plane defined by the other four atoms. The Cremer & Pople (1975) ring-puckering parameters are: cyclohexenedione: $q_2 = 0.353$ (4), $q_3 = -0.239$ (4), $Q = 0.426$ (4) Å, $\theta = 124.2$ (6), $\varphi = 124.4$ (7)°; cyclohexene: $q_2 = 0.337$ (4), $q_3 = -0.287$ (4), $Q = 0.442$ (4) Å, $\theta = 130.4$ (5), $\varphi = 276.8$ (7)°; cyclohexane: $q_2 = 0.004$ (4), $q_3 = 0.571$ (4), $Q = 0.571$ (4) Å, $\theta = 0.4$ (4), $\varphi = 9$ (59)°.

Experimental

Crystal data

$C_{18}H_{24}O_2$
$M_r = 272.39$
Monoclinic
$P2_1/n$
$a = 12.664$ (1) Å
$b = 9.424$ (1) Å
$c = 12.883$ (1) Å
$\beta = 107.53$ (1)°
$V = 1466.1$ (3) Å^3
$Z = 4$
$D_x = 1.23$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9-20°$
$\mu = 0.73$ mm^{-1}
$T = 291$ K
Irregular
$0.35 \times 0.39 \times 0.15$ mm
Yellow
Crystal source: from MeOH/H$_2$O (9:1)

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2410 measured reflections
2297 independent reflections
1311 observed reflections
$[I > 3\sigma(I)]$

$R_{int} = 0.020$
$\theta_{max} = 24°$
$h = -14 \rightarrow 13$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 14$
1 standard reflection
frequency: 60 min
intensity variation: ±1.4%

Refinement

Refinement on F
Final $R = 0.055$
$wR = 0.059$
$S = 1.16$
1311 reflections
182 parameters
$w = [\sigma^2(F) + 0.0005F^2]^{-1}$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Atomic scattering factors from SHELX76 (Sheldrick, 1976)

Fig. 1. The molecular structure of $C_{18}H_{24}O_2$ with 50% thermal ellipsoids showing the atom labeling.

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

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j B_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	0.5029 (2)	0.2458 (3)	0.4635 (2)	4.9 (1)
O(2)	0.9089 (2)	0.1916 (3)	0.4447 (3)	5.0 (1)
C(1)	0.7128 (3)	0.4441 (4)	0.5368 (3)	2.8 (1)
C(2)	0.6544 (3)	0.3696 (4)	0.4261 (3)	3.0 (1)
C(3)	0.5935 (3)	0.2371 (5)	0.4499 (3)	3.4 (1)
C(4)	0.6468 (4)	0.0969 (4)	0.4596 (3)	3.9 (1)
C(5)	0.7478 (3)	0.0752 (4)	0.4514 (3)	3.4 (1)
C(6)	0.8090 (3)	0.1968 (4)	0.4250 (3)	3.3 (1)

C(7)	0.7402 (3)	0.3221 (4)	0.3685 (3)	3.0 (1)
C(8)	0.8138 (3)	0.4444 (4)	0.3537 (3)	3.7 (1)
C(9)	0.8542 (3)	0.5340 (4)	0.4522 (3)	3.4 (1)
C(10)	0.8096 (3)	0.5352 (4)	0.5343 (3)	3.1 (1)
C(11)	0.8580 (3)	0.6212 (4)	0.6351 (3)	4.0 (1)
C(12)	0.8957 (3)	0.5241 (5)	0.7344 (3)	4.1 (1)
C(13)	0.8008 (3)	0.4304 (5)	0.7425 (3)	4.1 (1)
C(14)	0.7510 (3)	0.3456 (4)	0.6375 (3)	3.7 (1)
C(15)	0.5619 (3)	0.4679 (5)	0.3541 (3)	3.6 (1)
C(16)	0.5915 (4)	0.6228 (5)	0.3430 (4)	4.9 (2)
C(17)	0.5071 (4)	0.4054 (6)	0.2413 (4)	5.4 (2)
C(18)	0.8047 (4)	−0.0655 (5)	0.4694 (4)	5.2 (2)

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

O(1)—C(3)	1.215 (5)	O(2)—C(6)	1.214 (6)
C(1)—C(2)	1.562 (5)	C(1)—C(10)	1.505 (6)
C(1)—C(14)	1.549 (5)	C(2)—C(3)	1.546 (6)
C(2)—C(7)	1.555 (6)	C(2)—C(15)	1.561 (6)
C(3)—C(4)	1.472 (6)	C(4)—C(5)	1.331 (7)
C(5)—C(6)	1.479 (6)	C(5)—C(18)	1.493 (6)
C(6)—C(7)	1.517 (6)	C(7)—C(8)	1.530 (6)
C(8)—C(9)	1.481 (6)	C(9)—C(10)	1.341 (6)
C(10)—C(11)	1.496 (6)	C(11)—C(12)	1.528 (6)
C(12)—C(13)	1.520 (6)	C(13)—C(14)	1.534 (6)
C(15)—C(16)	1.525 (7)	C(15)—C(17)	1.527 (6)
C(2)—C(1)—C(10)	113.7 (3)	O(2)—C(6)—C(7)	122.9 (4)
C(2)—C(1)—C(14)	116.0 (3)	C(5)—C(6)—C(7)	116.6 (3)
C(10)—C(1)—C(14)	108.0 (3)	C(2)—C(7)—C(6)	112.2 (3)
C(1)—C(2)—C(3)	108.0 (3)	C(2)—C(7)—C(8)	112.5 (3)
C(1)—C(2)—C(7)	111.0 (3)	C(6)—C(7)—C(8)	111.3 (3)
C(1)—C(2)—C(15)	109.9 (3)	C(7)—C(8)—C(9)	112.9 (3)
C(3)—C(2)—C(7)	108.9 (3)	C(8)—C(9)—C(10)	124.2 (4)
C(3)—C(2)—C(15)	105.5 (3)	C(1)—C(10)—C(9)	123.5 (4)
C(7)—C(2)—C(15)	113.2 (3)	C(1)—C(10)—C(11)	114.4 (3)
O(1)—C(3)—C(2)	121.6 (4)	C(9)—C(10)—C(11)	122.0 (4)
O(1)—C(3)—C(4)	118.5 (4)	C(10)—C(11)—C(12)	110.2 (4)
C(2)—C(3)—C(4)	119.9 (4)	C(11)—C(12)—C(13)	110.6 (4)
C(3)—C(4)—C(5)	124.0 (4)	C(12)—C(13)—C(14)	111.4 (4)
C(4)—C(5)—C(6)	118.8 (4)	C(1)—C(14)—C(13)	111.6 (3)
C(4)—C(5)—C(18)	123.7 (4)	C(2)—C(15)—C(16)	117.5 (4)
C(6)—C(5)—C(18)	117.5 (4)	C(2)—C(15)—C(17)	112.4 (3)
O(2)—C(6)—C(5)	120.4 (4)	C(16)—C(15)—C(17)	109.5 (4)

Data were corrected for Lorentz and polarization 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 factor of 0.081 (3) Å. Programs used were: *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). The refinement was by full-matrix least-squares methods. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de São Carlos.

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1,5-Dihydro-3-(4,7-dihydro-1,3-dioxepin-2-yl)-8-methyl-3H-[1,3]dioxepino[5,6-c]-pyridinium-9-ol Maleate †

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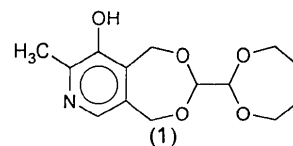
Abstract

Both dioxepine rings of the title compound, 1,5-dihydro-3-(4,7-dihydro-1,3-dioxepin-2-yl)-9-hydroxy-8-methyl-3H-[1,3]dioxepino[5,6-c]pyridinium maleate, adopt a twist-boat conformation. In the crystal structure the maleate anions are stacked exactly between the pyridine rings of the cations at an average distance of 3.5 Å.

Comment

As a part of our research on the chemistry of vitamin B6 (Dumić, Glunčić, Kovačević & Kujundžić, 1989), 1,5-dihydro-3-(4,7-dihydro-1,3-dioxepin-2-yl)-8-methyl-3H-[1,3]dioxepino[5,6-c]pyridin-9-ol (1) was prepared as the precursor for pyridoxine (vitamin B6) (Dumić & Butula, 1989, 1990). In order to establish the structure of the bis-1,3-dioxepin fragment of (1) the crystal structure analysis of its maleic acid salt (2) was undertaken. Details of the synthetic work will be published elsewhere (Dumić, Vinković, Butula & Jadrijević-Mladar, 1993).

(1)