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cis,trans-Tetrahydromitchelladione

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Abstract. $C_{30}H_{44}O_2$, $M_r = 436.68$, orthorhombic, $P2_12_12_1$, $a = 18.723$ (9), $b = 12.334$ (6), $c = 11.300$ (6) Å, $Z = 4$, $D_m = 1.100$ (2), $D_x = 1.112$ Mg m^{-3}. The structure was solved by direct methods with diffractometer data. Refinement of the structure gave a final value of $R = 0.073$ on F for 1325 non-zero reflections. The sesquiterpene dimer from the wood oil of *Eremophila mitchelli* exhibits a conformation in which the centres of the two halves of the molecule are as close as possible, most probably due to a dipolar interaction between them.

Introduction. From the wood oil of *Eremophila mitchelli*, two related sesquiterpene dimers have been isolated, and their gross structures have been determined by a combination of chemical and spectroscopic techniques (Lewis, 1978). The stereochemistry of the *C* ring could not, however, be determined, and consequently the structure determination of *cis,trans*-tetrahydromitchelladione [THM(I),† Fig. 1] was undertaken.

A mixture of (I) and (II) was obtained by reduction of the corresponding dihydro compound, and from this mixture suitable crystals of THM(I) were obtained by slow fractional crystallization from petroleum ether. THM(I) crystallized as colourless prisms elongated along *c*. Accurate cell parameters were obtained from the ω scans of the *h*00, 0*k*0 and 00*l* reflections. The space group $P2_12_12_1$ was assigned from the absence of

odd reflections from these classes. Integrated reflection intensities for the *hk*0–7 layers were collected out to $2\theta = 40°$ using a Stoe automatic Weissenberg diffractometer, fitted with a graphite monochromator, and Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) and ω scans. A standard reflection chosen for each layer was monitored after every 30 measurements and showed no significant change. Of the 1397 independent reflections collected, 72 were designated unobserved by the criterion $I_h < 2\sigma I_h$. The crystal used for data collection measured approximately $0.3 \times 0.3 \times 0.5$ mm. Lorentz and polarization corrections were applied, but absorption corrections were not applied [$\mu_{(MoK\alpha)} = 0.035$ mm^{-1}]. The structure was solved using the program *MULTAN* (Germain, Main & Woolfson, 1971). An *E* map computed from the set of phases with the highest absolute figure of merit (1.19) using 480 reflections with $E \geq 1.0$ revealed 31 of the 32 non-hydrogen atoms. The remaining carbon atom, C(29), was located from a difference map.
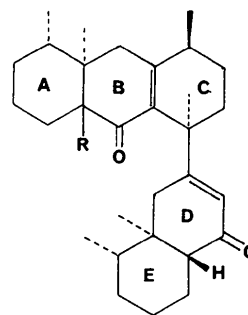
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† The full IUPAC name for THM is (1*S*,4*S*,5*S*,8a*S*,10a*R*)-1-[(4'a*R*,8'*S*,8'a*R*)-8',8'a-dimethyl-4'-oxo-1',4',4'a,5',6',7',8',8'a-octahydronaphthalen-2'-yl]-1,4,5,10a-tetramethyl-1,2,3,4,5,6,7,8,-8a,9,10,10a-dodecahydroanthracen-9-one.

Fig. 1. *cis,trans*-Tetrahydromitchelladione isomers [(I) $R = \cdots$H, (II) $R = $ H].

Table 1. *Atomic positional parameters* ($\times 10^4$)

	x	y	z
C(1)	934 (4)	1403 (6)	−2046 (8)
C(2)	1083 (4)	327 (6)	−1410 (8)
C(3)	908 (4)	−614 (6)	−1943 (9)
C(4)	528 (4)	−664 (6)	−3046 (9)
C(5)	224 (4)	381 (6)	−3563 (9)
C(6)	−49 (5)	275 (8)	−4795 (10)
C(7)	−360 (5)	1328 (8)	−5225 (10)
C(8)	187 (5)	2246 (8)	−5110 (10)
C(9)	451 (4)	2364 (6)	−3829 (9)
C(10)	791 (4)	1292 (6)	−3360 (8)
C(11)	936 (5)	3351 (7)	−3716 (11)
C(12)	1499 (4)	1021 (6)	−4044 (9)
C(13)	1369 (4)	384 (6)	−164 (9)
C(14)	696 (4)	622 (7)	624 (10)
C(15)	893 (5)	940 (8)	1868 (10)
C(16)	1325 (5)	1993 (7)	1876 (9)
C(17)	1904 (4)	1967 (7)	944 (9)
C(18)	2491 (5)	2778 (7)	1152 (10)
C(19)	2911 (4)	3133 (7)	83 (10)
C(20)	2457 (4)	3815 (7)	−803 (10)
C(21)	2831 (5)	4030 (8)	−2014 (10)
C(22)	3088 (5)	2945 (8)	−2582 (11)
C(23)	3556 (5)	2295 (8)	−1743 (11)
C(24)	3167 (4)	2066 (6)	−565 (10)
C(25)	2553 (4)	1262 (6)	−762 (9)
C(26)	1934 (4)	1269 (6)	41 (9)
C(27)	1712 (4)	−704 (6)	260 (10)
C(28)	818 (5)	2989 (8)	1667 (11)
C(29)	2211 (5)	4913 (7)	−267 (12)
C(30)	3594 (5)	3760 (7)	521 (11)
O(1)	432 (3)	−1536 (4)	−3563 (7)
O(2)	2596 (3)	606 (4)	−1557 (6)

Fig. 2. THM(1) structure with 50% probability ellipsoids.

Table 2. *Bond angles* (°)

C(10)−C(1)−C(2)	114·4 (9)	C(15)−C(16)−C(28)	110·1 (9)
C(1)−C(2)−C(3)	119·4 (8)	C(17)−C(16)−C(28)	110·2 (9)
C(1)−C(2)−C(13)	117·5 (8)	C(16)−C(17)−C(18)	113·6 (8)
C(3)−C(2)−C(13)	122·9 (8)	C(16)−C(17)−C(26)	125·2 (8)
C(2)−C(3)−C(4)	123·0 (8)	C(18)−C(17)−C(26)	121·1 (8)
C(3)−C(4)−C(5)	118·8 (8)	C(17)−C(18)−C(19)	116·7 (9)
C(4)−C(5)−C(6)	114·4 (9)	C(18)−C(19)−C(20)	112·8 (9)
C(4)−C(5)−C(10)	107·4 (9)	C(18)−C(19)−C(24)	106·7 (9)
C(6)−C(5)−C(10)	115·8 (9)	C(18)−C(19)−C(30)	108·3 (9)
C(5)−C(6)−C(7)	111·1 (9)	C(20)−C(19)−C(24)	108·5 (9)
C(6)−C(7)−C(8)	110·6 (9)	C(20)−C(19)−C(30)	112·4 (9)
C(7)−C(8)−C(9)	111·4 (9)	C(24)−C(19)−C(30)	108·0 (9)
C(8)−C(9)−C(10)	111·8 (9)	C(19)−C(20)−C(21)	114·2 (9)
C(8)−C(9)−C(11)	110·2 (9)	C(19)−C(20)−C(29)	112·5 (9)
C(10)−C(9)−C(11)	113·9 (9)	C(21)−C(20)−C(29)	109·1 (9)
C(1)−C(10)−C(9)	109·2 (9)	C(20)−C(21)−C(22)	110·7 (9)
C(1)−C(10)−C(5)	109·2 (9)	C(21)−C(22)−C(23)	112·0 (9)
C(1)−C(10)−C(12)	110·7 (9)	C(22)−C(23)−C(24)	111·2 (9)
C(9)−C(10)−C(5)	106·4 (9)	C(19)−C(24)−C(23)	113·0 (9)
C(9)−C(10)−C(12)	111·0 (9)	C(19)−C(24)−C(25)	112·2 (9)
C(5)−C(10)−C(12)	110·3 (9)	C(23)−C(24)−C(25)	110·3 (9)
C(2)−C(13)−C(14)	104·7 (9)	C(24)−C(25)−C(26)	119·8 (8)
C(2)−C(13)−C(26)	114·7 (9)	C(13)−C(26)−C(17)	122·2 (8)
C(2)−C(13)−C(27)	113·1 (9)	C(13)−C(26)−C(25)	116·4 (8)
C(14)−C(13)−C(26)	109·5 (9)	C(17)−C(26)−C(25)	120·6 (8)
C(14)−C(13)−C(27)	108·5 (9)	C(3)−C(4)−O(1)	121·3 (8)
C(26)−C(13)−C(27)	106·3 (9)	C(5)−C(4)−O(1)	120·0 (8)
C(13)−C(14)−C(15)	112·5 (9)	C(24)−C(25)−O(2)	119·2 (8)
C(14)−C(15)−C(16)	110·8 (9)	C(26)−C(25)−O(2)	121·0 (8)
C(15)−C(16)−C(17)	110·9 (9)		

The structure was then refined to convergence by least-squares (alternating full-matrix blocks) techniques with anisotropic temperature factors for hon-hydrogen atoms and isotropic temperature factors for H atoms. H atom parameters were not refined. The final R value based on all reflections was 0·075. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The function minimized was $\sum [w(|F_o| - |F_c|)^2]$. Programs used were those described previously (Snow, 1974). The final coordinates are given in Table 1.* Fig. 2 contains the bond lengths and Table 2 the bond angles.

Discussion. With the exception of the C(5)−C(6) and C(19)−C(24) bonds, all bond distances in the ring systems are within expected limits (Fig. 2). The molecule contains two conjugated systems, the α,β-unsaturated carbonyl systems of the B and D rings.

The B-ring system is nearly planar, the largest deviations from the plane of C(13), C(16), C(17), C(18), C(24), C(25), C(26) and O(2) being −0·043 (9) Å at C(16) and 0·046 (9) Å at C(26). In contrast to this, there are significant deviations from the plane of the D ring defined by C(2), C(3), C(4) and O(1), indicating a considerable degree of twist in the C(2)−C(3) bond. The two cyclohexane rings (A and E)

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are each in the chair conformation as shown by the deviations of C(7) [−0·67 (1) Å] and C(10) [0·69 (1) Å], and C(19) [−0·67 (1) Å] and C(22) [0·66 (1) Å] from the C(5)—C(6)···C(8)—C(9) and the C(20)—C(21)···C(23)—C(24) planes respectively. The conformation of the *C* ring is that of a slightly deformed cyclohexene half-chair. The dihedral angles between the C(11) and C(12) [59·3 (10)°] and the C(29) and C(30) methyl groups [57·8 (11)°] are not significantly different from the standard value for vicinal *cis* substituents of a chair cyclohexane ring. The two methyl groups of the *C* ring are both pseudo-axial.

The conformation of the molecule within the crystal is such that the centres of gravity of the two ring systems are as close as possible. In this conformation there are a number of strong non-bonded intra-molecular interactions, the shortest of which are C(1)H1···C(20)H, 1·80, C(3)H···C(27)H2, 1·80, C(1)H2···C(14)H1, 1·92, and C(11)H2···C(12)H1, 2·07 Å (11·89, 11·89, 6·81 and 4·22 kJ mol^{-1}). A qualitative examination of molecular models indicates that a number of conformations in which these non-bonded interactions are substantially reduced are accessible by rotation about the C(2)—C(13) bond. There is only one short non-bonded contact between non-hydrogen atoms, and this occurs between O(2) and C(2). The contact distance, 2·80 Å, is considerably less than the sum of the van der Waals radii of C and O (1·7 and 1·4 Å respectively). There are only two independent intermolecular non-bonded contacts, and these are related to a second pair of contacts by the crystal symmetry. Furthermore, the magnitudes of these interactions are not sufficiently great by comparison with the intramolecular interactions to allow the rationalization of the crystal conformation of the molecule solely on the basis of packing constraints.

The structure of THM(I) may be written as the Lewis resonance form given in Fig. 3. In this form it is
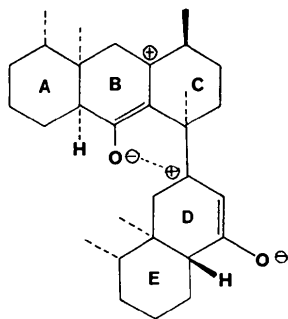
apparent that there exists a dipole–dipole interaction between C(2) and O(2). It therefore appears reasonable to assert that the preferred crystal conformation of the molecule may be due to such an interaction. Furthermore, the geometry at C(2), in particular the O(2)—C(2)—C(3) angle, is very similar to that predicted by the empirical rules proposed by Baldwin (1976) and Baldwin, Cutting, Dupont, Kruse, Silberman & Thomas (1976) for the transition state of nucleophilic 1,4-addition reactions to α,β-unsaturated ketones, and one may therefore postulate that the interaction O(2)···C(2) may be of partial bonding character. Such an interaction may also account for the deviations of C(1) and C(13) from the ideal planar geometry of the C(2)—C(3) bond.

Alternatively, the differences between the two conjugated systems, in particular the distortion of the *D* ring, may be explained in terms of ring strain. *cis*-Fused decalin systems are known to be conformationally labile and to undergo facile ring inversion, whereas the corresponding *trans*-fused systems are conformationally rigid (Eliel, 1962). In view of the fact that the introduction of extended planar systems into the *B* and *D* rings would most probably result in a large degree of strain, it appears reasonable to rationalize the differences between the *B*- and *D*-ring geometries in terms of the abilities of the *A* and *E* rings to accommodate part of this strain energy. By analogy with the decalin systems, it is reasonable to propose that in the *AB* ring system, which is *cis*-fused, the strain may be readily partitioned over the entire bicyclic system, thus allowing the *B* ring to adopt a nearly planar conformation, whereas in the *trans*-fused *DE* ring system this release of strain energy may occur only by bond-angle distortion, and hence the *D*-ring geometry is much less planar.

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Fig. 3. Principal resonance form of THM(I).