

substituents at C(4), C(9) and C(10) and therefore a hemispherical conformation for the entire molecule. This result allows prediction of the steric course of subsequent reactions (Trost, 1983) and prediction of the orientation of similar Diels–Alder reactions (Woodward & Hoffmann, 1970).

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Structure of 9,9-Dimethyl-8-oxatricyclo[4.3.0.0^{1,3}]nonan-6-ol

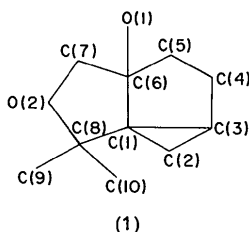
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Abstract. C₁₀H₁₆O₂, $M_r = 168.24$, monoclinic, $P2_1$, $a = 8.390$ (2), $b = 10.052$ (3), $c = 12.163$ (2) Å, $\beta = 108.65$ (2)°, $V = 971.9$ (3) Å³, $Z = 4$, $D_x = 1.150$ g cm⁻³, $\lambda = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 0.73$ cm⁻¹, $F(000) = 368$, $T = 298$ K, $R = 0.045$ for 1333 observed reflections. There are two independent molecules in the asymmetric unit which are essentially identical. They are hydrogen bonded to each other and to neighbouring symmetry-related ones, giving rise to infinite helical chains of molecules along the direction of the twofold screw axis.

Experimental. The synthesis of compound (1) has been reported previously (Marsaioli, Nurnberg, Sarragiotto & Castellano, 1989).



The data collection and refinement parameters are summarized in Table 1. The structure was solved using standard direct-methods and difference-

Fourier techniques. In the final cycles of least-squares refinement, all non-H atoms were treated anisotropically. The origin in the polar axis was fixed by splitting the normal matrix into two blocks, one for each of the independent molecules. H atoms were included as fixed contributors at positions found in difference syntheses, slightly modified on stereochemical grounds, all with a common isotropic temperature factor that refined to $U = 0.070$ Å². Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for the H atoms from Stewart, Davidson & Simpson (1965). Programs used were *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). All calculations were performed on a VAX 11/780 computer.

Atomic coordinates are listed in Table 2* and bond lengths and angles in Table 3. Fig. 1 is a stereoscopic projection of the unit-cell contents.

Related literature. Crystals were obtained as previously described (Marsaioli, Nurnberg, Sarragiotto

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52968 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Crystallographic summary for (1)

Data collection*	
Mode	θ - 2θ
Scan rate ($^{\circ}$ min ⁻¹)	2.6-6.7
θ range ($^{\circ}$)	0-25
Range of hkl	$-9 \leq h \leq 9, 0 \leq k \leq 11, 0 \leq l \leq 14$
Total reflections measured	1805
Unique reflections	1687
R_{int}	0.017
Crystal dimensions (mm)	$\sim 0.5 \times 0.5 \times 0.3$
Structure refinement†	
Reflections used [$I > 3\sigma(I)$]	1333
No. of variables	218
R, wR	0.045, 0.051
Max. shift/e.s.d.	0.013
Max. min. density in final difference map ($e \text{ \AA}^{-3}$)	0.20, -0.16
S	0.93

* Unit-cell parameters by least-squares refinement of the setting angles of 15 reflections with $11 < \theta < 17^{\circ}$. Enraf-Nonius CAD-4 diffractometer with a graphite monochromator. One standard reflection (512) measured every half an hour of radiation time showed no significant variation. No correction for absorption.

† Function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = [\sigma^2(F_o) + 0.004F_o^2]$.

Table 2. Fractional atomic coordinates and isotropic temperature factors (\AA^2) for non-H atoms

	x	y	z	B_{iso}
O(11)	-0.2293 (3)	-0.0875 (3)	-0.5214 (2)	4.75 (7)
O(12)	-0.0278 (3)	-0.1212 (3)	-0.2702 (2)	5.12 (8)
C(11)	-0.1666 (4)	-0.2867 (3)	-0.3951 (2)	3.28 (8)
C(12)	-0.2129 (5)	-0.4072 (4)	-0.4689 (3)	4.8 (1)
C(13)	-0.2836 (5)	-0.3876 (4)	-0.3716 (3)	4.6 (1)
C(14)	-0.4545 (5)	-0.3246 (5)	-0.3943 (3)	5.3 (1)
C(15)	-0.4497 (4)	-0.2015 (5)	-0.4643 (3)	5.1 (1)
C(16)	-0.2657 (4)	-0.1604 (3)	-0.4326 (3)	3.47 (8)
C(17)	-0.1989 (4)	-0.0812 (4)	-0.3220 (3)	4.5 (1)
C(18)	0.0055 (4)	-0.2483 (3)	-0.3154 (3)	3.80 (9)
C(19)	0.1293 (4)	-0.2284 (5)	-0.3795 (4)	6.1 (1)
C(110)	0.0755 (5)	-0.3394 (5)	-0.2128 (3)	6.1 (1)
O(21)	0.2405 (3)	-0.0269 (3)	-0.1243 (2)	4.84 (8)
O(22)	0.2894 (3)	-0.2589 (3)	-0.2759 (2)	5.23 (8)
C(21)	0.3206 (4)	-0.2572 (3)	-0.0808 (3)	3.86 (9)
C(22)	0.3803 (6)	0.2697 (4)	0.0479 (3)	5.6 (1)
C(23)	0.2457 (6)	0.3605 (4)	-0.0231 (3)	5.1 (1)
C(24)	0.0649 (6)	0.3269 (5)	-0.0413 (4)	6.1 (1)
C(25)	0.0449 (5)	0.1832 (4)	-0.0821 (3)	5.4 (1)
C(26)	0.1824 (4)	0.1611 (3)	-0.1372 (3)	3.70 (8)
C(27)	0.1398 (4)	0.2083 (4)	-0.2626 (3)	4.5 (1)
C(28)	0.4171 (4)	0.2823 (4)	-0.1643 (3)	4.2 (1)
C(29)	0.5545 (5)	0.1799 (6)	-0.1496 (4)	6.7 (2)
C(210)	0.4814 (6)	0.4224 (5)	-0.1636 (4)	6.1 (1)

& Castellano, 1989). There are two independent molecules in the asymmetric unit which are essentially identical: a least-squares fit (Kabsch, 1976) gives a mean deviation between equivalent atoms of 0.041 \AA and a root-mean-square deviation of 0.061 \AA . All O atoms are involved in strong hydrogen bonds: O(11)···O(22) ($-x, -1/2 + y, -1 - z$) = 2.815 (3) \AA , O(12)···O(21) = 2.807 (3) \AA , O(11)—H(O11)···O(22) = 177.2 (4) $^{\circ}$, O(21)—H(O21)···O(12)

Table 3. Interatomic bond distances (\AA) and angles ($^{\circ}$) for non-H atoms

O(11)—C(16)	1.417 (4)	O(21)—C(26)	1.426 (4)
O(12)—C(18)	1.453 (4)	O(22)—C(28)	1.454 (4)
O(12)—C(17)	1.429 (5)	O(22)—C(27)	1.411 (4)
C(16)—C(15)	1.524 (5)	C(26)—C(25)	1.524 (6)
C(16)—C(11)	1.506 (5)	C(26)—C(21)	1.496 (5)
C(16)—C(17)	1.508 (5)	C(26)—C(27)	1.527 (4)
C(15)—C(14)	1.510 (6)	C(25)—C(24)	1.519 (6)
C(14)—C(13)	1.510 (6)	C(24)—C(23)	1.500 (7)
C(13)—C(12)	1.497 (6)	C(23)—C(22)	1.493 (6)
C(13)—C(11)	1.501 (5)	C(23)—C(21)	1.499 (5)
C(12)—C(11)	1.483 (5)	C(22)—C(21)	1.488 (4)
C(11)—C(18)	1.509 (5)	C(21)—C(28)	1.509 (5)
C(18)—C(110)	1.507 (5)	C(28)—C(210)	1.507 (6)
C(18)—C(19)	1.498 (5)	C(28)—C(29)	1.513 (6)
C(18)—O(12)—C(17)	111.6 (3)	C(28)—O(22)—C(27)	111.6 (3)
O(11)—C(16)—C(15)	113.3 (3)	O(21)—C(26)—C(25)	111.7 (3)
O(11)—C(16)—C(11)	115.7 (3)	O(21)—C(26)—C(21)	111.9 (3)
O(11)—C(16)—C(17)	107.3 (3)	O(21)—C(26)—C(27)	111.5 (3)
C(15)—C(16)—C(11)	105.3 (3)	C(25)—C(26)—C(21)	106.8 (3)
C(15)—C(16)—C(17)	115.2 (3)	C(25)—C(26)—C(27)	115.2 (3)
C(11)—C(16)—C(17)	99.4 (3)	C(21)—C(26)—C(27)	99.0 (3)
C(16)—C(15)—C(14)	106.7 (3)	C(26)—C(25)—C(24)	105.2 (3)
C(15)—C(14)—C(13)	104.6 (3)	C(25)—C(24)—C(23)	105.3 (4)
C(14)—C(13)—C(12)	120.3 (3)	C(24)—C(23)—C(22)	119.3 (4)
C(14)—C(13)—C(11)	108.8 (3)	C(24)—C(23)—C(21)	109.3 (3)
C(12)—C(13)—C(11)	59.3 (2)	C(22)—C(23)—C(21)	59.7 (3)
C(13)—C(12)—C(11)	60.5 (2)	C(23)—C(22)—C(21)	60.4 (3)
C(16)—C(11)—C(13)	107.2 (3)	C(26)—C(21)—C(23)	106.4 (3)
C(16)—C(11)—C(12)	119.5 (3)	C(26)—C(21)—C(22)	119.2 (3)
C(16)—C(11)—C(18)	107.5 (3)	C(26)—C(21)—C(28)	107.7 (3)
C(13)—C(11)—C(12)	60.2 (2)	C(23)—C(21)—C(22)	60.0 (3)
C(13)—C(11)—C(18)	126.9 (3)	C(23)—C(21)—C(28)	126.5 (3)
C(12)—C(11)—C(18)	127.5 (3)	C(22)—C(21)—C(28)	128.4 (3)
O(12)—C(18)—C(11)	102.0 (3)	O(22)—C(28)—C(21)	102.0 (3)
O(12)—C(18)—C(110)	107.0 (3)	O(22)—C(28)—C(210)	108.2 (3)
O(12)—C(18)—C(19)	109.2 (3)	O(22)—C(28)—C(29)	107.8 (3)
C(11)—C(18)—C(110)	114.6 (3)	C(21)—C(28)—C(210)	114.9 (3)
C(11)—C(18)—C(19)	112.3 (3)	C(21)—C(28)—C(29)	111.1 (3)
C(110)—C(18)—C(19)	111.1 (3)	C(210)—C(28)—C(29)	112.2 (3)
O(12)—C(17)—C(16)	106.2 (3)	O(22)—C(27)—C(26)	107.1 (3)

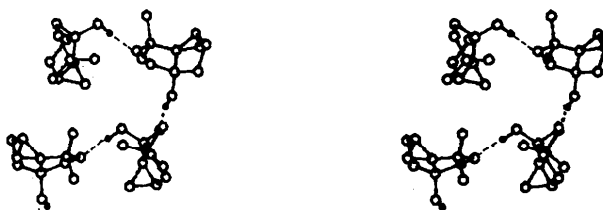


Fig. 1. Stereoscopic projection of the unit-cell contents.

= 166.7 (4) $^{\circ}$. The compound is a novel rearrangement product isolated from the oxidation reaction of β -pinene with potassium permanganate which should find wide application in the synthesis of *o*-menthanes and thujanenes (Marsaioli, Nurnberg, Sarragiotto & Castellano, 1989, and references therein).

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Acta Cryst. (1990). **C46**, 1975–1976

Structure of 5,5,15,15-Tetramethyl-6,16-dioxapentacyclo[9.6.1.0^{1,13}.0^{2,10}.0^{3,8}]-octadeca-3(8),12-diene-7,17-dione

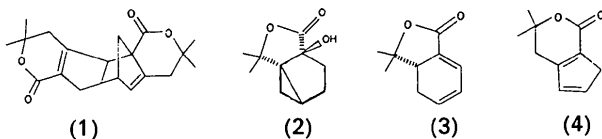
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(Received 26 February 1990; accepted 6 April 1990)

Abstract. C₂₀H₂₄O₄, *M_r* = 328.41, monoclinic, *P*₂₁/*n*, *a* = 10.546 (5), *b* = 8.774 (2), *c* = 18.931 (9) Å, β = 101.88 (4)°, *V* = 1714 (1) Å³, *Z* = 4, *D_x* = 1.272 g cm⁻³, λ = 0.71073 Å, μ(Mo Kα) = 0.82 cm⁻¹, *F*(000) = 704, *T* = 298 K, *R* = 0.047 for 1889 observed reflections. The compound is obtained by a Diels–Alder cycloaddition between two 7,7-dimethyl-8-oxabicyclo[4.3.0]-nona-1,3-dien-9-one molecules. The folding along the common bond between the five-membered and the cyclohexene ring, plus the boat conformation of the latter, force the molecule to adopt an overall hemispherical conformation.

Experimental. The synthesis of compound (1) has been reported previously (Marsaioli, Nurnberg, Sarragiotto & Castellano, 1989).



The data collection and refinement parameters are summarized in Table 1. The structure was solved using standard direct-methods and difference-Fourier techniques. In the final cycles of full-matrix least-squares refinement all non-H atoms were treated anisotropically. H atoms were included as fixed contributors at positions found in difference syntheses, slightly modified when possible on stereochemical grounds, all with a common isotropic temperature factor that refined to *B* = 4.50 Å².

Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for the H atoms from Stewart, Davidson & Simpson (1965). Programs used were *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). All calculations were performed on a VAX 11/780 computer.

Atomic coordinates are listed in Table 2* and bond lengths and angles in Table 3. Fig. 1 is a stereoscopic projection of the molecule.

Related literature. The title compound is one of the two dimers formed in an attempt to transform (2) into lactone (3), treating (2) with perchloric acid (Marsaioli, Nurnberg, Sarragiotto & Castellano, 1989, and references therein). The structure deter-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52969 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

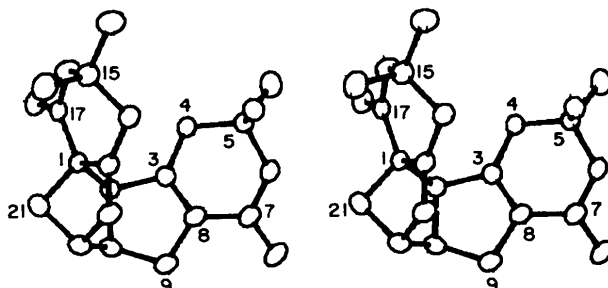


Fig. 1. Stereoscopic projection of compound (1).