hydrododecaborate monohydrate (Shiro, Aono & Watanabe, 1970). The B—H distances range from 0·89 (7) to 1·26 (7) Å. The C—N bonds in the trimethylammonium ions average 1·464 (4) Å, but range in the broad region of 1·439–1·487 Å owing to the inaccurate positions of the C atoms subject to the large thermal motion.

The N—H bond of a cation points to the S atom and forms the hydrogen bond N—H···S, the distance between N and S being 3·242 (4) Å. There are no other contacts shorter than the sum of van der Waals radii.

We thank Dr T. Nakagawa for his continuing interest throughout this investigation.

References

Dobrott, R. D. & Lipscomb, W. N. (1962). *J. Chem. Phys.* **37**, 1779–1784.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Komura, M., Nakai, H. & Shiro, M. (1987). *J. Chem. Soc. Dalton Trans.* In the press.

Main, P., Germain, G. & Woolfson, M. M. (1974). *MULTAN74. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Shiro, M., Aono, K. & Watanabe, H. (1970). *Chem. Ind. (London)*, p. 564.

Acta Cryst. (1987). C**43**, 1422–1424

Conformation of a Cycloundeca-1,5-diene Ring: Structure of (6*R*,12*R*)-6-Acetoxy-12,16-dihydroxydolabella-3,7-diene

By Joseph D. Connolly and George A. Sim

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

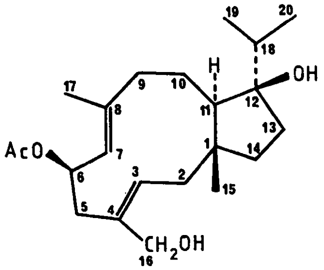
and Akihiko Matsuo

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730, Japan

(*Received* 23 *January* 1987; *accepted* 18 *March* 1987)

Abstract. $C_{22}H_{36}O_4$, $M_r = 364{\cdot}55$, monoclinic, $P2_1$, $a = 9{\cdot}304\ (3)$, $b = 9{\cdot}606\ (9)$, $c = 12{\cdot}371\ (13)$ Å, $\beta = 100{\cdot}69\ (4)°$, $V = 1086\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}11$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 400$, $T = 293$ K, $R = 0{\cdot}031$ for 1667 reflections $[I/\sigma(I) \geq 2{\cdot}5]$. The 11-membered ring exhibits a conformation that is one of the low-energy forms found for cycloundeca-1,5-diene by molecular-mechanics calculations. The C—C(sp^3)—C angles in the 11-membered ring are 110·3–119·5°, mean 114·7°. The fusion distance, 1·578 (4) Å, is long due to torsional strain.

Introduction. The conformational properties of odd-numbered organic rings of medium size ($n = 9,11,13$) are not as well characterized as those of even-numbered rings and only limited information is available about the conformations of 11-membered rings (Anet & Rawdah, 1978). Such rings occur in various natural products, *e.g.* cytochalasins, dolabellane diterpenoids, and pyrrolizidine alkaloids, and studies of these compounds provide conformational details of substituted 11-membered rings. An X-ray study of the title compound was undertaken to determine the conformation of its cycloundeca-1,5-diene ring.



Experimental. Colourless crystal, dimensions 0·15 × 0·20 × 0·40 mm. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation. Cell dimensions from setting angles of 25 independent reflections with θ *ca* 12°; 2136 intensities surveyed in range 1·5–25·0°; $h\ \bar{1}\bar{1}$–11, k 0–11, l 0–14; 2034 independent reflections after deletion of systematic absences and averaging of equivalent reflections, 1667 reflections with $I > 2{\cdot}5\sigma(I)$, $R_{\text{int}} = 0{\cdot}022$. Two reference reflections monitored periodically showed no significant variation in intensity.

0108-2701/87/071422-03$01.50

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

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
C(1)	−0·7512 (2)	−0·5124 (3)	−0·8980 (2)	0·045 (2)
C(2)	−0·6202 (3)	−0·5103 (4)	−0·9599 (2)	0·049 (2)
C(3)	−0·4959 (3)	−0·4200 (4)	−0·9101 (2)	0·050 (2)
C(4)	−0·3556 (3)	−0·4534 (4)	−0·8713 (2)	0·053 (2)
C(5)	−0·2557 (3)	−0·3429 (4)	−0·8127 (2)	0·062 (2)
C(6)	−0·2579 (3)	−0·3383 (4)	−0·6891 (2)	0·053 (2)
C(7)	−0·4093 (3)	−0·3197 (3)	−0·6685 (2)	0·050 (2)
C(8)	−0·4848 (3)	−0·4095 (3)	−0·6197 (2)	0·046 (1)
C(9)	−0·6469 (3)	−0·3910 (3)	−0·6287 (2)	0·055 (2)
C(10)	−0·7401 (3)	−0·5159 (4)	−0·6786 (2)	0·048 (1)
C(11)	−0·7057 (2)	−0·5866 (3)	−0·7829 (2)	0·037 (1)
C(12)	−0·7784 (2)	−0·7339 (3)	−0·7975 (2)	0·042 (1)
C(13)	−0·8226 (3)	−0·7527 (4)	−0·9216 (2)	0·051 (2)
C(14)	−0·8691 (3)	−0·6084 (4)	−0·9619 (2)	0·053 (2)
C(15)	−0·8118 (4)	−0·3651 (4)	−0·8938 (3)	0·064 (2)
C(16)	−0·2895 (3)	−0·5914 (5)	−0·8816 (3)	0·070 (3)
C(17)	−0·4199 (4)	−0·5344 (4)	−0·5585 (3)	0·063 (2)
C(18)	−0·6840 (3)	−0·8524 (3)	−0·7387 (2)	0·050 (2)
C(19)	−0·5340 (4)	−0·8675 (5)	−0·7708 (3)	0·071 (2)
C(20)	−0·7653 (5)	−0·9916 (4)	−0·7553 (4)	0·077 (3)
C(21)	−0·1108 (3)	−0·2075 (4)	−0·5446 (3)	0·066 (2)
C(22)	−0·0182 (8)	−0·0817 (8)	−0·5196 (5)	0·132 (6)
O(1)	−0·91560 (16)	−0·73260	−0·75818 (15)	0·049 (1)
O(2)	−0·1653 (2)	−0·2174 (3)	−0·6511 (2)	0·075 (2)
O(3)	−0·1356 (2)	−0·2896 (3)	−0·4772 (2)	0·067 (1)
O(4)	−0·2092 (3)	−0·6358 (4)	−0·7784 (2)	0·094 (2)

No absorption correction. Structure determined by direct phasing using *MITHRIL* (Gilmore, 1984). The y coordinate of O(1) was fixed to define the origin; for the absolute configuration, see below. H atoms located in difference Fourier syntheses. Full-matrix least-squares calculations on F with anisotropic thermal parameters for C and O atoms and isotropic parameters for H atoms. Convergence at $R = 0{\cdot}031$, $wR = 0{\cdot}037$, $S = 1{\cdot}91$ for 378 parameters, $\Delta/\sigma < 0{\cdot}35$, $w = 1/\sigma^2(|F_o|)$. Final $\Delta\rho$ max. 0·16, min. −0·12 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations on an SEL 32/27 computer with the *GX* system of programs (Mallinson & Muir, 1985).

Discussion. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.* Fig. 1, drawn with *ORTEP* (Johnson, 1965), illustrates the molecular geometry. The absolute configuration was assumed to be the same as that of 6*β*-(*p*-bromobenzoyloxy)-12*β*-hydroxydolabella-3,7-diene (Matsuo, Uohama, Yoshida, Nakayama, Hayashi, Connolly & Sim, 1985).

The torsion angles for the 11-membered ring (Table 3) establish that the conformation is essentially the same as those in the related dolabellane diterpenoids (3*S*,4*S*,7*S*,8*S*,10*R*)-10,18-dihydroxy-3,4;7,8-diepoxydolabellane, (*E*)-(3*S*,4*S*,10*R*)-10,18-diacetoxy-3,4-epoxydolabell-7-ene and (3*S*,4*S*,7*S*,8*S*)-18-acetoxy-3,4;7,8-diepoxydollabellane (Huneck, Baxter, Cameron, Connolly, Harrison, Phillips, Rycroft & Sim, 1986); substitution of an epoxide group for a C=C double bond has little effect on the molecular conformation. X-ray studies of the bis(silver nitrate) adduct of humulene (McPhail & Sim, 1966) and of humulene diepoxide (Cradwick, Cradwick & Sim, 1973) and humulene triepoxide (Murray-Rust & Murray-Rust, 1977) found a common conformation for the 11-membered ring in these compounds.

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

C(1)—C(2)	1·556 (4)	C(1)—C(11)	1·578 (4)
C(1)—C(14)	1·535 (5)	C(1)—C(15)	1·528 (5)
C(2)—C(3)	1·485 (5)	C(3)—C(4)	1·344 (4)
C(4)—C(5)	1·506 (5)	C(4)—C(16)	1·477 (6)
C(5)—C(6)	1·534 (4)	C(6)—C(7)	1·488 (4)
C(6)—O(2)	1·470 (5)	C(7)—C(8)	1·326 (4)
C(8)—C(9)	1·502 (4)	C(8)—C(17)	1·486 (5)
C(9)—C(10)	1·540 (5)	C(10)—C(11)	1·544 (4)
C(11)—C(12)	1·564 (5)	C(12)—C(13)	1·525 (4)
C(12)—C(18)	1·535 (5)	C(12)—O(1)	1·448 (3)
C(13)—C(14)	1·509 (6)	C(16)—O(4)	1·420 (5)
C(18)—C(19)	1·526 (5)	C(18)—C(20)	1·531 (6)
C(21)—C(22)	1·483 (9)	C(21)—O(2)	1·324 (4)
C(21)—O(3)	1·201 (5)		

C(2)—C(1)—C(11)	110·3 (2)	C(2)—C(1)—C(14)	107·7 (3)
C(2)—C(1)—C(15)	109·4 (3)	C(11)—C(1)—C(14)	103·9 (3)
C(11)—C(1)—C(15)	115·3 (3)	C(14)—C(1)—C(15)	109·9 (3)
C(1)—C(2)—C(3)	115·1 (3)	C(2)—C(3)—C(4)	129·7 (4)
C(3)—C(4)—C(5)	118·4 (4)	C(3)—C(4)—C(16)	125·2 (4)
C(5)—C(4)—C(16)	116·4 (3)	C(4)—C(5)—C(6)	112·3 (3)
C(5)—C(6)—C(7)	111·2 (2)	C(5)—C(6)—O(2)	103·1 (3)
C(7)—C(6)—O(2)	111·6 (3)	C(6)—C(7)—C(8)	126·7 (3)
C(7)—C(8)—C(9)	119·9 (3)	C(7)—C(8)—C(17)	123·9 (3)
C(9)—C(8)—C(17)	116·1 (3)	C(8)—C(9)—C(10)	114·9 (3)
C(9)—C(10)—C(11)	119·3 (3)	C(1)—C(11)—C(10)	119·5 (3)
C(1)—C(11)—C(12)	105·5 (2)	C(10)—C(11)—C(12)	110·0 (2)
C(11)—C(12)—C(13)	104·7 (3)	C(11)—C(12)—C(18)	114·8 (2)
C(11)—C(12)—O(1)	110·0 (3)	C(13)—C(12)—C(18)	114·4 (3)
C(13)—C(12)—O(1)	104·4 (2)	C(18)—C(12)—O(1)	108·1 (2)
C(12)—C(13)—C(14)	103·4 (3)	C(1)—C(14)—C(13)	104·3 (3)
C(4)—C(16)—O(4)	110·5 (3)	C(12)—C(18)—C(19)	114·7 (3)
C(12)—C(18)—C(20)	111·0 (3)	C(19)—C(18)—C(20)	109·6 (4)
C(22)—C(21)—O(2)	111·5 (4)	C(22)—C(21)—O(3)	124·7 (4)
O(2)—C(21)—O(3)	123·8 (4)	C(6)—O(2)—C(21)	117·9 (3)

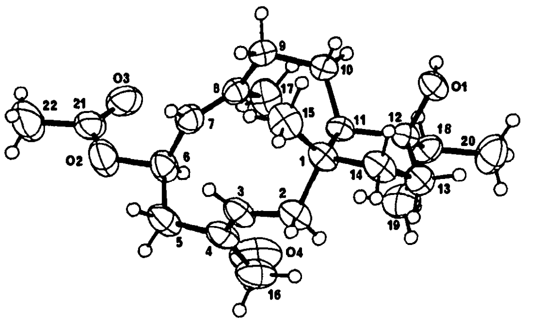


Fig. 1. Molecular structure and atomic numbering. The thermal ellipsoids of the C and O atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0·1 Å.

---

* Lists of coordinates and bond lengths for H atoms, structure factors, anisotropic thermal parameters and torsion angles with their e.s.d.'s have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43887 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of the torsion angles* (°) *in the* 11-*membered ring* (*column A*) *with molecular-mechanics results for cycloundeca*-1,5-*diene conformations of lowest energy* (*column B*) *and next lowest energy* (*column C*)

	A	*B*	*C*
11–1–2–3	−68	−57	−78
1–2–3–4	120	119	103
2–3–4–5	−173	−177	−172
3–4–5–6	88	104	94
4–5–6–7	−55	−56	−46
5–6–7–8	116	100	110
6–7–8–9	−166	−171	−171
7–8–9–10	122	78	127
8–9–10–11	−45	64	−43
9–10–11–1	−75	−151	−71
10–11–1–2	131	100	146

The low-energy conformations of cycloundeca-1,5-diene have been derived by molecular-mechanics calculations (Russell, Sim & White, unpublished results) using the force field developed by White & Bovill (1977). Comparison with the X-ray results (see Table 3) shows that the title compound adopts the cycloundeca-1,5-diene conformation with second lowest energy, 3·1 kJ mol^{-1} above the global minimum-energy form which is seen in two other dolabellane diterpenoids 6*β*-(*p*-bromobenzoyloxy)-12*β*-hydroxydolabella-3,7-diene and 6*β*-acetoxy-3,4-epoxy-3,4-dihydroodontoschismenol (Matsuo *et al.*, 1985). There is very reasonable agreement between the torsion angles in columns *A* and *C* of Table 3, the differences ranging from 1 to 17° with a mean difference of 7°.

One of the bond angles at the junction between the 11-membered and five-membered rings in the title compound, C(2)—C(1)—C(11), is about tetrahedral, 110·3°, whereas the adjacent angle at this junction, C(1)—C(11)—C(10), is considerably greater than tetrahedral, 119·5°. The other angles at C(sp^3) atoms in the 11-membered ring are all greater than tetrahedral, most notably C(9)—C(10)—C(11), 119·3°. The mean value of the seven C—C(sp^3)—C angles in the 11-membered ring is 114·7°, comparable with values for other 11-membered rings, *e.g.* 115·6° in cycloundecanone phenylsemicarbazone and 115·2° in cycloundecylmethyl naphthylurethane (Freer, Gilmore, Russell, Sim & White, unpublished results).

The highly substituted bond C(1)—C(11) has a length of 1·578 (4) Å whereas the equally highly substituted bond C(12)—C(18) has a length of 1·535 (5) Å. The distinct lengthening of the former bond can be attributed to torsional strain; the torsion angle C(14)—C(1)—C(11)—C(12), 10·8 (3)°, deviates appreciably from the ideal staggered value of 60° whereas the angle C(11)—C(12)—C(18)—C(19), −56·5 (3)°, is close to the ideal value. Similar results were obtained for (3*S*,4*S*,7*S*,8*S*,10*R*)-10,18-dihydroxy-3,4;7,8-diepoxydolabellane, (*E*)-(3*S*,4*S*,10*R*)-10,18-diacetoxy-3,4-epoxydolabell-7-ene and (3*S*,4*S*,-7*S*,8*S*)-18-acetoxy-3,4;7,8-diepoxydolabellane (Huneck *et al.*, 1986).

References

Anet, F. A. L. & Rawdah, T. N. (1978). *J. Am. Chem. Soc.* **100**, 7810–7814.

Cradwick, M. E., Cradwick, P. D. & Sim, G. A. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 404–407.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Huneck, S., Baxter, G. A., Cameron, A. F., Connolly, J. D., Harrison, L. J., Phillips, W. R., Rycroft, D. S. & Sim, G. A. (1986). *J. Chem. Soc. Perkin Trans.* 1, pp. 809–814.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

McPhail, A. T. & Sim, G. A. (1966). *J. Chem. Soc. B*, pp. 112–120.

Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.

Matsuo, A., Uohama, K., Yoshida, K., Nakayama, M., Hayashi, S., Connolly, J. D. & Sim, G. A. (1985). *Chem. Lett.* pp. 935–938.

Murray-Rust, P. & Murray-Rust, J. (1977). *Acta Cryst.* B**33**, 3931–3933.

White, D. N. J. & Bovill, M. J. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1610–1623.