Structure of the *ABC* Ring Subunit of 3-Hydroxy-2-oxodendrobine

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Abstract. (1S^*,4S^*,5R^*,6S^*,8S^*,11R^*)-5,6-Epoxy-1-hydroxy-6-isopropyl-3,11-dimethyl-3-azatricyclo-[6.2.1.0^{4,11}]undecan-2-one, $C_{15}H_{23}NO_3$, M_r = 265·35, triclinic, $P\bar{1}$, a = 7·2170 (6), b = 8·5578 (10), c = 12·4342 (14) Å, α = 97·017 (9), β = 91·733 (8), γ = 109·799 (8)°, V = 715·04 (13) Å^3, Z = 2, D_x = 1·23 g cm^{-3} (298 K), λ(Mo $K\alpha$) = 0·7107 Å, μ = 0·7949 cm^{-1}, $F(000)$ = 288, T = 298 K, R = 0·0482 for 2464 reflections. The molecules exist as hydrogen-bonded dimers in the crystal involving the hydroxyl group and the carbonyl O atom [O13···O14 (related by 2 − x, − y, − z) 2·719 (2) Å; H13···O14 1·90 (2) Å; O13—H13···O14 165 (2)°]. The bonds from the bridgehead atom of the tricyclic ring to other ring atoms appears to be elongated [av. 1·557 (1) Å] compared to the other Csp^3—Csp^3 bonds in the molecule. The lactam ring is essentially planar [maximum deviation is 0·010 (3) Å for N3].

Experimental. (1) was synthesized by an intramolecular Diels–Alder reaction of the corresponding trienamide. Details of the synthetic procedure are

(1)
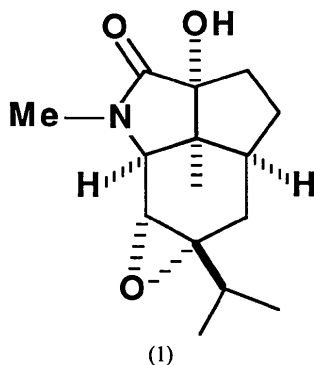
described elsewhere (Li, 1988). Colorless crystals were obtained by slow evaporation from diethyl ether. The data crystal was a long needle and had approximate dimensions 0·21 × 0·31 × 0·73 mm. The data were collected at room temperature on a Nicolet $P3$ diffractometer using a graphite monochromator. Lattice parameters were obtained from

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the least-squares refinement of 24 reflections with 20·4 < 2θ < 30·2°. Data were collected using the ω-scan technique (6562 reflections, 3281 unique, R_{int} = 0·0228), with a 2θ range from 4·0–55°, using a 1·2° ω scan at 3–6° min^{-1} (h = −10→9, k = −12→11, l = −17→16). Four reflections (0$\bar{4}$0; 103; 400; 1$\bar{2}\bar{3}$) were remeasured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was <4%). The data were also corrected for Lp effects but not for absorption. Data reduction and decay correction were performed using the Nicolet XRD *SHELXTL-PLUS* software package (Sheldrick, 1987). Reflections having $F_o < 4\sigma(F_o)$ were considered unobserved (817 reflections). The structure was solved by direct methods (Sheldrick, 1987) and refined by full-matrix least-squares procedures (Sheldrick, 1976) with anisotropic thermal parameters for the non-H atoms. H atoms were obtained from a ΔF map and refined with isotropic thermal parameters. 264 parameters were refined. The function $\Sigma w(|F_o| - |F_c|)^2$, was minimized, where w = $1/[\sigma(F_o)]^2$ and $\sigma(F_o)$ = $0·5kI^{-1/2}\{[\sigma(I)]^2 + (0·02I)^2\}^{1/2}$. The intensity I is given by ($I_{peak} - I_{background}$) × (scan rate); 0·02 is a factor to downweight intense reflections and to account for instrument instability and k

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

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

	x	y	z	$U_{eq}(\text{Å}^2)$
C1	0·8335 (2)	0·1226 (2)	0·13177 (14)	0·0420 (6)
C2	0·8588 (2)	0·2096 (2)	0·03118 (14)	0·0413 (6)
N3	0·7498 (2)	0·3082 (2)	0·03322 (10)	0·0403 (5)
C4	0·6322 (2)	0·3053 (2)	0·12673 (13)	0·0384 (6)
C5	0·6649 (2)	0·4808 (2)	0·18065 (13)	0·0424 (6)
C6	0·7108 (3)	0·5354 (2)	0·29777 (13)	0·0467 (7)
C7	0·7323 (3)	0·4090 (3)	0·3666 (2)	0·0552 (8)
C8	0·8023 (3)	0·2760 (2)	0·30589 (14)	0·0461 (6)
C9	1·0171 (3)	0·3346 (3)	0·2771 (2)	0·0534 (7)
C10	1·0276 (3)	0·1845 (3)	0·2037 (2)	0·0532 (7)
C11	0·6837 (2)	0·1842 (2)	0·19742 (13)	0·0400 (6)
C12	0·4948 (3)	0·0440 (3)	0·2157 (2)	0·0566 (8)
O13	0·7589 (2)	−0·05295 (15)	0·09832 (12)	0·0577 (5)
O14	0·9633 (2)	0·1914 (2)	−0·04277 (11)	0·0573 (5)
C15	0·7196 (4)	0·3876 (3)	−0·0595 (2)	0·0535 (8)
O16	0·5119 (2)	0·4944 (2)	0·24862 (11)	0·0592 (5)
C17	0·8057 (4)	0·7213 (2)	0·3385 (2)	0·0616 (9)
C18	0·7123 (7)	0·7702 (4)	0·4394 (2)	0·094 (2)
C19	1·0286 (4)	0·7737 (4)	0·3557 (3)	0·0878 (12)

is the correction due to Lp effects and decay. $\sigma(I)$ was estimated from counting statistics; $\sigma(I) = [(I_{peak} + I_{background})^{1/2} \times (\text{scan rate})]$. The final $R = 0.0482$ for 2464 reflections, $wR = 0.0551$ ($R_{all} = 0.0678$, $wR_{all} = 0.0588$) and a goodness of fit $= 1.811$. The maximum $|\Delta/\sigma| < 0.1$ in the final refinement cycle and the minimum and maximum peaks in the final ΔF map were -0.21 and 0.23 e Å^{-3}, respectively. The scattering factors for the non-H atoms were obtained from Cromer & Mann (1968), with anomalous-dispersion corrections taken from Cromer & Liberman (1970), while scattering factors for the H atoms are from Stewart, Davidson & Simpson (1965). The linear absorption coefficient was calculated from values in *International Tables for X-ray Crystallography* (1974). Thermal ellipsoid plots were generated using *SHELXTL-PLUS* (Sheldrick, 1987). Positional and thermal parameters for the non-H atoms are listed in Table 1,* while the bond lengths and angles

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* Tables of anisotropic thermal parameters, positional and thermal parameters for the H atoms, bond distances and angles involving the H atoms, torsion angles, structure factor amplitudes and a unit-cell packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52595 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
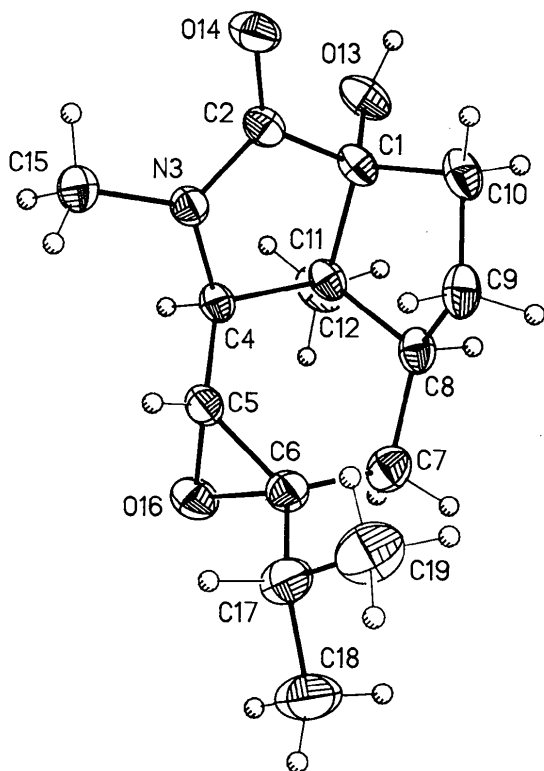

Fig. 1. View of (1) showing the atomic labelling scheme. Thermal ellipsoids are scaled to the 30% probability level. H atoms are scaled to an arbitrary size.

Table 2. Bond lengths (Å) and angles (°)

1	2	3	1—2	1—2—3
C2	C1	C10	1·517 (3)	110·30 (13)
C2	C1	C11		105·28 (15)
C10	C1	C11	1·533 (2)	106·39 (14)
C10	C1	O13		114·2 (2)
C11	C1	O13	1·564 (3)	111·94 (12)
O13	C1	C2	1·416 (2)	108·38 (13)
N3	C2	O14	1·333 (2)	124·5 (2)
N3	C2	C1		110·12 (15)
O14	C2	C1	1·235 (2)	125·4 (2)
C4	N3	C15	1·458 (2)	121·3 (2)
C4	N3	C2		114·96 (14)
C15	N3	C2	1·454 (3)	122·7 (2)
C5	C4	C11	1·505 (2)	117·18 (13)
C5	C4	N3		110·61 (13)
C11	C4	N3	1·564 (3)	105·19 (14)
C6	C5	O16	1·466 (2)	60·03 (11)
C6	C5	C4		123·8 (2)
O16	C5	C4	1·437 (2)	114·12 (13)
C7	C6	O16	1·502 (3)	113·70 (14)
C7	C6	C17		119·8 (2)
C7	C6	C5		117·5 (2)
O16	C6	C17	1·452 (2)	111·9 (2)
O16	C6	C5		59·02 (11)
C17	C6	C5	1·516 (2)	118·9 (2)
C8	C7	C6	1·524 (3)	113·7 (2)
C9	C8	C11	1·527 (3)	104·20 (14)
C9	C8	C7		116·33 (15)
C11	C8	C7	1·544 (2)	115·8 (2)
C10	C9	C8	1·507 (3)	102·68 (14)
C1	C10	C9		104·0 (2)
C12	C11	C1	1·526 (2)	114·14 (14)
C12	C11	C4		109·59 (15)
C12	C11	C8		111·6 (2)
C1	C11	C4		104·43 (13)
C1	C11	C8		103·96 (13)
C4	C11	C8		112·89 (13)
C5	O16	C6		60·96 (11)
C18	C17	C19	1·522 (4)	112·7 (2)
C18	C17	C6		110·8 (2)
C19	C17	C6	1·517 (4)	111·8 (2)

for the non-H atoms are listed in Table 2. The atomic labelling scheme is shown in Fig. 1. The least-squares planes program was provided by Cordes (1983); other computer programs are listed in reference 11 of Gadol & Davis (1982).

Related literature. The crystal structure of the α-phenylethyl analog of (1) has been reported previously and references cited therein (Lynch, Li & Martin, 1988) contain related literature.

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Structure of a Tetrazole

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Abstract. 2-Phenyl-1,2,3,4-tetrazole-5-carbonitrile, $C_8H_5N_5$, $M_r = 171\cdot1$, monoclinic, $P2_1/a$, $a = 10\cdot028$ (1), $b = 11\cdot747$ (1), $c = 7\cdot205$ (1) Å, $\beta = 102\cdot94$ (1)°, $V = 827\cdot1$ (1) Å^3, $Z = 4$, $D_x = 1\cdot374$ Mg m^{-3}, $\lambda(Cu\ K\alpha_1) = 1\cdot54050$ Å, $\mu = 0\cdot78$ mm^{-1}, $F(000) = 352$, $T = 293$ K, final $R = 0\cdot059$
for 730 reflexions. The dihedral angle between the phenyl and tetrazole rings is $1\cdot9$ (5)°. Bond lengths and planarity indicate extensive electron delocalization in the tetrazole ring.

Experimental. A colorless prism, $0\cdot15 \times 0\cdot10 \times 0\cdot45$ mm, by recrystallization from $C_2H_5OC_2H_5/C_6H_{14}$. Rigaku AFC5 four-circle diffractometer used with θ–2θ-scan method, ω-scan width $(1\cdot3 + 0\cdot41 \tan\theta)°$ and scan speed $16°$ min^{-1}. Lattice parameters obtained from least-squares analysis of 20 reflexions with 2θ values ranging from 54 to 60°. Out of 1466 reflexions scanned within index range $h\ -11$–11, $k\ 0$–13, $l\ 0$–8 up to $(\sin\theta)/\lambda = 0\cdot56$ Å^{-1} including 112 equivalent reflexions ($R_{int} = 0\cdot014$), 1229 unique reflexions classified as observed. Three standard reflexions measured every 120 reflexions, no significant intensity variation. Intensities corrected for Lorentz and polarization factors, but absorption correction not applied. Structure solved using the program package *SAPI*85 (Yao, Zheng, Qian, Han, Gu & Fan, 1985), a version of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The refinement was carried out by the

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
N(1)	0·4563 (3)	0·2743 (3)	0·2259 (4)	5·92 (28)
N(2)	0·5360 (3)	0·3632 (2)	0·2789 (4)	5·41 (28)
N(3)	0·6629 (3)	0·3358 (3)	0·3690 (5)	7·09 (29)
N(4)	0·6661 (3)	0·2233 (4)	0·3773 (5)	7·56 (30)
C(5)	0·5401 (4)	0·1896 (4)	0·2887 (7)	6·15 (29)
C(6)	0·5024 (4)	0·0722 (5)	0·2658 (7)	7·78 (32)
N(7)	0·4723 (5)	−0·0209 (4)	0·2457 (7)	11·31 (33)
C(8)	0·4906 (3)	0·4783 (3)	0·2462 (5)	5·06 (28)
C(9)	0·3566 (4)	0·4974 (4)	0·1572 (6)	6·06 (30)
C(10)	0·3135 (5)	0·6089 (4)	0·1259 (6)	6·93 (32)
C(11)	0·4015 (5)	0·6975 (4)	0·1793 (7)	7·17 (31)
C(12)	0·5354 (5)	0·6764 (4)	0·2696 (8)	7·10 (31)
C(13)	0·5805 (4)	0·5655 (4)	0·3024 (6)	6·15 (30)

Table 2. *Bond lengths* (Å) *and angles* (°)

|			
N(1)—C(5)	1·316 (6)		
N(1)—N(2)	1·318 (5)	C(8)—C(9)	1·372 (6)
N(2)—N(3)	1·332 (5)	C(9)—C(10)	1·382 (7)
N(3)—N(4)	1·323 (6)	C(10)—C(11)	1·364 (7)
N(4)—C(5)	1·342 (6)	C(11)—C(12)	1·376 (7)
C(5)—C(6)	1·429 (8)	C(12)—C(13)	1·383 (7)
C(6)—N(7)	1·135 (8)	C(13)—C(8)	1·364 (6)
N(2)—C(8)	1·429 (5)		
N(1)—N(2)—N(3)	113·6 (3)	N(3)—N(2)—C(8)	122·9 (3)
N(2)—N(3)—N(4)	105·9 (3)	N(2)—C(8)—C(13)	119·7 (3)
N(3)—N(4)—C(5)	105·2 (3)	N(2)—C(8)—C(9)	118·3 (3)
N(4)—C(5)—N(1)	113·6 (4)	C(8)—C(9)—C(10)	118·0 (4)
C(5)—N(1)—N(2)	101·5 (3)	C(9)—C(10)—C(11)	121·1 (4)
C(5)—C(6)—N(7)	179·2 (7)	C(10)—C(11)—C(12)	119·8 (4)
N(4)—C(5)—C(6)	122·4 (4)	C(11)—C(12)—C(13)	119·8 (4)
N(1)—C(5)—C(6)	123·9 (4)	C(12)—C(13)—C(8)	119·2 (4)
N(1)—N(2)—C(8)	123·4 (3)	C(13)—C(8)—C(9)	121·9 (4)
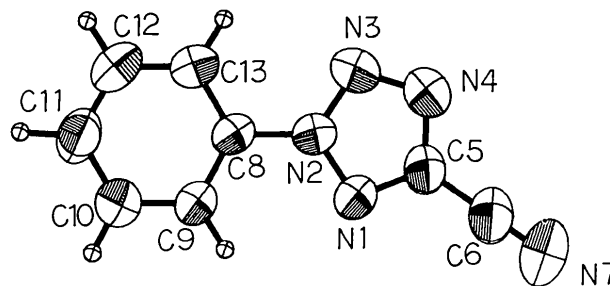
Fig. 1. Thermal-ellipsoid plot. Ellipsoids are drawn at the 50% probability level while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.