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Acta Cryst. (1991). C**47**, 2107–2109

Structure of 10-*tert*-Butyl-7*β*-ethynyl-7*α*-hydroxyspiro[5.5]undec-1-en-3-one*

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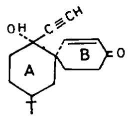
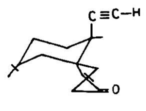
(*Received* 10 *September* 1990; *accepted* 6 *March* 1991)

Abstract. $C_{17}H_{24}O_2$, $M_r = 260{\cdot}36$, monoclinic, $P2_1/c$, $a = 10{\cdot}712$ (3), $b = 11{\cdot}817$ (3), $c = 12{\cdot}318$ (3) Å, $\beta = 107{\cdot}75$ (2)°, $V = 1485{\cdot}0$ (4) Å^3, $Z = 4$, $D_m = 1{\cdot}16$ (2), $D_x = 1{\cdot}168$ g cm^{-3}, graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 5{\cdot}47$ cm^{-1}, $F(000) = 568$, $T = 298$ K, final $R = 0{\cdot}040$, $wR = 0{\cdot}037$ for 2087 reflections with $I > 2\sigma(I)$. One of the cyclohexane rings is in the chair conformation and the other is in the half-chair conformation. Molecules are stabilized by O—H···O intermolecular hydrogen bonds.

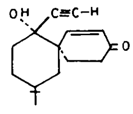
Introduction. The title compound was studied mainly to learn the geometry of the spiro carbinol (1). In particular the relative orientation of the unsaturated rings is of unusual importance in understanding the mechanism of base-catalyzed rearrangements of oxy-Cope systems (Seshu Sekhara Rao, Kumar, Rajagopalan & Swaminathan, 1982; Swaminathan, 1984). This carbinol (m.p. 405–406 K) was obtained (Ravikumar, 1985) by the ethynylation of the spiro diketone (4) and assigned the stereochemistry indicated in structure (1), also represented conformationally in structure (2). This assignment was tentative based on the assumptions (i) that the sp^2 C atom at the spiro junction is more likely to have an axial orientation with respect to ring *A* in the diketone (4) and (ii) that the attack of the acetylide ion occurs axially as has been established for 2,2-disubstituted cyclohexanones (Milas, Macdonald & Black, 1948; Attenburrow, Cameron, Chapman, Evans, Hems, Jansen & Walker, 1952). It was of interest therefore to determine unequivocally the structure of (1) by X-ray analysis.



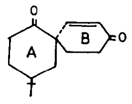
(1)



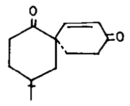
(2)



(3)



(4)



(5)

Experimental. The title compound was synthesised in the Department of Organic Chemistry, University of Madras, and its density was measured by flotation. White needle-shaped crystals from benzene, 0·40 × 0·20 × 0·50 mm, Enraf–Nonius CAD-4 single-crystal diffractometer, $\omega/2\theta$ scan, cell parameters from 20 accurately centred reflections, $30 \leq 2\theta \leq 60°$. Lp correction but no absorption correction, three check reflections measured every 100 reflections showed a 3% change in the intensity of standard reflections, $0 \leq h \leq 11$, $0 \leq k \leq 14$, $-14 \leq l \leq 14$, 2251 unique reflections, $R_{\rm int} = 0{\cdot}067$, 2087 reflections with $I > 2\sigma(I)$ used in the least-squares refinement. Structure

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Table 1. *Positional parameters of non-*H *atoms and* B_{eq} *values with e.s.d.'s in parentheses*

Anisotropically refined atoms are given in the form: $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ac(\cos\beta)B(1,3)]$.

	x	y	z	B(Å^2)
C1	0·4243 (2)	0·2337 (2)	0·9915 (1)	3·18 (4)
C2	0·5298 (2)	0·1705 (2)	1·0339 (2)	3·62 (4)
O1	0·6385 (1)	0·0312 (1)	1·1642 (1)	4·91 (4)
O2	0·3981 (1)	0·3580 (1)	1·1934 (1)	4·28 (3)
C3	0·5454 (2)	0·0964 (2)	1·1325 (2)	3·50 (4)
C4	0·4461 (2)	0·1090 (2)	1·1944 (2)	4·16 (5)
C5	0·3110 (2)	0·1382 (2)	1·1155 (2)	3·47 (4)
C6	0·3051 (2)	0·2370 (2)	1·0321 (1)	2·71 (3)
C7	0·2953 (2)	0·3542 (2)	1·0868 (2)	3·12 (4)
C8	0·1621 (2)	0·3698 (2)	1·1073 (2)	3·48 (4)
C9	0·0460 (2)	0·3502 (2)	1·0001 (2)	3·40 (4)
C10	0·0527 (2)	0·2321 (2)	0·9517 (1)	2·91 (4)
C11	0·1834 (2)	0·2226 (2)	0·9253 (1)	2·98 (4)
C12	0·3153 (2)	0·4476 (2)	1·0135 (2)	3·80 (4)
C13	0·3352 (2)	0·5239 (2)	0·9599 (2)	5·43 (6)
C14	−0·0687 (2)	0·1989 (2)	0·8494 (2)	3·53 (4)
C15	−0·0527 (2)	0·0770 (2)	0·8135 (2)	4·65 (5)
C16	−0·1924 (2)	0·2040 (2)	0·8879 (2)	5·42 (6)
C17	−0·0873 (2)	0·2780 (2)	0·7470 (2)	4·57 (5)

Table 2. *Bond distances* (Å) *and bond angles* (°) *of non-*H *atoms with e.s.d.'s in parentheses*

C1	C2	1·323 (3)	C10	C14	1·559 (2)
C2	C3	1·465 (3)	C11	C6	1·553 (2)
C4	C3	1·492 (3)	C12	C13	1·175 (3)
C4	C5	1·517 (2)	C14	C16	1·540 (3)
C6	C5	1·544 (3)	C14	C15	1·532 (3)
C6	C1	1·507 (3)	C14	C17	1·534 (3)
C7	C6	1·557 (3)	O1	C3	1·225 (2)
C7	C8	1·534 (3)	C9	C8	1·531 (2)
C7	O2	1·435 (2)	C10	C9	1·528 (3)
C7	C12	1·483 (3)	C10	C11	1·535 (3)

C6	C1	C2	126·3 (2)	O2	C7	C12	108·7 (1)
C1	C2	C3	122·2 (2)	C8	C7	C12	109·0 (2)
O1	C3	C2	121·0 (2)	C6	C7	C12	110·9 (2)
O1	C3	C4	122·5 (2)	C9	C8	C7	113·1 (2)
C2	C3	C4	116·4 (2)	C10	C9	C8	110·6 (1)
C3	C4	C5	112·6 (2)	C9	C10	C11	107·7 (1)
C6	C5	C4	115·8 (2)	C9	C10	C14	114·7 (1)
C1	C6	C5	109·5 (1)	C11	C10	C14	113·6 (2)
C7	C6	C5	112·3 (1)	C10	C11	C6	113·4 (1)
C11	C6	C1	107·1 (1)	C7	C12	C13	176·8 (2)
C11	C6	C5	109·5 (1)	C10	C14	C15	109·3 (1)
C11	C6	C7	108·3 (1)	C10	C14	C16	109·0 (2)
C7	C6	C1	110·0 (1)	C10	C14	C17	112·2 (2)
O2	C7	C6	106·9 (1)	C16	C14	C15	108·0 (2)
C8	C7	C6	111·5 (1)	C16	C14	C17	108·8 (2)
O2	C7	C8	109·8 (2)	C17	C14	C15	109·5 (2)

solution by direct methods, all H atoms obtained from ΔF map, full-matrix least-squares refinement on F_o, anisotropic temperature factors for all non-H atoms and isotropic temperature factors for all H atoms. $R = 0·040$, $wR = 0·037$, $w = 1/[\sigma^2(F_o) + 0·04(F_o)^2]$, $S = 0·647$, $(\Delta/\sigma)_{\max} = 0·19$, final ΔF map featureless, final peaks in the $\Delta\rho$ synthesis are $-0·14$ to $+0·17$ e Å^{-3}; no correction for secondary extinction. Atomic scattering factors and f', f'' values from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations peformed using the *SDP* (Frenz, 1978) package on a VAX 11/730 computing system.

Discussion. Final positional parameters of all non-H atoms are given in Table 1[*] and bond lengths and bond angles in Table 2. A stereo diagram of the molecule (*PLUTO*; Motherwell & Clegg, 1978) is given in Fig. 1. The cyclohexane ring *A* is in a chair conformation. The bond lengths and bond angles agree with other cyclohexane systems (Nethaji, 1987). The average bond length around the ring is 1·539 (12) Å and average bond angle is 110 (3)°. Ring *B* is in a half-chair conformation.

The mean planes of the two rings make an angle of 100·1 (1)°. X-ray analysis shows that the equatorial sp^2 C atom at the spiro junction is *cis* to the axial *sp* C atom and the structure (1) must now be revised to structure (3); it follows that the starting spiro

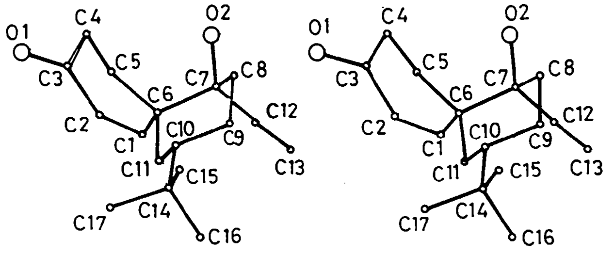

Fig. 1. Stereo diagram of the molecule.

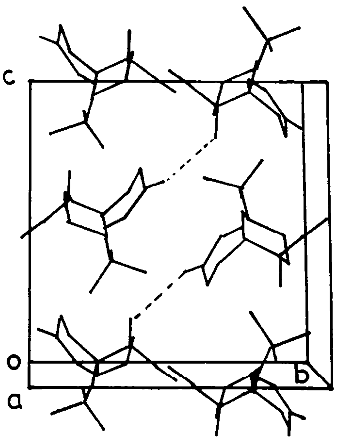

Fig. 2. View of the contents of the unit cell down the *a* axis.

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[*] Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles, least-squares planes, hydrogen-bond geometry and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54066 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

diketone (4) must be represented by structure (5). Such a structure is expected to favour the base-catalyzed rearrangement of the system in structure (3) by a concerted mechanism.

Unit-cell packing of the molecules down the *a* axis is shown in Fig. 2. The molecules in the unit cell are stabilized by O2—HO2···O1 intermolecular hydrogen bonds, distance O2···O1 2·799 (2), O2—HO2 1·01 (3) and HO2···O1 1·79 (3) Å and angle O2—HO2···O1 179 (2)°.

We thank Professor Swaminathan for supplying the compound and for discussions. Thanks are also due to Professor R. Srinivasan for discussions. One of the authors (VG) thanks the CSIR for financial assistance.

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Acta Cryst. (1991). C**47**, 2109–2112

Application of the Haller–Bauer Reaction in the Synthesis of Taxol-Related Diterpenes: Structure of the Intramolecular Lactam of 2-Amino-5-hydroxy-4,8,11-trimethylbicyclo[5.3.1]undeca-3,8-diene-11-carboxylic Acid

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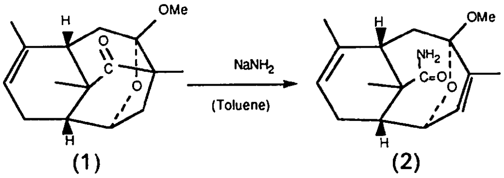
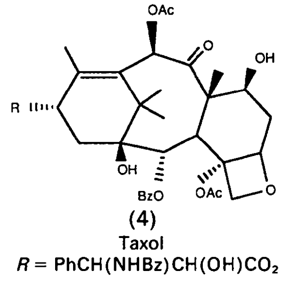
(*Received* 26 *October* 1990; *accepted* 18 *February* 1991)

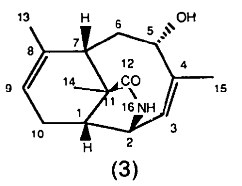
Abstract. 4-Hydroxy-3,7,13-trimethyl-11-azatricyclo[4.4.3.$0^{10,13}$]trideca-2,7-dien-12-one (3), $C_{15}H_{21}NO_2$, M_r = 247·34, triclinic, $P\bar{1}$, a = 13·454 (4), b = 12·701 (3), c = 13·376 (3) Å, α = 106·18 (5), β = 112·13 (4), γ = 95·80 (5)°, V = 1978·2 Å^3, Z = 6, D_x = 1·241 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 4·59 cm^{-1}, $F(000)$ = 798, T = 293 K, R = 0·062 for 5781 observed reflections. The result of the Haller–Bauer reaction was found unexpectedly to be a lactam instead of a dihydrofuran acyclic amide. The molecules of the asymmetric unit are associated in compact trimeric clusters stabilized by six hydrogen bonds with only weak interactions between the clusters.

Introduction. In the course of taxol-derivative synthesis (Andriamialisoa, Fétizon, Hanna, Pascard & Prangé, 1984; Cervantes, Do Khac, Fétizon, Guir, Beloeil, Lallemand & Prangé, 1986), general access to the taxane backbone has been investigated. The ring expansion of the compound (1) (Guir, 1990) was thought to be one of the possible routes to synthesize the *A*/*B* structural moiety of the taxol molecule (4), a strong antimitotic natural diterpene (Wani, Taylor, Wall, Coggon & MacPhail, 1971).





(4)
Taxol
R = PhCH(NHBz)CH(OH)CO_2



(3)
Numbering of the molecule
′ is added for molecule 2
″ is added for molecule 3

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