Tetrahedron Vol. 39, No. 7, pp 1181 to 1185, 1983
Printed in Great Britain.

0040-4020/83/071181-05$03.00/0
Pergamon Press Ltd.

THE TWIN-CHAIR CONFORMATION OF BICYCLO[3.3.1]NONANE. DIFFERENTIAL DISTORTIONS OF THE RINGS IN 9-CYCLOHEXYLBICYCLO[3.3.1]NONAN-9-OL AN X-RAY DIFFRACTION STUDY

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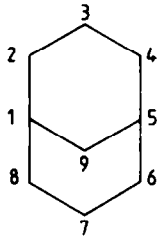
(*Received in UK 2 March* 1981)

Abstract—9-Cyclohexylbicyclo[3.3.1]nonan-9-ol has a twin-chair conformation with C(3)...C(7) transannular separation of 3.134(3) Å. In the twin chair, the ring carrying the 9-C_6H_{11} group in the axial position is flattened to a greater extent than the ring with the 9-OH group axial. The crystals are monoclinic, space group $P2_1/n$, with $a = 11.629(3)$, $b = 6.507(2)$, $c = 17.122(3)$Å, $\beta = 93.80(2)°$, and $Z = 4$. The crystal structure was determined by direct phasing and the atomic co-ordinates were subsequently adjusted by least-squares calculations which converged at $R = 0.047$ for 1764 diffractometer $|F_o|$ values.

In a twin-chair conformer of bicyclo[3.3.1]nonane (I) composed of six-membered rings with tetrahedral angles, the C(3)...C(7) separation would be 2.5Å and the H...H 3,7-separation would have the physically impossigle value of *ca* 0.75 Å. Several X-ray diffraction studies of bicyclo[3.3.1]nonane derivatives have disclosed molecules with a modified twin-chair conformation in which the C(3)...C(7) separation is enlarged to *ca.* 3.1Å; the H...H 3,7-separation is not yet known with precision but appears to be shorter than 2Å.[1] Molecular-mechanics calculations have yielded a range of estimates for the various conformational parameters of the twin-chair conformer[2] and the geometry of this species accordingly provides a useful test of the relative merits of the empirical force fields employed in conformational calculations.



An X-ray structural analysis of 9-cyclohexylbicyclo[3.3.1]-nonan-9-ol was undertaken to investigate the effect on bicyclo[3.3.1]nonane conformation of an unsymmetrical pattern of substituents at position 9. Earlier X-ray studies of derivatives of bicyclo[3.3.1]nonan-9-ol did not provide information about possible differences between the rings because of disorder which effectively superposed and averaged the two six-membered rings.[3]

The crystal structure was determined by direct phasing procedures and the atomic parameters were adjusted by full-matrix least-squares calculations. The molecular structure is illustrated in Fig. 1 and the atomic co-ordinates, bond lengths, interbond angles and torsion angles are in Tables 1–4. The bicyclononane six-membered ring which has the 9-hydroxyl group in axial orientation has been numbered to contain C(3) and the ring which has the 9-cyclohexyl group in axial orientation has been numbered to contain C(7).

The C–C–C–C torsion angles in the cyclohexyl substituent range from 53.2 to 56.7° (mean 55.3°) whereas those in the six-membered rings of the bicyclononane moiety range from 38.1 to 64.6°; the contrast provides a striking demonstration of the steric forces operative here. Since corresponding torsion angles on opposite sides of the plane through C(3), C(9) and C(7) differ only very slightly in magnitude, the bicyclononane rings are not skewed. On the other hand, the torsion angles C(5)–C(6)–C(7)–C(8) and C(6)–C(7)–C(8)–C(1) in the C(7)-ring are substantially smaller than the angles C(1)–C(2)–C(3)–C(4) and C(2)–C(3)–C(4)–C(5) in the C(3)-ring, a result which indicates that the C(7)-ring has been flattened to a greater extent than the C(3)-ring. This differential

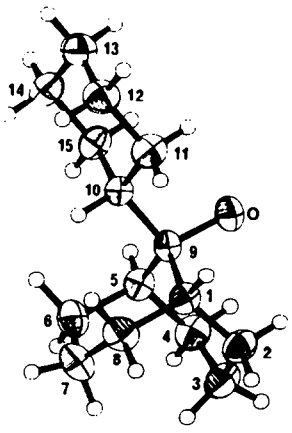


Fig. 1. Molecular structure of 9-cyclohexylbicyclo[3.3.1]-nonan-9-ol. The thermal ellipsoids of the C and O atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0.1Å. The H atom of the hydroxyl group has been omitted, since its position is uncertain.

Table 1. Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	x	y	z
C(1)	7369(2)	1105(3)	4585(1)
C(2)	8013(2)	1539(3)	5379(1)
C(3)	8671(2)	3572(4)	5416(1)
C(4)	7951(2)	5331(3)	5057(1)
C(5)	7306(2)	4815(3)	4268(1)
C(6)	8101(2)	4515(3)	3594(1)
C(7)	8819(2)	2538(3)	3638(2)
C(8)	8176(2)	0662(3)	3928(1)
C(9)	6546(1)	2897(3)	4346(1)
C(10)	5772(1)	2424(2)	3591(1)
C(11)	4987(2)	0566(3)	3693(1)
C(12)	4225(2)	0088(4)	2953(1)
C(13)	3522(2)	1934(4)	2679(1)
C(14)	4304(2)	3763(4)	2551(1)
C(15)	5046(2)	4265(3)	3292(1)
O(1)	5804(1)	3231(2)	4979(1)
H(1)	6908(17)	-0051(35)	4684(12)
$H(2_1)$	8543(19)	0403(39)	5536(14)
$H(2_2)$	7461(20)	1534(38)	5767(14)
$H(3_1)$	9403(19)	3396(35)	5117(13)
$H(3_2)$	8907(24)	3861(43)	5944(18)
$H(4_1)$	7382(19)	5711(37)	5436(15)
$H(4_2)$	8483(18)	6572(38)	5006(13)
H(5)	6791(16)	6006(31)	4146(11)
$H(6_1)$	8625(21)	5682(41)	3577(14)
$H(6_2)$	7572(20)	4618(39)	3070(16)
$H(7_1)$	9146(25)	2243(40)	3141(19)
$H(7_2)$	9550(26)	2812(41)	4002(17)
$H(8_1)$	7697(20)	-0023(39)	3449(15)
$H(8_2)$	8765(21)	-0329(40)	4144(14)
H(10)	6313(16)	2053(31)	3178(12)
$H(11_1)$	4464(21)	0894(39)	4085(16)
$H(11_2)$	5437(21)	-0646(44)	3828(15)
$H(12_1$	3702(22)	-1054(41)	3047(16)
$H(12_2)$	4732(22)	-0226(38)	2555(16)
$H(13_1)$	3028(25)	1567(49)	2201(19)
$H(13_2)$	2996(22)	2342(36)	3044(16)
$H(14_1)$	4858(19)	3426(35)	2166(14)
$H(14_2)$	3863(20)	4947(40)	2358(15)
$H(15_1)$	5591(22)	5433(43)	3205(15)
$H(15_2)$	4552(22)	4671(40)	3668(16)

distortion of the rings can be attributed to the repulsive interactions in the C(7)-ring between the bulky axial cyclohexyl group at C(9) and the axial H atoms at C(6) and C(8) being greater than the corresponding repulsive interaction in the C(3)-ring between the axial OH group and the axial H atoms at C(2) and C(4).

The conformational differences between the rings may be described by the following parameters:

Let

$$\omega_A = \tfrac{1}{2}(|\omega(5\text{–}6\text{–}7\text{–}8)| + |\omega(6\text{–}7\text{–}8\text{–}1)|)$$
$$\omega_B = \tfrac{1}{2}(|\omega(9\text{–}5\text{–}6\text{–}7)| + |\omega(7\text{–}8\text{–}1\text{–}9)|)$$
$$\omega_C = \tfrac{1}{2}(|\omega(1\text{–}9\text{–}5\text{–}6)| + |\omega(8\text{–}1\text{–}9\text{–}5)|)$$
$$\omega_D = \tfrac{1}{2}(|\omega(1\text{–}2\text{–}3\text{–}4)| + |\omega(2\text{–}3\text{–}4\text{–}5)|)$$
$$\omega_E = \tfrac{1}{2}(|\omega(9\text{–}1\text{–}2\text{–}3)| + |\omega(3\text{–}4\text{–}5\text{–}9)|)$$
$$\omega_F = \tfrac{1}{2}(|\omega(5\text{–}9\text{–}1\text{–}2)| + |\omega(4\text{–}5\text{–}9\text{–}1)|).$$

Here, ω(5–6–7–8), ω(6–7–8–1), etc. are defined as the torsion angles C(5)–C(6)–C(7)–C(8), C(6)–C(7)–C(8)–C(1), etc.

Then

$$\Delta_1 = \omega_A - \omega_D$$
$$\Delta_2 = \omega_B - \omega_E$$
$$\Delta_3 = \omega_C - \omega_F.$$

The results obtained for 9-cyclohexylbicyclo-[3.3.1]nonan-9-ol are shown in Table 5. Molecular-mechanics calculations for 9-cyclohexylbicyclo-

Table 2. Bond lengths (Å)

C(1)–C(2)	1.534(3)	C(3)–H(3_2)	0.95(3)
C(1)–C(8)	1.539(3)	C(4)–H(4_1)	0.99(2)
C(1)–C(9)	1.546(2)	C(4)–H(4_2)	1.03(2)
C(2)–C(3)	1.527(3)	C(5)–H(5)	0.99(2)
C(3)–C(4)	1.523(3)	C(6)–H(6_1)	0.98(3)
C(4)–C(5)	1.539(3)	C(6)–H(6_2)	1.06(3)
C(5)–C(6)	1.538(3)	C(7)–H(7_1)	0.97(3)
C(5)–C(9)	1.540(2)	C(7)–H(7_2)	1.04(3)
C(6)–C(7)	1.533(3)	C(8)–H(8_1)	1.06(3)
C(7)–C(8)	1.532(3)	C(8)–H(8_2)	0.99(3)
C(9)–C(10)	1.557(2)	C(10)–H(10)	1.01(2)
C(9)–O(1)	1.446(2)	C(11)–H(11_1)	0.96(3)
C(10)–C(11)	1.532(3)	C(11)–H(11_2)	0.97(3)
C(10)–C(15)	1.533(3)	C(12)–H(12_1)	0.98(3)
C(11)–C(12)	1.529(3)	C(12)–H(12_2)	0.95(3)
C(12)–C(13)	1.510(3)	C(13)–H(13_1)	1.00(3)
C(13)–C(14)	1.522(3)	C(13)–H(13_2)	0.94(3)
C(14)–C(15)	1.522(3)	C(14)–H(14_1)	0.98(2)
C(1)–H(1)	0.95(2)	C(14)–H(14_2)	0.97(3)
C(2)–H(2_1)	0.99(2)	C(15)–H(15_1)	1.01(3)
C(2)–H(2_2)	0.95(3)	C(15)–H(15_2)	0.93(3)
C(3)–H(3_1)	1.03(2)		

[3.3.1]nonane, 9-cyclohexyl-9-methylbicyclo-[3.3.1]-nonane, and bicyclo[3.3.1]nonane were performed with the hydrocarbon force fields developed by Allinger (A)[4] and by White & Bovill (WB)[5] and are also summarized in Table 5. It is gratifying that the results for the 9–C_6H_{11}, 9–CH_3 hydrocarbon mirror in sign the experimental pattern found for the 9–C_6H_{11},9–OH compound.

Results in Table 5 indicate that substituents at C(9) have little effect on the C...C and H...H 3,7-separations which are calculated to be essentially unchanged from those in bicyclo[3.3.1]nonane. The C(3)–C(7) and H(3_1)...H(7_2) separations for 9-cyclohexylbicyclo[3.3.1]nonan-9-ol are 3.134(3) and 1.97(4)Å. The C(3)–H(3_1) and C(7)–H(7_2) lengths, however, are shorter than the normal spectroscopic

Table 3. Bond angles (deg.)

C(2)–C(1)–C(8)	113.3(2)	C(1)–C(9)–C(10)	112.6(1)
C(2)–C(1)–C(9)	110.6(1)	C(1)–C(9)–O(1)	107.8(1)
C(8)–C(1)–C(9)	110.2(1)	C(5)–C(9)–C(10)	113.0(1)
C(1)–C(2)–C(3)	114.3(2)	C(5)–C(9)–O(1)	108.6(1)
C(2)–C(3)–C(4)	111.9(2)	C(10)–C(9)–O(1)	108.2(1)
C(3)–C(4)–C(5)	114.4(2)	C(9)–C(10)–C(11)	112.1(1)
C(4)–C(5)–C(6)	113.9(2)	C(9)–C(10)–C(15)	113.4(1)
C(4)–C(5)–C(9)	110.4(1)	C(11)–C(10)–C(15)	109.6(1)
C(6)–C(5)–C(9)	109.9(1)	C(10)–C(11)–C(12)	112.5(2)
C(5)–C(6)–C(7)	115.0(2)	C(11)–C(12)–C(13)	111.6(2)
C(6)–C(7)–C(8)	114.1(2)	C(12)–C(13)–C(14)	110.5(2)
C(1)–C(8)–C(7)	115.0(2)	C(13)–C(14)–C(15)	111.1(2)
C(1)–C(9)–C(5)	106.6(1)	C(14)–C(15)–C(10)	112.3(2)

Table 4. Torsion angles (deg.)

C(8)-C(1)-C(2)-C(3)	69 2(2)	C(6)-C(5)-C(9)-C(1)	64.6(2)
C(9)-C(1)-C(2)-C(3)	-55.2(2)	C(6)-C(5)-C(9)-C(10)	-59.6(2)
C(2)-C(1)-C(8)-C(7)	-72.8(2)	C(6)-C(5)-C(9)-O(1)	-179.6(1)
C(9)-C(1)-C(8)-C(7)	51.8(2)	C(5)-C(6)-C(7)-C(8)	38.7(3)
C(2)-C(1)-C(9)-C(5)	62.0(2)	C(6)-C(7)-C(8)-C(1)	-38.1(3)
C(2)-C(1)-C(9)-O(1)	-54.4(2)	C(1)-C(9)-C(10)-C(11)	61.6(2)
C(2)-C(1)-C(9)-C(10)	-173.6(1)	C(1)-C(9)-C(10)-C(15)	-173.6(1)
C(8)-C(1)-C(9)-C(5)	-64.1(2)	C(5)-C(9)-C(10)-C(11)	-177.6(1)
C(8)-C(1)-C(9)-O(1)	179.5(1)	C(5)-C(9)-C(10)-C(15)	-52.8(2)
C(8)-C(1)-C(9)-C(10)	60.3(2)	O(1)-C(9)-C(10)-C(11)	-57.4(2)
C(1)-C(2)-C(3)-C(4)	45.3(2)	O(1)-C(9)-C(10)-C(15)	67.4(2)
C(2)-C(3)-C(4)-C(5)	-45.3(2)	C(9)-C(10)-C(11)-C(12)	-180.0(2)
C(3)-C(4)-C(5)-C(6)	-68.8(2)	C(15)-C(10)-C(11)-C(12)	53.2(2)
C(3)-C(4)-C(5)-C(9)	55.4(2)	C(9)-C(10)-C(15)-C(14)	179.7(2)
C(4)-C(5)-C(6)-C(7)	71.5(2)	C(11)-C(10)-C(15)-C(14)	- 54.1(2)
C(9)-C(5)-C(6)-C(7)	-52.9(2)	C(10)-C(11)-C(12)-C(13)	-55.2(2)
C(4)-C(5)-C(9)-C(1)	-61.9(2)	C(11)-C(12)-C(13)-C(14)	55.9(2)
C(4)-C(5)-C(9)-C(10)	174.0(1)	C(12)-C(13)-C(14)-C(15)	-56.7(2)
C(4)-C(5)-C(9)-O(1)	54.0(2)	C(13)-C(14)-C(15)-C(10)	56.7(2)

value for C(sp^3)–H bonds, a characteristic artifact of structure analysis by X-ray diffraction, and when $H(3_1)$ and $H(7_2)$ are displaced along the C–H vectors to make these bond lengths 1.10 Å the H...H transannular distance becomes 1.89Å. The Allinger and White and Bovill force fields yield estimates of *ca* 2Å for the H...H 3,7-separation in bicyclo[3.3.1] nonane and appear to exaggerate slightly the transannular repulsion. The C(3)...C(7) separation reported here for 9-cyclohexylbicyclo[3.3.1]nonan-9-ol is in excellent agreement with X-ray results for related compounds, e.g. 3.120(4)Å in 2,6-dichloro-9-thiabicyclo[3.3.1]nonane-9,9-dioxide,[6] and is a little longer than the value of 3.10Å obtained in an electron-diffraction study of bicyclo[3.3.1]nonane.[7]

Although 9-cyclohexylbicyclo[3.3.1]nonan-9-ol contains a hydroxyl group, there is no hydrogen bonding between molecules in the crystal. The shortest O...O intermolecular distance is 2.97 Å, indicative of a van der Waals interaction.

EXPERIMENTAL

The X-ray intensities were measured on an Enraf-Nonius CAD4 diffractometer with Mo-K_α radiation; 1764 independent reflections in the range $\theta \leq 28.0°$ satisfied the criterion $I > 3\sigma(I)$. The crystal structure was elucidated with a version of MULTAN[8] adapted for the Glasgow University ICL 2976 computer by Dr. C. J. Gilmore. Subsequent Fourier and least-squares calculations were performed with SHELX.[9] Molecular diagrams were prepared with ORTEP.[10]

The co-ordinates and isotropic temperature factors of the C and O atoms were adjusted by full-matrix least-squares calculations with unit weights, after which the H atoms, apart from that of the 9-OH group, were located in a

Table 5. Conformational parameters for bicyclo[3.3.1] nonanes with substituents R_1, R_2 at position 9. Results for $R_1 = C_6H_{11}$, $R_2 = OH$ were obtained by X-ray diffraction, and those for $R_1 = C_6H_{11}$, $R_2 = H$; $R_1 = C_6H_{11}$, $R_2 = CH_3$; $R_1 = H$, $R_2 = H$ were obtained from molecular-mechanics calculations with the Allinger (A) and White & Bovill (WB) force fields

	C_6H_{11},OH	C_6H_{11},CH_3		C_6H_{11},H		H,H	
		A	WB	A	WB	A	WB
Δ_1	-6.9°	-2.0	-1.2	-2.5	-1.6	0	0
Δ_2	-2.9°	-0.5	-0.1	-2.0	-1.7	0	0
Δ_3	2.4°	2.1	1.9	-1.8	-1.6	0	0
$C_3...C_7$	3 13Å	3.17	3.16	3.18	3.16	3.18	3.16
$H_3...H_7$	1.89Å	2.04	1.99	2.03	1.98	2.03	1.97

difference map. The C and O atoms were then assigned anisotropic thermal parameters, the weighting scheme was altered to

$$w = \{\sigma^2(F) + 0.0069|F|^2\}^{-1}$$

and the positional and isotropic thermal parameters of the H atoms were included as variables. The calculations converged at $R = 0.047$, $R_w = 0.053$.

The highest features in a final difference map were two peaks of 0.15Å^{-3} situated about 0.6Å from the oxygen atom, suggesting that the H atom of the hydroxyl group is disordered over two sites. Other features of the map were below $0.1\text{e}\text{Å}^{-3}$.

Acknowledgements—I thank Professor N. L. Allinger for the molecular-mechanics results calculated with his force field and the Science Research Council for a grant towards the purchase of the diffractometer.

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