

The present structure is an interesting example of a substrate molecule unable to bind efficiently to a host site but capable of binding through the mediation of water molecules. Such processes may be of importance in the secondary binding interactions of substrates to enzyme or receptor sites. The bond is strong enough to orient the substrate but weak enough to be broken readily through changes of conformation or solvation.

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9,9'-Bibicyclo[3.3.1]nonylidene

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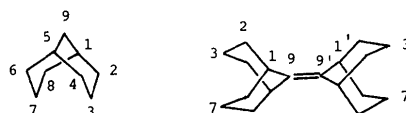
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Abstract. $C_{18}H_{28}$, $M_r = 244.42$, monoclinic, $C2/m$, $a = 14.257$ (6), $b = 15.015$ (6), $c = 6.895$ (2) Å, $\beta = 93.21$ (3)°, $V = 1474$ (1) Å³, $Z = 4$, $D_c = 1.10$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.057$ mm⁻¹. Full-matrix least-squares refinement (non-H atoms anisotropic, H atoms isotropic) based on 790 observed reflections led to an R of 0.045 and R_w of 0.078. The two independent molecules sit on sites of C_{2h} ($2/m$) symmetry. In one molecule the twofold crystallographic axis is along the C=C bond while in the other it is perpendicular to this bond. The bicyclo[3.3.1]non-9-ylidene molecules exhibit all-chair conformations with transannular H...H contacts of 1.99 (3) and 1.81 (8) Å.

Introduction. In the liquid state bicyclo[3.3.1]nonane (1) exists as an equilibrium mixture of the dichair, boat-chair and diboat conformations with the dichair conformation being more stable by about 11.3 kJ mol⁻¹ (Fisch, Smallcombe, Gramain, McKervey & Anderson, 1970; Russell & Keske, 1970). With *endo* substituents at C(3) and C(7), the boat-chair conformation is most stable (Binsch & Roberts, 1965). The

close approach of the C(3) and C(7) *endo* H atoms is reflected in the unusually high C–H bending and stretching frequencies of 2990 and 1490 cm⁻¹, respectively (Eglington, Martin & Parker, 1965). The structures of 1-(*p*-bromobenzenesulfonyloxymethyl)-5-methylbicyclo[3.3.1]nonan-9-ol (Brown, Martin & Sim, 1965) and 3-azabicyclo[3.3.1]nonane hydrobromide (Dobler & Dunitz, 1964) have been reported. Both structures exhibit chair-chair conformations in the solid state with estimated H(3)...H(7) distances of 1.7 and 1.8 Å, respectively. The crowded molecular environment also affects the NMR chemical shifts. The compressed protons are deshielded and exhibit nuclear Overhauser effects. Transannular hydride shifts have been observed in these systems (Appleton & Graham, 1965).



(1)

(2)

9,9'-Bibicyclo[3.3.1]nonylidene (2) should exhibit the same transannular interactions as observed in bicyclo[3.3.1]nonane and C-H stretching and bending frequencies of 2985 and 1488 cm^{-1} are observed. The proton NMR shows four H-atom resonances centered at 2.8 δ and a 24-H-atom envelope at 1.4-2.2 δ . The ^{13}C NMR spectrum contains resonances at 132.3 [C(9)], 34.0 [C(2,4,6,8)], 32.1 [C(1,5)] and 22.5 δ

Table 1. Atomic positional parameters ($\times 10^4$ for C and $\times 10^3$ for H) and U_{eq} ($\times 10^3$)

	x	y	z	U_{eq}^* (\AA^2)
C(1)	259 (1)	1027 (1)	-1680 (3)	52 (1)
C(2)	1125 (2)	1588 (2)	-1042 (4)	66 (2)
C(3)	1048 (2)	2113 (2)	811 (4)	70 (2)
C(4)	601 (2)	1577 (2)	2384 (4)	64 (2)
C(5)	0 †	444 (2)	0 †	46 (1)
C(21)	3962 (1)	-819 (1)	4257 (3)	50 (1)
C(22)	3658 (2)	-841 (2)	2086 (4)	75 (2)
C(23)	3169 (4)	0 †	1344 (5)	79 (3)
C(24)	3140 (2)	-839 (2)	5588 (4)	65 (2)
C(25)	2552 (2)	0 †	5564 (6)	66 (2)
C(26)	4552 (2)	0 †	4693 (4)	48 (2)
H(1)	44 (2)	65 (2)	-280 (3)	59 (6) \ddagger
H(2a)	127 (2)	198 (2)	-207 (4)	77 (8)
H(2b)	172 (2)	115 (2)	-82 (4)	78 (8)
H(3a)	167 (2)	231 (2)	131 (4)	89 (9)
H(3b)	66 (2)	269 (2)	55 (4)	64 (6)
H(4a)	108 (2)	111 (2)	291 (4)	92 (9)
H(4b)	38 (2)	197 (2)	343 (4)	72 (7)
H(21)	435 (2)	-135 (2)	460 (3)	65 (7)
H(22a)	324 (2)	-140 (2)	191 (4)	76 (8)
H(22b)	420 (2)	-88 (2)	145 (4)	82 (9)
H(23a)	249 (4)	0 †	188 (9)	141 (22)
H(23b)	325 (3)	0 †	-14 (7)	94 (13)
H(24a)	342 (2)	-87 (2)	698 (4)	79 (8)
H(24b)	273 (2)	-135 (2)	523 (4)	79 (8)
H(25a)	208 (3)	0 †	674 (7)	93 (11)
H(25b)	215 (3)	0 †	436 (6)	79 (11)

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

† Special positions.

$\ddagger U_{iso} \times 10^3$.

Table 2. Interatomic distances (\AA) and valence angles ($^\circ$)

Molecule A		Molecule B	
C(1)-C(2)	1.539 (4)	C(21)-C(22)	1.535 (4)
C(1)-C(5)	1.514 (3)	C(21)-C(24)	1.530 (4)
C(2)-C(3)	1.510 (4)	C(21)-C(26)	1.510 (3)
C(3)-C(4)	1.518 (4)	C(22)-C(23)	1.518 (4)
C(4)-C(1')	1.535 (4)	C(24)-C(25)	1.512 (4)
C(5)-C(5'')	1.332 (4)	C(26)-C(26'')	1.324 (4)
C(2)C(1)C(4')	114.2 (2)	C(22)C(21)C(24)	113.6 (2)
C(2)C(1)C(5)	108.9 (2)	C(22)C(21)C(26)	109.6 (2)
C(4)C(1')C(5)	109.2 (2)	C(24)C(21)C(26)	109.4 (2)
C(1)C(2)C(3)	115.6 (2)	C(21)C(22)C(23)	114.2 (3)
C(2)C(3)C(4)	112.4 (2)	C(22)C(23)C(22')	112.6 (4)
C(3)C(4)C(1')	114.7 (2)	C(21)C(24)C(25)	114.8 (2)
C(1)C(5)C(1')	109.3 (2)	C(21)C(26)C(21')	109.1 (2)
C(1)C(5)C(5'')	125.3 (1)	C(21)C(26)C(26'')	125.5 (1)
		C(24)C(25)C(24')	112.8 (3)

[C(3,7)]. We would like to report details of the structure of 9,9'-bicyclo[3.3.1]nonylidene.

The title compound was prepared from 9,9-dibromobicyclo[3.3.1]nonane by a Wurtz-type reaction and was recrystallized from ethyl acetate. The material sublimes readily and decomposes upon exposure to X-rays in the presence of air. A crystal of dimensions 0.42 \times 0.58 \times 0.75 mm was sealed in a quartz capillary and was used for all X-ray measurements. Intensity data were collected on a Syntex $P2_1$ diffractometer system by the $\theta:2\theta$ scanning technique using a variable scan speed, Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflections whose angles were measured by a centering routine associated with the diffractometer. The unit cell was found to be monoclinic, and systematic absences were consistent with space group $C2/m$. A periodically monitored reflection showed no significant change in intensity. Of the 1190 reflections measured ($2\theta \leq 48$), 790 had intensities greater than $3\sigma(I)$. Lorentz and polarization corrections were applied, but no absorption corrections were made.

Application of the direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) revealed the positions of the 11 independent heavy atoms. After several cycles of refinement H-atom positions were calculated and included in the refinement. C atoms were refined with anisotropic thermal parameters while H atoms were refined isotropically. The refinement was terminated at a final R value of 0.045 and R_w of 0.078, where R and R_w are defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$ and $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$.

Atomic scattering factors were calculated by the XRAY 76 program (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The largest peak in the difference Fourier map was 0.25 $e \text{ \AA}^{-3}$, and the

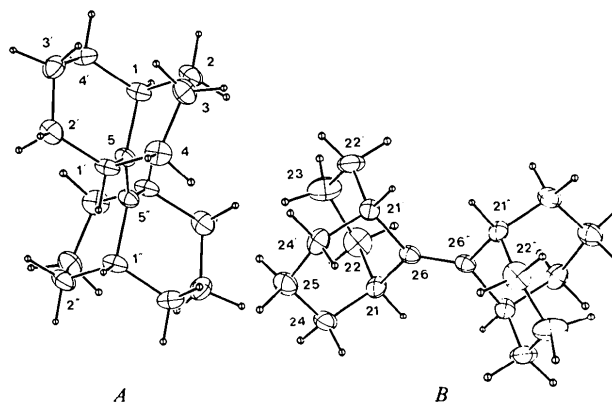


Fig. 1. ORTEP drawing of 9,9'-bicyclo[3.3.1]nonylidene. The thermal ellipsoids are drawn at the 35% probability level.

average shift/error during the final cycle of refinement was 0.27. Atomic positional parameters are presented in Table 1 while interatomic distances and valence angles are given in Table 2.* The numbering scheme used in Fig. 1 and in all tables reflects molecular symmetry and does not correspond to *Chemical Abstracts* notation.

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of the two independent 9,9'-bibicyclo[3.3.1]nonylidene molecules. The molecules exist in the all-chair conformation which leads to a strong transannular interaction between (H3*b*)...H(3*b'*) and H(23*a*)...H(25*b*) of 1.99 (3) and 1.81 (8) Å, respectively. This interaction is responsible for the flattening of the cyclohexane rings as indicated by four torsion angles of less than 55.8° (Bucourt & Hainaut, 1965) and three valence angles of greater than 112°. The short transannular contact is consistent with the observed shifts in the IR and proton NMR spectra.

The double bonds with attached atoms form planar systems which bring atoms H(1')...H(1''), H(21')...H(21'') and the symmetry-related pairs within 1.95 (4) and 1.90 (4) Å, respectively. Since the title molecule serves as a model for compounds such as tetraisopropylethylene, it confirms the predicted strong steric interaction expected for tetra-*tert*-butylethylene which has yet to be synthesized. Although the H(1')...H(1'') and H(21')...H(21'') distances are short, there are apparently no significant shifts in the IR or proton NMR absorptions for these atoms.

9,9'-Bibicyclo[3.3.1]nonylidene reacts with peroxides to give an epoxide and with singlet oxygen to

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38042 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

yield a dioxetane (Keul, 1975). The instability of the compound upon exposure to X-rays in the presence of air is more likely due to reaction with oxygen to give an epoxide.

The 9,9'-bibicyclo[3.3.1]nonylidene molecule can be considered to have D_{2h} symmetry, although not required by crystallographic symmetry.

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Structure of the 1 : 1 Complex of Resorcinol and Urea

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Abstract. $C_6H_6O_2 \cdot CO(NH_2)_2$, orthorhombic, $P2_12_12_1$, $a = 7.142$ (2), $b = 7.798$ (2), $c = 15.428$ (5) Å, $D_m = 1.321$, $D_x = 1.314$ Mg m⁻³, $Z = 4$. 1297 observed diffractometer-measured intensities were used to determine and refine the structure ($R = 0.050$). The structure is hydrogen-bonded with O—H...O (urea) distances 2.696 and 2.679 Å and N—H...O (resor-

cinol) distances 2.944 and 3.128 Å. There are no short contacts between molecules of the same type.

Introduction. Urea forms 1:1 complexes with all three benzenediols, the structure of the one with hydroquinone having already been reported (Mahmoud & Wallwork, 1975). The title compound is frequently