

Conformational behavior of 3-borabicyclo[3.3.1]nonanes. Intramolecular p– σ and p– π interactions in 3,7-*endo*-disubstituted 3-borabicyclo[3.3.1]nonanes

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Received 5 October 2000; accepted 27 February 2001

Dedicated to Professor O.M. Nefedov on the occasion of his 70th birthday (November 25, 2001)

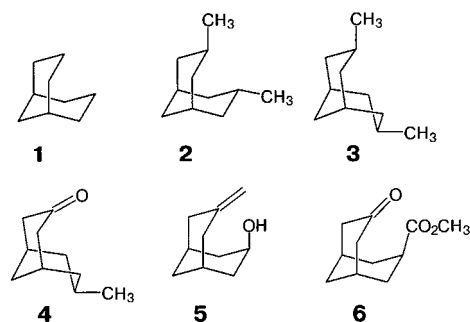
Abstract

Intramolecular interactions between the unoccupied p-orbital of the boron atom and the σ - (Me) or π -orbital (Ph) of the 7-*endo*-substituent lead to an unusual stability of the chair–chair conformation in 3-borabicyclo[3.3.1]nonanes. X-ray analysis of 3,7 α -dimethyl-3-borabicyclo[3.3.1]nonane (**7**) and 3-methyl-7 α -phenyl-3-borabicyclo[3.3.1]nonane (**8**), and single point ab initio calculation (B3LYP/6-31G*) of **8** have confirmed the existence of this specific attractive interaction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 3-Borabicyclo[3.3.1]nonanes; Conformation analysis; p– σ and p– π interactions; X-ray analysis

1. Introduction

Studies of the conformational equilibria in various bicyclo[3.3.1]nonanes, including heterosubstituted compounds, contributed significantly to the formation of



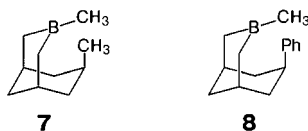
Scheme 1.

the modern concept of conformational analysis [1]. Extensive investigations of the representative series of structurally similar bicycles made it possible to achieve a rather accurate understanding of the spatial and electronic interactions inside the bicyclo[3.3.1]nonane skeleton that result in the relative stability of a certain conformation. This, in turn, gives reasons to consider any deviations from the general regularities in the conformational preferences of bicyclo[3.3.1]nonanes as caused by some additional effects, increasing the stability of an unexpected conformation.

According to electrographic data [2] unsubstituted bicyclo[3.3.1]nonane **1** at 65°C exists predominantly (95%) in a double chair (cc) conformation [2a]. The chair–boat (cb) conformation is about 2.5 kcal mol^{–1} less stable, owing to a greater number of torsional repulsions. At 400°C, the equilibrium concentration of the cc conformation is lower (75%) [2b].

The insertion of neutral substituents in 3-*endo* or 7-*endo* positions makes the cb conformation more sta-

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Scheme 2.

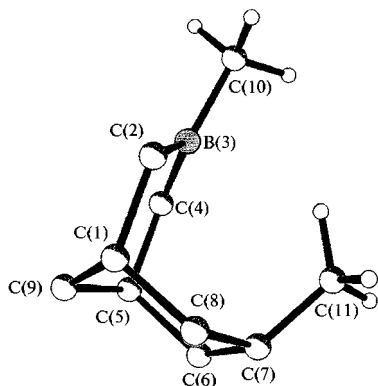


Fig. 1. General view of the molecule **7** and atom numbering scheme. Important bond lengths and bond angles: B(3)–C(2), 1.556(4); B(3)–C(4), 1.569(5); B(3)–C(10), 1.569(5); C(7)–C(11), 1.530(4) Å; C–C bond lengths in the 3-borabicyclo[3.3.1]nonane skeleton 1.522–1.537(5) Å; bond angles: C(2)–B(3)–C(4), 118.2(3); C(2)–B(3)–C(10), 121.1(3); C(4)–B(3)–C(10), 120.2(3); C(2)–C(1)–C(8), 113.5(3); C(4)–C(5)–C(6), 114.1(2); C(1)–C(9)–C(5), 110.5(3); C(6)–C(7)–C(8), 111.0(3); C(6)–C(7)–C(11), 113.2(2); C(8)–C(7)–C(11), 114.0(3)°. Intramolecular distances B(3)⋯C(11), 3.108 Å; B(3)⋯H(11C), 2.23 Å.

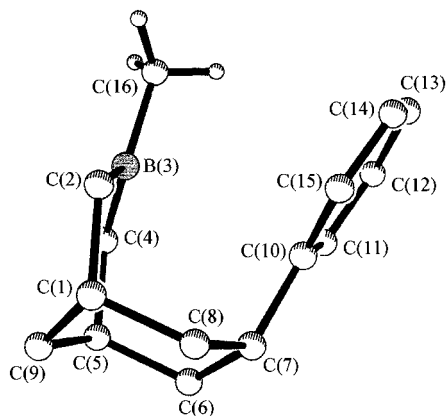


Fig. 2. General view of the molecule **8** and atom numbering scheme. Important bond lengths and bond angles: B(3)–C(2), 1.573(3); B(3)–C(4), 1.576(3); B(3)–C(16), 1.569(3); C(7)–C(10), 1.538(3); C–C bond lengths in the 3-borabicyclo[3.3.1]nonane skeleton 1.535–1.553(3) Å; bond angles: C(2)–B(3)–C(4), 117.0(2); C(2)–B(3)–C(16), 121.0(2); C(4)–B(3)–C(16), 121.3(2); C(2)–C(1)–C(8), 112.9(2); C(4)–C(5)–C(6), 112.9(2); C(1)–C(9)–C(5), 110.2(2); C(6)–C(7)–C(8), 109.2(1); C(6)–C(7)–C(10), 114.8(2); C(8)–C(7)–C(10), 115.8(2); C(7)–C(10)–C(11), 121.5(2); C(7)–C(10)–C(15), 121.3(2); C(11)–C(10)–C(15), 116.9(2)°. Intramolecular distance B(3)⋯C(10), 2.938(3) Å.

ble owing to increased transannular interactions in the cc conformation (3,7-repulsion). Thus, for example, 3β,7β-dimethylbicyclo[3.3.1]nonane **2** occurs predomi-

nantly in the cc conformation, whereas for the 3α,7β derivative **3**, the cb conformation is the most stable one [3] (Scheme 1).

When a methylene group in position 3 is replaced by a trigonal atom, 3,7-interactions are somewhat reduced but usually not enough to make the cc conformation more stable than the cb conformation. Thus 7α-methylbicyclo[3.3.1]nonan-3-on (**4**) acquires the solid state cb conformation according to the X-ray data [4]. The predominance of the cc conformation in the case of 3-methylene-7α-hydroxybicyclo[3.3.1]nonane (**5**) was shown to be caused by an intramolecular hydrogen bond between the *exo*-methylene double bond and the hydroxy group [5]. Apparently a similar reason, viz. the intramolecular dipole–dipole interaction, may be proposed to explain the predominance of the cc conformation in the case of 7α-carboxymethylbicyclo[3.3.1]nonan-3-on (**6**) [5].

In this respect, the fact that in a series of 3,7α-disubstituted 3-borabicyclo[3.3.1]nonanes the cc conformation was found to predominate (according to NMR data) [6] deserves further investigation. In this work, the conformational equilibria in the 3,7α-dimethyl-3-borabicyclo[3.3.1]nonane (**7**) and 3-methyl-7α-phenyl-3-borabicyclo[3.3.1]nonane (**8**) are studied in solid state (Scheme 2).

Special techniques were used to obtain single crystals of air-sensitive liquids (**7**) for X-ray crystallography.

2. Results and discussion

The molecular structures and important structural data for compounds **7** and **8** are shown in Figs. 1 and 2, respectively. Both compounds have a cc conformation with the axial orientation of the methyl (**7**) and phenyl (**8**) substituents at the C(7) atom, and a rather flattened chair conformation of the six-membered boron heterocycle. This flattening is more pronounced in the case of compound **7**: the boron atom B(3) deviates from the plane C(1,2,4,5) by 0.211 Å, and the C(9) atom deviates from the same plane by 0.742 Å in the opposite direction (in compound **8**, the corresponding deviations are 0.299 and 0.754 Å).

The double chair conformations of compounds **7** and **8** cause the shortened intramolecular contacts between the boron atom and C(11) methyl group in **7** (2.23 Å B–H, 3.1 Å B–C) and between the boron atom and the Ph group (2.98 Å B–C(10)) as well as between the methyl group C(16) and Ph (2.83 Å H(16A)–C(13), C(16)–H(16)–C(13) 160°) in **8**. These distances are significantly shorter than the sum of the van der Waals radii (3.7 Å), and normally should lead to the predominance of the cb conformation due to the steric repulsion in the cc conformation. Therefore, the X-ray structures of **7** and **8** directly indicate the existence of

some intramolecular attractive interaction, strong enough to overcome the 3,7-repulsion.

Additionally, this interaction manifests itself in the small deviations of the boron atom from the plane of its C-atom neighbors toward 7 α -substituent by 0.061 (7) and 0.076 Å (8). A similar deviation is observed for the C(10) atom in 8 (0.052 Å).

The intramolecular interaction observed in compounds 7 and 8 may be caused by the vacant 2p-AO of the boron atom. In compound 8 it may be explained by the overlap of the 2p-AO of the boron with the π -system of the phenyl ring. This conclusion is strongly supported by the structural data since the angle between the normal to the phenyl-ring plane and the normal to the C(2)–B–C(4) plane (the direction of the 2p-AO of boron) is equal to 163°, i.e. the phenyl ring is oriented almost perpendicular to the axis of the vacant 2p-AO which should be expected, if they overlap.

Since the structural features of compound 7 are similar to those of compound 8, we conclude that the p– σ conjugation of the 2p-AO of boron and the C–H bonds of the methyl group in 7 may also cause an attractive interaction strong enough to overcome the severe steric 3,7-repulsion.

It should be kept in mind that routine X-ray analysis gives only information about the interatomic distances and says nothing about the real nature of the intramolecular shortening found in 7 and 8. Therefore, topological analysis of the electron density function $\rho(\mathbf{r})$ in 8 obtained by the single point ab initio calculation (B3LYP/6-31G*) using X-ray geometry was carried out [7]. This approach is based on the quantum theory ‘Atoms in molecules’ (QTAM) developed by Bader and co-workers [8], and gives an opportunity to explore the presence and nature of the chemical bond between atoms in question in terms of the critical point (CP) of $\rho(\mathbf{r})$ [8]. The advantage of this approach in the investigation of the transannular interactions was recently demonstrated [9].

Analyses of the CP $\rho(\mathbf{r})$ in 8 have revealed that CP (3, –1) were observed not only on all expected chemical bonds, but also in the interatomic B(3)C(10) and H(16A)C(13) lines, thus indicating that the boron atom and the methyl group exhibit attractive interactions with the Ph ring π -system. The transannular interactions in 8 are characterized by the small values of $\rho(\mathbf{r})$ (0.02 and 0.006 a.e.) and positive values of the Laplacian of the electron density ($\nabla^2\rho(\mathbf{r})$) and local energy density, which are characteristic of the closed-shell interaction [8]. In contrast, the topology of $\rho(\mathbf{r})$ in the CP (3, –1) for B–C, C–C and C–H bonds corresponds to the typical shared-type interaction in terms of the QTAM [8a].

The values of $\rho(\mathbf{r})$ in CP (3, –1) (which correlate with the bond order [8a]) in the interatomic regions of the B(3)C(10) and H(16a)C(13) are similar to the corre-

sponding values found for the SiN interaction in 1-methylsilatarane (0.04 a.e.) [9c] and C=C \cdots HCl (0.006 a.e.) in C₄H₄·HCl [10], respectively. It is noteworthy that the energy of the latter interaction according to the MP2/6-311++G(d,p) calculation is equal to 3.8 kcal mol^{–1} [10].

In conclusion, the X-ray study of the 3,7 α -dimethyl-3-borabicyclo[3.3.1]nonane (7) and 3-methyl-7 α -phenyl-3-borabicyclo[3.3.1]nonane (8), and (B3LYP/6-31G*) calculation of 8 have shown that a specific attractive interaction between the vacant p-orbital of the boron atom and the π - or σ -orbitals of 7-endo-substituents leads to the unusual stability of the cc conformations in these bicyclic compounds.

3. Experimental

All manipulations with organoboron compounds were performed in dry argon. Compound 7 was prepared according to Ref. [6], ¹¹B-NMR (128 MHz, CD₂Cl₂, BF₃·OEt₂): 83.4 (25°C), 82.7 (–60°C). Bicyclic compound 8 was synthesized by the action of the ethereal solution of methylmagnesium iodide (from 0.6 g Mg and 3.55 g (25 mmol) MeI) on 5 g (22 mmol) 7 α -phenyl-3-methoxy-3-borabicyclo[3.3.1]nonane [11]. Yield 3.7 g (80%), b.p. 123–124°C (1.5 mmHg). Anal. Found: C, 84.65; H, 10.15; B, 4.88. Calc. for C₁₅H₂₁B: C, 84.84; H, 9.98; B, 5.19%. ¹H-NMR (CDCl₃, 400 MHz, 20°C, TMS, δ ppm): –0.14 (t, ³J(H,H) = 1.3 Hz, 3H, CH₃); 0.95 (br dd, ²J(H-2 α ,H-2 β) = 17.7 Hz, ³J(H-2 β ,H-1) = 5.5 Hz, 2H, H-2 β ,4 β), 1.58 (dm, ²J(H-9_{syn},H-9_{anti}) = 12.6 Hz, ³J(H-9_{syn},H-1) = 2.7 Hz, 1H, H-9_{syn}), 1.63 (br dm, ²J(H-2 α ,H-2 β) = 17.7 Hz, 2H, H-2 α ,4 α), 1.92 (dm, ²J(H-9_{syn},H-9_{anti}) = 12.6 Hz, ³J(H-9_{anti},H-1) = 2.8 Hz, 1H, H-9_{anti}), 2.12 (ddd, ²J(H-6 β ,H-6 α) = 14.2 Hz, ³J(H-6 β ,H-1) = 5.9 Hz, ³J(H-6 β ,H-7) = 5.4 Hz, 2H, H-6 β , H-8 β), 2.32 (m, 2H, H-1, H-5), 2.39 (dm, ²J(H-6 β ,H-6 α) = 14.2 Hz, 2H, H-6 α , H-8 α), 3.10 (m, 1H, H-7), 7.17 (tm, 1H, *p*-Ph), 7.29 (tm, 2H, *m*-Ph), 7.49 (dm, 2H, *o*-Ph). ¹³C-NMR (CDCl₃): 11.37 (Me), 28.70 (C(1,5)), 34.52 (C(9)), 35.8 (C(6,8)), 37.0 (C(2,4)), 37.10 (C(7)), 126.38 (*p*-Ph), 129.02 and 129.06 (*m,o*-Ph), 144.10 (*ipso*-Ph). ¹¹B-NMR (128 MHz, CD₂Cl₂, BF₃·OEt₂): 82.0 (25°C), 80.7 (–60°C).

X-ray analysis of 7. C₁₀H₁₉B, *M* = 150.1, monoclinic, space group *P*2₁/*n*, at –80°C: *a* = 6.623(3), *b* = 14.247(6), *c* = 10.646(4) Å, β = 103.87(2)°, *V* = 975.3(7) Å³, *Z* = 4, *D*_{calc} = 1.022 g cm^{–3}, μ = 0.055 mm^{–1}. A single crystal of 7 of the cylinder form was grown from the melt in the thin-walled capillary diameter ca. 0.4 mm directly on a diffractometer by the very slow cooling of the liquid near the melting point (–35°C) [12].

Intensities of 2117 reflections were measured at -80°C with a Sintex P2₁ diffractometer (Mo–K α radiation, graphite monochromator, $\theta/2\theta$ -scan, $2\theta = 2-60^{\circ}$), and 1128 independent observable reflections with $F > 4\sigma(F)$ were used in the structure solution and refinement. Full-matrix anisotropic–isotropic least-squares refinement (the H-atoms were located from the difference Fourier electron density synthesis and refined using a ‘riding model’), 100 refined parameters, $R = 0.0678$, $R_w = 0.0786$, GOF = 1.02. All calculations were performed using SHELXTL PLUS programs.

X-ray analysis of **8**. C₁₅H₂₁B, $M = 212.1$, orthorhombic, space group $Pbca$, $a = 7.374(3)$, $b = 15.550(7)$, $c = 21.536(10)$ Å, $V = 2457$ Å³, $Z = 8$, $D_{\text{calc}} = 1.147$ g cm⁻³, $\mu = 0.063$ mm⁻¹. A single crystal of **8** of the cylinder form (diameter 0.3 mm) was grown from the melt in the thin-walled capillary directly on a diffractometer near the melting point (ca. -10°C) using a miniature zone-melting technique with the IR-laser beam producing a molten zone in the capillary [12].

Intensities of 4004 reflections were measured at -153°C with a Siemens R3m/V diffractometer (Mo–K α radiation, graphite monochromator, Wyckoff-scan technique, $2\theta = 2-60^{\circ}$), 2831 independent reflections were obtained ($R_{\text{int}} = 0.05$), and 2015 independent observable ones with $F > 4.0\sigma(F)$ were used in the structure solution and refinement. Full-matrix anisotropic–isotropic least-squares refinement (the H-atoms were located from the Fourier electron density synthesis and refined using a ‘riding model’), 145 refined parameters, $R = 0.0544$, $R_w = 0.0605$, GOF = 1.58. All calculations were performed using SHELXTL PLUS programs.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 161836 for compound **7**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project Nos. 98-03-32993a, 00-15-97378 and 00-03-32807a).

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