



Boron analogs of the 2-norbornyl cation

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Abstract—The relative stability of classical versus nonclassical mono- and bis-boron analogs of the 2-norbornyl cation was investigated by ab initio and density functional methods. Nonclassical structures were preferred in carbon bridged isoelectronic 1,2-diboranorbornyl anions having the following substituents on boron: H, CH₃ and CN. The difluoro analog preferred the classical structure. The mono-boron analog preferred an open structure. © 2001 Elsevier Science Ltd. All rights reserved.

The 2-norbornyl system occupies a special niche in the history of physical organic chemistry as a result of the intense efforts to define the electronic structure of the intermediate cation involved in the solvolysis of 2-norbornyl derivatives.^{1–3} Representation of this ion evolved from that of a classical ion to a variety of symmetrical nonclassical bridged or π -complexed structures (Fig. 1). This ion and many related nonclassical structures can be described in molecular orbital terms as a cyclic three-center two-electron array whose generation leads to enhanced ionization rates and stereoselective product formation. Recent computational studies of the norbornyl cation confirmed its C_s symmetry in agreement with results of spectroscopic and chemical studies.^{2,3} Structures having geometry expected for the classical

2-norbornyl cation proved to be first order saddle points rather than energy minima.²

The question of the uniqueness of carbon in these structures aroused our interest, i.e. could other elements lead to bridged intermediates in preference to classical structures?⁴ In this communication we address this question with a study of the relationships between boron/carbon analogs of the types shown in Figs. 2 and 5 (vide infra).

It will be noted that these anions are isoelectronic with the 2-norbornyl cation having the requisite three-center two-electron array.⁵ Comparisons of structures and relative energies of a series of classical and bridged forms

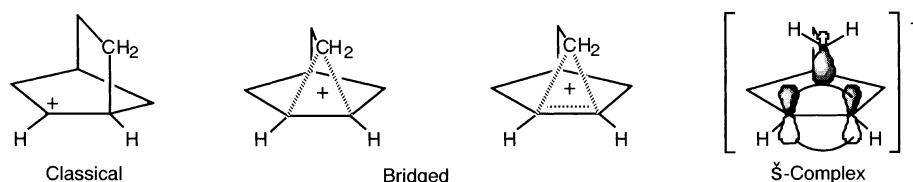


Figure 1. Representations of the 2-norbornyl cation.

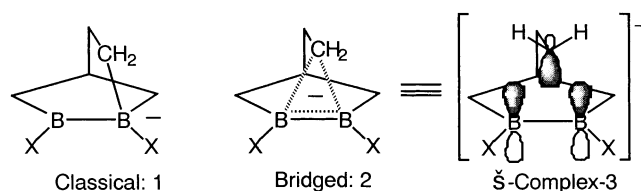


Figure 2. Representations of the diboro anion.

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of these boranes will provide insight into the preferences between the two forms and the structural dependency on boron substitution.

Computational methodology. All structures were fully optimized by analytical gradient methods using the Gaussian98 suite.⁶ Density functional (DFT) calculations used the exchange potentials of Becke⁷ and the correlation functional of Lee, Yang and Parr.⁸ Electron correlation was included via optimizations utilizing Møller–Plesset methods.⁹ Frequencies were computed by analytical methods. Reported enthalpies were corrected for zero-point energy differences (ZPVE) (unscaled) and thermal effects at 298.150 K.

Results and discussion. The prototype structures **1** and **2** (X=H) were examined at several computational levels including: HF/6-31G(d), B3LYP/6-31G(d), B3LYP/6-311+G(d), MP2/6-31G(d), and MP2/6-31+G(d). The classical ion C_1 form (Fig. 3) proved to be a minimum energy stationary point at these levels, as determined by harmonic vibrational analyses. Select geometrical features are listed in Table 1 for this structure.

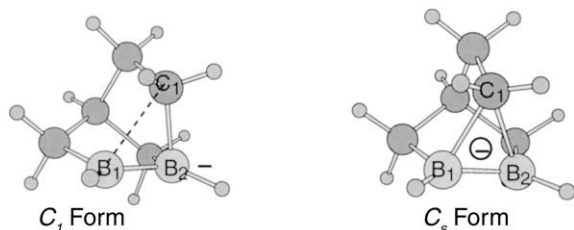


Figure 3. Reference structures for Table 1.

Table 1. Geometry and relative energy^a of 1,2-diboronbornane anions

Method/basis set	C_1 Form Bond lengths (Å)			C_s Form Bond lengths (Å)			$\Delta H_{C_s} - \Delta H_{C_1}$
	C_1-B_1	C_1-B_2	$B_1 \cdots B_2$	C_1-B_1 C_1-B_2	$B_1 \cdots B_2$	ν_i (cm ⁻¹)	
HF/6-31G*	2.570	1.667	1.719	1.976	1.624	318.58	4.88
B3LYP/6-31G*	2.211	1.775	1.652	1.952	1.620	221.50	0.423
B3LYP/6-311+G*	2.243	1.770	1.614	1.954	1.619	205.16	0.396
MP2/6-31G*	2.008	1.804	1.627	1.906	1.616	163.30	-0.337
MP2/6-31+G*	1.975	1.841	1.627	1.908	1.622	97.62	-0.541
MP2/6-311+G*	1.912	1.912	1.626	1.913	1.626	NA	0.015

^a kcal/mol @298.150 K.

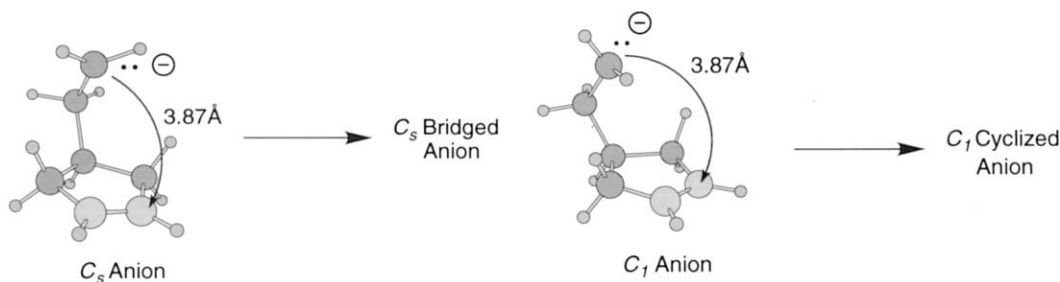


Figure 4. Open chain anionic systems.

Optimization of the C_s form (Fig. 3) gave rise to a structure with one imaginary frequency at each of these levels, i.e. a first-order saddle point. The computed energy barrier between the two forms decreased as the level of computation improved (Table 1) and became slightly negative at the MP2/6-31+G(d) level. Concurrently, the single imaginary frequency for the C_s form also gradually decreased and fell to 97 cm⁻¹. A natural bond order population analysis calculation¹⁰ (MP2/6-31+G*) showed a small positive charge on each boron atom (0.066) and a large negative charge on the bridging carbon atom (-0.725). A computed Wiberg bond index between the bridging carbon and boron was 0.48 and the index for the B–B bond was 1.09.¹¹

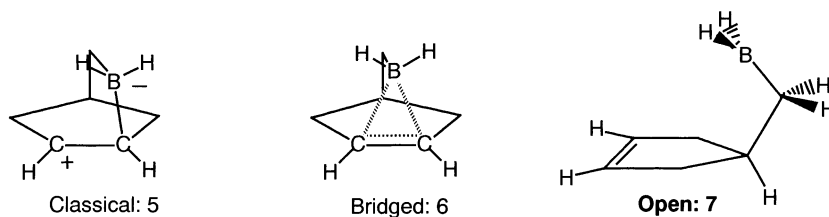
Finally, optimizations at the MP2/6-311+G(d) level starting from either the classical form or the C_s structure led to the C_s form 2B(X=H) with equal bond lengths of 1.912–1.913 Å ($\Delta H_{(298.15)} = 0.015$ kcal/mol (Table 1)). We believe that the trends in the DFT results coupled with the MP2 calculations are best interpreted in terms of a preference for a nonclassical structure for anion 2B(X=H). It is noteworthy that the geometry of this ion is very similar to that computed for the norbornyl cation for which distances from the bridging atom to the 2-carbon base are 1.83 Å with a C–C separation of the basal carbon atoms of 1.39 Å [MP2/6-311G(d,p)].

We next devised two computational experiments designed to estimate the energetics of bridging by comparisons of the energy of the bridged form with open-chain analogs **3** (C_s) and **4** (C_1) (Fig. 4). Despite the significant initial separation of the anionic centers and the B–B array by 3.87 Å, the C_s system smoothly

Table 2. Geometry and energy of substituted 1,2-diboronornbornane anions^a

I: X=	<i>C</i> ₁ Form Bond lengths (Å)				<i>C</i> _s Form Bond lengths (Å)			$\Delta H_{C_s} - \Delta H_{C_1}$
	<i>C</i> ₁ –B ₁	<i>C</i> ₁ –B ₂	X–B ₁	X–B ₂	<i>C</i> ₁ –B ₁ <i>C</i> ₁ –B ₂	X–B	ν_i (cm ⁻¹)	
H	2.243	1.770	1.216	1.222	1.954	1.216	205.2	0.40
	<i>1.975</i>	<i>1.841</i>	<i>1.217</i>	<i>1.218</i>	<i>1.908</i>	<i>1.218</i>	<i>97.6</i>	<i>-0.54</i>
CH ₃	2.448	1.726	1.594	1.629	1.980	1.610	218.2	1.91
	<i>2.022</i>	<i>1.836</i>	<i>1.608</i>	<i>1.615</i>	<i>1.922</i>	<i>1.612</i>		<i>0.34</i>
CN	2.302	1.742	1.544	1.562	1.933	1.550	183.0	0.34
	<i>1.943</i>	<i>1.832</i>	<i>1.555</i>	<i>1.556</i>	<i>1.888</i>	<i>1.555</i>		<i>-0.025</i>
F	2.619	1.682	1.376	1.454	2.008	1.409	268.8	5.51
	<i>2.607</i>	<i>1.674</i>	<i>1.387</i>	<i>1.463</i>	<i>1.951</i>	<i>1.424</i>		<i>3.37</i>

^akcal/mol @298.150 K. Plain type: B3LYP/6-311+G*; italics: X=H; MP2/6-31+G*; all others: MP2/6-31+G**/MP2/6-31G*+ZPE B3LYP/6-311+G*.

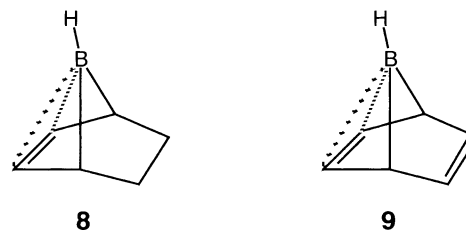
**Figure 5.** Mono-boro systems.

cyclized to the bridged form 1B(X=H) on optimization at the MP2/6-31+G* level. The *C*₁ anion **4**, on the other hand, optimized to the higher energy *C*₁ structure described above 2B(X=H) (cf. Table 1). At higher MP2 computational levels, both open anions produced the *C*_s form. The overall enthalpic energy change for bridging is estimated to be ca. 84 kcal/mol.¹² Synthetic attempts to generate these bridged ions may benefit from this difference.

We extended this study to include three derivatives of **1** and **2**: X=F, CN⁻ and CH₃ to test the effects of resonance and inductive interactions on the relative stability and structure of the classical and bridged forms. Spectroscopic and chemical studies on substituted norbornyl cations have shown that the classical form is stabilized by electron-donating substituents, e.g. alkyl, phenyl, methoxy.^{1,3} In this study a decrease in barrier heights between the two forms was found with increasing computational level for all substituents (Table 2).¹³

By analogy to the behavior of the unsubstituted system, it appears very likely that the dimethyl and dicyano derivatives also prefer bridged structures. The barrier for the difluoro derivative at the highest level was significant: 5.51–3.37 kcal/mol. Evidently, the strong resonance interaction of the lone pairs on fluorine with the vacant p-orbital on boron in preferentially stabilizes the open form. The calculated bond lengths for the two kinds of B–F bonds in **1-B** are consistent with this idea: 1.37–1.39 Å (B₁···F) versus 1.45–1.46 Å (B₂···F⁻). None of the other systems show a comparable disparity.

Lastly, the structure and energy of mono-boron systems **5** and **6** were examined (Fig. 5). The zwitterionic classical form rearranged to the bridged structure **6** at the HF/6-31G* level analogous to the behavior of the norbornyl system. Computations initiated from the *C*_s structure **6** led to weakly bridged structures with B···C bond distances of 2.165 Å (B3LYP/6-31G*, $\nu \geq 147$ cm⁻¹) and 2.226 Å (B3LYP/6-311+G*, $\nu \geq 124$ cm⁻¹). No evidence for bridging was found at the MP2/6-31+G* level as B···C distances expanded to 3.87 Å leading to the cyclopentylethyl borane **7** (*C*_s). Vibrational analysis revealed one imaginary frequency that corresponded to torsion about the CH₂–BH₂ bond. Relaxation of the symmetry led to a true minimum structure that was 3.1 kcal/mol lower in energy. Although the nonclassical structure is not an energy minimum, a combination of electron withdrawing groups on boron and electron donating groups on carbon might be sufficient to stabilize the bridged form. In a computational study of related complexes in hydroboration reactions, Houk et al. found that similar π -complexes were not true minima when correlation is included.¹⁴ In contrast, Schulman et al. provided computational evi-

**Figure 6.**

dence (MP2/6-31G*) based on homodesmotic comparisons that homoconjugative stabilizations of 7-boranorbornene (**8**) and 7-boranorbornadiene (**9**) (Fig. 6) are comparable to those of the isoelectronic carbocationic systems.¹⁵ The fixed geometry and proximity of the boron atom relative to the π -system is clearly an important factor in these molecules.

In summary, these calculations lead to the prediction that bridged ions with two boron atoms at the basal positions in **2** are preferred over equilibrating classical counterparts **1** except for the bis-fluoro substituted boron system. A classical structure **7** is preferred when the putative bridging atom is boron.

Acknowledgements

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