Decisive Evidence for Nonclassical Bonding in Five-Vertex *closo*-Boranes, $X_2B_3H_3$, X = N, CH, P, SiH, BH^-

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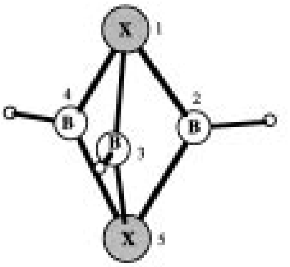
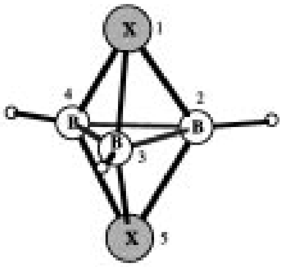
The 1,5-$X_2B_3H_3$ (X = N, CH, P, SiH, BH^-) members of the *closo*-borane family are unique, since both classical (**1**) and nonclassical (**2**) bonding alternatives are possible. The electronic structures of these five-vertex species have been discussed many times in the literature (Table 1).[1−12] With merely three exceptions (Table 1), all earlier analyses favored classical (Lewis) descriptions (**1**) for X = N, CH, P, SiH, and BH^-. In contrast to the conclusions of other research groups, nonclassical structures (**2**) were proposed for X = BH^- only by Lipscomb and co-workers,[2] for X = CH only by Williams,[10] and for X = N only by Burdett and Eisenstein (BE).[11] We now present *ab initio* computations of the bonding, energetic, and magnetic properties that challenge almost all previous interpretations.[2,4,6−9,11]





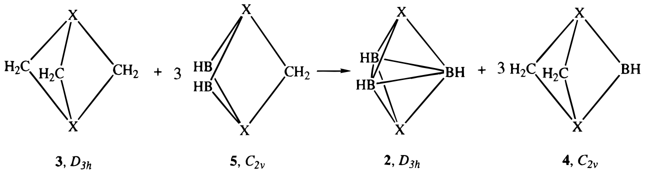
1, D_{3h} X = N, CH, P, SiH and BH^- **2**, D_{3h}

Most of the earlier conclusions were based on analyses of the wave functions.[2,7−9,11] Lipscomb and co-workers[2] employed the Boys procedure and deduced that classical localization is not favored for $B_5H_5^{2-}$. Bader's *Atoms in Molecules* bonding analysis[12] found 1,5-$C_2B_3H_5$ to be "electron precise" in contrast to the "electron-deficient" character of 1,6-$C_2B_4H_6$[7a] and higher *closo*-carboranes. Jemmis *et al*. concluded similarly that $B_5H_5^{2-}$ and 1,5-$Si_2B_3H_5$ have classical Lewis structures (**1**, Table 1).[7b] Jemmis and Subramanian[9] and BE[11] both applied the Mulliken overlap population (MOP) analysis but arrived at *opposite* conclusions for X = N (Table 1). Because of the well-known drawbacks of the Mulliken approach,[13a] we now employ the natural population analysis (NPA) of Weinhold, Reed, and Weinstock[13] to characterize the nature of bonding (**1**, **2**) in the present investigation. However, our support for nonclassical bonding descriptions (**2**) is based primarily on the results of quantitative evaluations of the energetic and magnetic properties, which have not been considered earlier.[1−11]

Table 1. References Concerning the Principle Character of Bonding (**1**, **2**) in *closo*-1,5-$X_2B_3H_3$ Cages (X = N, CH, P, SiH, BH^-)

X	**1**	**2**
N	9	11
CH	2, 6−9, 11	10
P	9, 11	
SiH	7b, 9, 11	
BH^-	4, 7b, 9, 11	2

The 1,5-$X_2B_3H_3$ geometries, as well as those of the reference molecules **3**−**5** employed in eq 1, were optimized at MP2(fc)/6-31+G* (MP2).[14] The MP2 aromatic stabilization energy (ASE) values and the CSGT-HF/6-311+G**//MP2[16] diamagnetic susceptibility exaltation (Λ)[15] values were computed using the homodesmotic reaction (eq 1). Recently, the chemical shifts of endohedral He species have been used as measures of fullerene aromaticity.[17] While the five-vertex cages are much too small to accommodate He or other atoms, the chemical shieldings computed at the cage centers offer simple alternatives. Such data (nucleus independent chemical shifts, NICS)[18a]



X = N, CH, P, SiH and BH^-

(1)

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Table 2. Total (hartrees) and Zero-Point Energies (ZPE, kcal/mol), Interatomic Distances (D, Å), Wiberg Bond Indices (WBI), Natural Atomic Orbital Bond Orders (NAO), Aromatic Stabilization Energies (ASE, kcal/mol), Magnetic Susceptibility Exaltation (Λ, ppm cgs) Values, and the Nucleus Independent Chemical Shifts (NICS, ppm) of 1,5-$X_2B_3H_3$ (X = N, CH, P, SiH, BH^-) Molecules

			B−X			B−B[c]					
molecule	total energy[a]	ZPE[b]	D	WBI	NAO	D	WBI	NAO	ASE[d]	Λ[e]	NICS[f]
$N_2B_3H_3$	−185.28891	30.6	1.516	0.871	0.848	1.759	0.165	0.343	−8.3	0.5	−10.2
$C_2B_3H_5$	−153.19126	45.3	1.554	0.933	0.888	1.844	0.202	0.345	−19.8	−6.9	−17.1
$P_2B_3H_3$	−757.71502	26.4	1.909	0.935	0.805	1.856	0.445	0.513	−21.9	−23.3	−18.2
$Si_2B_3H_5$	−655.07456	33.5	1.941	0.917	0.875	2.078	0.437	0.439	−29.2	−36.6	−22.4
$B_5H_5^{2-}$	−126.58335	36.6	1.684	0.926	0.882	1.811	0.452	0.490	−34.8	−46.1	−28.1

[a] MP2(fc)/6-31+G*. [b] Frequency computations show all D_{3h} structures to be minima. [c] Equatorial plane of the 1,5-$X_2B_3H_3$ cage. [d] Calculated using eq 1 at MP2(FC)/6-31+G* (ZPE not included). [e] Calculated using eq 1 at CSGT-HF/6-311+G**//MP2(fc)/6-31+G*. [f] GIAO-HF/6-311+G**//MP2(fc)/6-31+G*.

evaluated at GIAO-HF/6-311+G**//MP2[19] (Table 2) are proving to be highly effective as an aromaticity criterion.[18]

The equatorial B−B distances, ranging from 1.76 Å (X = N) to 2.08 Å (X = SiH) for various X substituents (Table 2), may be compared to the reference single B−B bond length in planar B_2H_4 (1.747 Å at MP2(fc)/6-31+G*). As pointed out earlier,[11] the variations in B−B distances (Table 2) of the *closo*-diheteroboranes correlate with the electronegativity of the capping X groups and are not necessarily related to the degree of bonding. Indeed, the B−B Wiberg bond indices (WBI) and the overlap-weighted natural atomic orbital (NAO) bond orders,[13] which suggest moderate bonding interactions between the borons, are *smallest* for X = N (Table 2).[20] Natural localized molecular orbital analysis[13] reveals delocalization on each deltahedral face, also supporting depiction **2**. These NPA bonding analyses favoring the nonclassical interpretation (**2**) contradict the basically classical descriptions (**1**) claimed by BE[11] (X = CH, P, SiH, BH^-) and by other groups (Table 1).

Since the various wave function analyses lead to different conclusions,[2,7−9,11] we examined the energies and magnetic properties to ascertain if the five-vertex cages are classical (**1**) or nonclassical (**2**). Delocalized bonding (three-dimensional aromaticity)[1,3,5] in five-vertex cages is supported and quantified by the evaluations of the aromatic stabilization energy (ASE) values, by the magnetic susceptibility exaltations (Λ), and by the NICS values.[18,21,22] We have chosen the homodesmotic reaction (eq 1) to evaluate ASE and Λ. This equation, employing classical reference molecules based on bicyclo[1.1.1]-pentane and its dihetero analogs (**3**, $X_2C_3H_6$; **4**, $X_2C_2BH_5$; **5**, $X_2CB_2H_4$), compensates for the angle strain, hyperconjugation, and zero-point energy differences. The ASE values favor **2** (Table 2) since they are quite exothermic (with the exception of −8.3 kcal/mol for 1,5-$N_2B_3H_3$, the smallest stabilization). The −34.8 kcal/mol ASE for $B_5H_5^{2-}$ (the most strongly stabilized) agrees with the Lipscomb *et al.*[2a] nonclassical description (**2**) but contradicts the conclusions of Aihara[4] and others.[6−9,11]

Additional evidence for nonclassical bonding (**2**) is obtained from the evaluation of the diamagnetic susceptibility exaltation (Λ) values.[21,22] Three-dimensional aromatics exhibit large exaltations (negative Λ value; e.g., −49.6 ppm cgs for *closo*-$B_6H_6^{2-}$).[22] The Λ values (Table 2), also evaluated from eq 1, show that most of the 1,5-$X_2B_3H_3$ cages have large exaltations that range from −46.1 ppm cgs for $B_5H_5^{2-}$ to 0.5 ppm cgs for 1,5-$N_2B_3H_3$ (a negligible value).

Further evidence for cage delocalization is provided by NICS,[18] a new criterion based on computed magnetic shieldings introduced recently to characterize aromaticity. Among the five-vertex deltahedra, $B_5H_5^{2-}$ has the most strongly diatropic NICS (−28.1 ppm) and 1,5-$N_2B_3H_3$ (−10.2 ppm) has the smallest. Not only do the trends of the NICS results agree with the ASE and Λ data, but also qualitatively with the WBI and NAO B−B bond orders (Table 2). All these criteria support the nonclassical bonding description (**2**) for X = CH, P, SiH, and BH^-. Although the B−B distance is shortest in 1,5-$N_2B_3H_3$, WBI, NAO, ASE, Λ, and NICS all agree that it has the *least* delocalized character. This contradicts BE,[11] who claimed 1,5-$N_2B_3H_3$ to be nonclassical. At the other extreme, the three-dimensional aromaticity of $B_5H_5^{2-}$ is largest among the systems investigated.

The 1,5-$X_2B_3H_3$ cages have large three-dimensional aromatic stabilization energies, exalted diamagnetic susceptibilities, and diatropically shielded NICS values. The ordering follows the electronegativity of X in each row (BH^- > CH > N; SiH > P). Starting with 1,5-$N_2B_3H_3$ (a borderline case), we conclude that these results increasingly favor the nonclassical bonding descriptions (**2**) for the five-vertex cages, contradicting the localized picture (**1**) proposed in the literature (Table 1).

Note Added in Proof: Deformation electron density (DED) data obtained by the multipole refinement of the X-ray diffraction analysis for 1,5-$C_2B_3(Et)_5$ by Antipin et al. (Antipin, M.; Boese, R.; Bläser, D.; Maulitz, A. *J. Am. Chem. Soc.* **1996**, accepted for publication) and the population analysis of pair densities for 1,5-$C_2B_3H_5$ employing the semiempirical SINDO1 method (Ponec, R.; Jug, K. *Int. J. Quantum Chem.* **1996**, *60*, 75) support deltahedral face delocalization in agreement with our NLMO analysis. Note that our energetic analysis balances the number of B−X−B faces on both sides (structures **2** and **5**) of eq 1.

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Supporting Information Available: NBO bonding analyses for the five-vertex cages and total energies and magnetic susceptibilities (χ) of the reference molecules used in eq 1 (2 pages). See any current masthead page for ordering and Internet access instructions.

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