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Theoretical *Ab Initio* Study of Neutral and Charged B_3H_n ($n = 3-9$) Species. Importance of Aromaticity in Determining the Structural Preferences

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The geometries and stabilization energies (SE) of B_3H_n molecules and ions were computed *ab initio* at MP2-(FULL)/6-31+G* + ZPE(HF/6-31+G*). QCISD(T)/6-311+G**//MP2(FULL)/6-31+G* (QCI) single point energies and MP2(FC)/6-31+G* analytical frequencies also were calculated for some of these species. The lowest energy isomers of the electron and hydrogen deficient boron hydrides B_3H_3, $B_3H_4^+$, $B_3H_4^-$, B_3H_5, and $B_3H_6^+$ have the greatest aromatic stabilization. The aromatic SEs of $B_3H_4^-$, B_3H_5, $B_3H_6^+$, $B_3H_3^{-2}$, and $B_3H_3Li_2$, estimated from appropriate isodesmic equations, approach the large value of the 2π-electron cyclopropenium ion. The relative energies and even the character of B_3H_n stationary points are influenced strongly by electron correlation. The BB distances vary considerably and depend on the bonding character as well as nonbonded repulsions. The isoelectronic and isostructural analogies between boron and carbon species guide searches for the new boron hydride isomers.

Introduction

The considerable current interest in three-membered boron rings is documented by numerous experimental[1,2] and theoretical[2r,3−13] papers. The three-boron cyclic systems are implicated in the mechanism of diborane pyrolysis.[1,8e] It is possible that besides B_3H_7 and B_3H_9 other three-membered boron intermediates also may be involved in the reaction of BH_3 with B_2H_6. In this regard, note the novel mechanism proposed recently for the formation of H_2BNH_2 from B_2H_6 and NH_3.[13e] $B_3H_4^+$ and $B_3H_6^+$ cations were reported in electron impact mass-spectrometric studies on B_4H_8CO.[2g]

This *ab initio* study of B_3H_3 (**1**),[3] $B_3H_4^+$ (**2**), $B_3H_4^-$ (**3**),[3] B_3H_5 (**4**),[3,4] $B_3H_6^+$ (**5**),[4] $B_3H_6^-$ (**6**),[3] B_3H_7 (**7**),[3,5−8] $B_3H_8^+$ (**8**),

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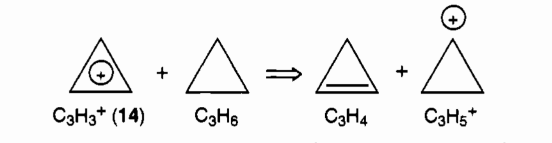
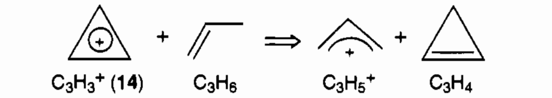
$B_3H_8^-$ (**9**),[5,9,10] B_3H_9 (**10**),[4,5,8,11,12] $B_3H_3^{-2}$ (**11**), $B_3H_3Li^-$ (**12**), and $B_3H_3Li_2$ (**13**) summarizes and extends earlier investigations.[3-13] We demonstrate that the global minima of **1**–**5**, as well as the dianion **11** and its lithium complexes **12** and **13**, benefit from aromatic (cyclic 3-center-2π-electron) delocalization.

Hückel π aromaticity ($4n + 2$ electrons) is recognized to be largest per atom in three-membered rings.[14,15] The stabilization energy (SE) of the D_{3h} cyclopropenium cation, **14** (as defined by eq 1), is 64.1 kcal/mol.[14c,15] The aromatic (cyclic) stabilization energy (ASE) may be obtained from eq 2, which employs the allyl cation as the reference species.[14c] Similarly defined ASEs (at MP2/6-31+G* + ZPE(HF/6-31+G*) of C_{2v} borirene[2l-n,13f-i,15] (eq 3) and of the C_{2v} diboriranyl anion[2o,2p] (eq 4) are about half of the value for **14**.[14c]



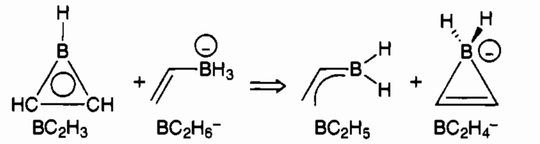
(1)

ΔE = 64.1 kcal/mol at MP2/6-31+G* + ZPE(HF/6-31+G*)[14c]



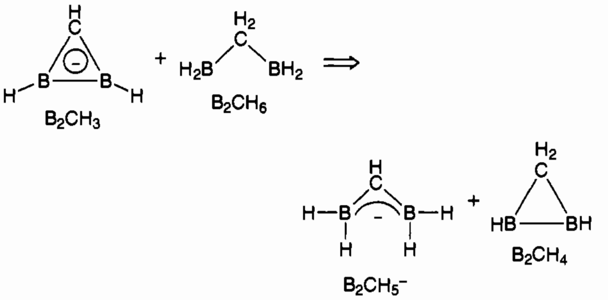
(2)

ΔE = 35.7 kcal/mol at MP2/6-31+G* + ZPE(HF/6-31+G*)[14c]



(3)

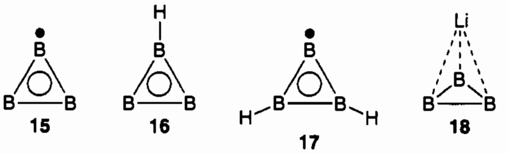
ΔE = 20.8 kcal/mol at MP2/6-31+G* + ZPE(HF/6-31+G*)[14c]



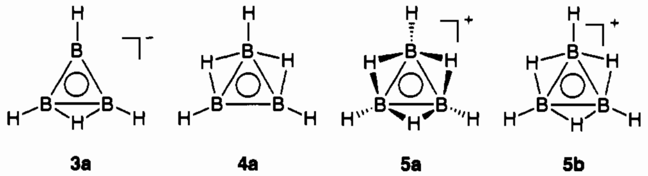
(4)

ΔE = 17.8 kcal/mol at MP2/6-31+G* + ZPE(HF/6-31+G*)[14c]

How does aromaticity influence the structures and energies of three-boron hydrides? In recent *ab initio* studies, Simons and co-workers established that the global minima structures of B_3 (**15**),[13a] B_3H (**16**), and B_3H_2 (**17**)[13b] contain three-membered rings with cyclic π electron delocalization. The substitution of H in **16** by Li to give B_3Li leads to the electrostatically favored pyramidal structure **18**,[13c] which has some 4c–2e bonding[13d] arising from the interaction of the empty s orbital of Li^+ with the 3c–2e π bond of the B_3^- anion.



The most favorable cyclic structures of $B_3H_4^-$ (**3a**),[3a] B_3H_5 (**4a**), and $B_3H_6^+$ (**5a**)[4] (all isoelectronic with **14**) also display 3c–2e aromatic ring π delocalization. The C_{3v} $B_3H_6^+$ (**5a**) with three out-of-plane bridged hydrogens was declared to be the "first three-membered nonplanar 2π aromatic" species.[4] Indeed, **5a** is 42–45 kcal/mol more stable than the planar D_{3h} structure **5b**. The "extra stability" relative to **14** was deduced from *nonisodesmic*[16] eqs 5 and 6.[4]



$2B_3H_6^+$ (**5a**) + $2C_3H_6$ (D_{3h}) -> $2C_3H_3^+$ (**14**) + $3B_2H_6$ ΔE = 59 kcal/mol[4] (5)

$B_3H_6^+$ (**5a**) + C_3H_6 (D_{3h}) -> $C_3H_3^+$ (**14**) + B_3H_9 (C_{3v}) ΔE = 42 kcal/mol (6)

Thus, the literature shows the importance of aromaticity in establishing structures of three-boron hydrides. Our goals in this paper are (1) to estimate ASEs of the three-membered ring aromatic species **3**–**5**, **11**, and **13**, (2) to study the three-membered ring aromatics (**1**–**5**) and the reference B_3H_n species (**6**–**10**) involved in isodesmic equations, and (3) to examine the structure and stability of Li^+ (**12**) and $2Li^+$ (**13**) complexes of the aromatic dianion **11**. The literature data, where available, are compared with our results.

Methods

All geometries were optimized at HF/6-31+G* and MP2(FULL)/6-31+G* (simply designated HF and MP2 in the following text) using the GAUSSIAN 92 program package.[17] Analytical frequencies were obtained at HF/6-31+G*. Zero point energies were scaled by 0.89, as recommended.[15d] The energy comparisons are at MP2(FULL)/6-31+G* + ZPE(HF/6-31+G*) unless otherwise noted. For a limited number of structures, single point QCISD(T)/6-311+G**//MP2(FULL)/6-31+G* (designated QCI) energy and MP2(FC)/6-31+G* analytical

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(16) These estimates are imperfect, as the number of CH and BH bonds as well as the B and C hybridizations differ in the species on both sides of eqs 5 and 6.

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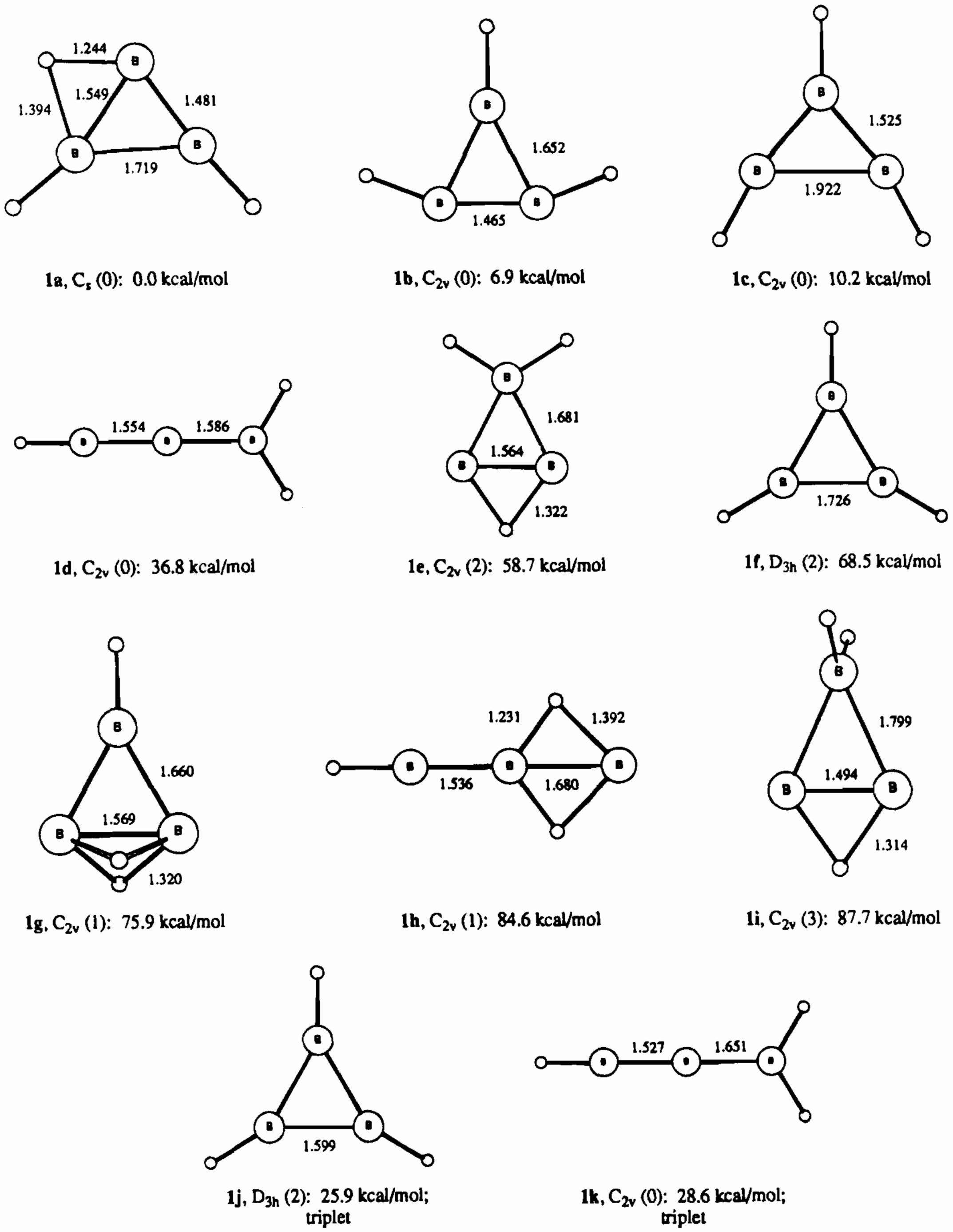

1a, C_s (0): 0.0 kcal/mol

1b, C_{2v} (0): 6.9 kcal/mol

1c, C_{2v} (0): 10.2 kcal/mol

1d, C_{2v} (0): 36.8 kcal/mol

1e, C_{2v} (2): 58.7 kcal/mol

1f, D_{3h} (2): 68.5 kcal/mol

1g, C_{2v} (1): 75.9 kcal/mol

1h, C_{2v} (1): 84.6 kcal/mol

1i, C_{2v} (3): 87.7 kcal/mol

1j, D_{3h} (2): 25.9 kcal/mol; triplet

1k, C_{2v} (0): 28.6 kcal/mol; triplet

Figure 1. B_3H_3 structures. The number of imaginary frequencies is given in parentheses.

frequency computations were performed to determine the effect of electron correlation on relative energies and the nature of stationary states. The energies are presented in Table 1, and the geometries, in Figures 1–9. The number of imaginary frequencies (NIMAG) characterizes each stationary point: 0 = minimum; 1 = transition state (TS), etc. The numbering of the boron atoms (when not shown on figures) is from left to right unless indicated specifically. A detailed study of all possible forms and excited states of three-membered boron hydrides is beyond the scope of this paper. We computed some triplets only in cases where lower energies were expected.

The HF/6-31+G*//MP2/6-31+G* wave functions are characterized by natural bond orbital (NBO) charges (q), Wiberg bond indices (WBI), and Mulliken bond populations (MBP).[18,19] In particular cases, we have also considered the Mulliken gross populations of pπ orbitals (MPP).

Results and Discussion

Different definitions and measures of "aromaticity" based on structures, energies, electron distributions, and magnetic and chemical properties have been suggested and discussed extensively.[20] The qualitative attributes applicable to three-membered

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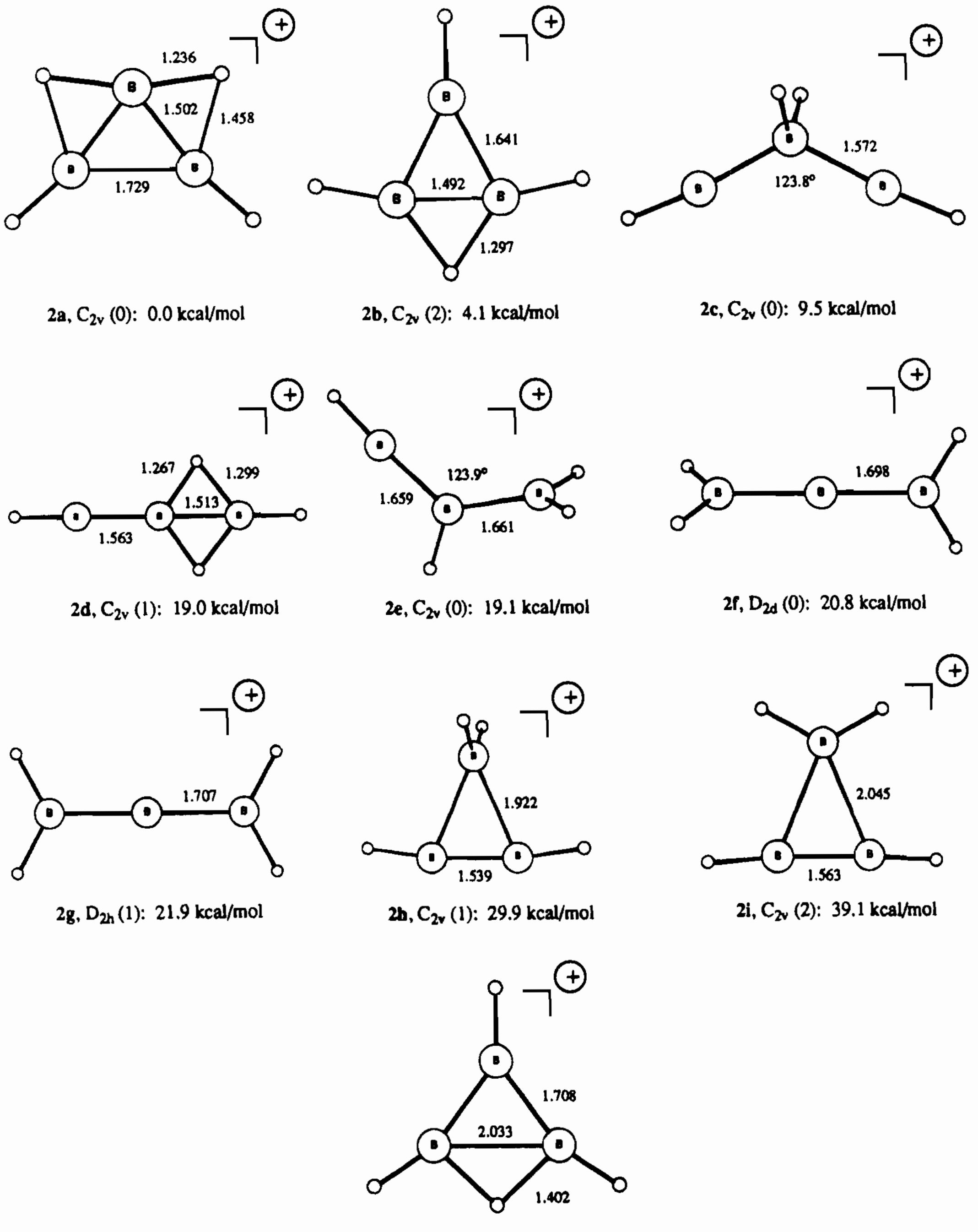


2a, C_{2v} (0): 0.0 kcal/mol

2b, C_{2v} (2): 4.1 kcal/mol

2c, C_{2v} (0): 9.5 kcal/mol

2d, C_{2v} (1): 19.0 kcal/mol

2e, C_{2v} (0): 19.1 kcal/mol

2f, D_{2d} (0): 20.8 kcal/mol

2g, D_{2h} (1): 21.9 kcal/mol

2h, C_{2v} (1): 29.9 kcal/mol

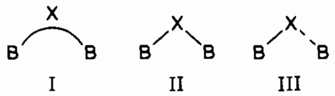
2i, C_{2v} (2): 39.1 kcal/mol

2j, C_{2v} (2): 43.1 kcal/mol

Figure 2. $B_3H_4^+$ structures. The number of imaginary frequencies is given in parentheses.

aromatic species include the following: (1) a delocalized 3c–2e π bonding orbital perpendicular to the cyclic plane; (2) equalization of the internal bond lengths to values intermediate between those of corresponding single and double bonds; (3) aromatic stabilization energy (ASE) defined with respect to appropriate reference species.[21] If the ASE energy is substantial, the cyclic isomer with 3c–2e π bonding usually is the global minimum. Bond lengths also are influenced by strain and electrostatic interactions, etc. Since the choice of reference species for evaluating of ASEs often is not unambiguous, the electronic structure may provide the best criteria of aromaticity in some cases.[21b]

The different kinds of bridged bonds have been found here. As there is no unique way to display such bonds,[1] we have employed different modes of representation. Mode I gives the



electron count (one line, curved or straight, for two electrons), while mode II displays the coordination number and shows the geometry (bond lengths and bond angles) perspective. Mode III indicates that the bridging is quite unsymmetrical.

B_3H_3 (Figure 1). The "classical" three-membered ring D_{3h} isomer **1f** ($1a_1'^2 1e'^4 2a_1'^2 2e'^4 3a_1'^2 3e'^4$) does not have a favorable electronic structure (there are no π electrons[3b]) and is higher in energy than other alternatives. The strain energy in **1f**, estimated

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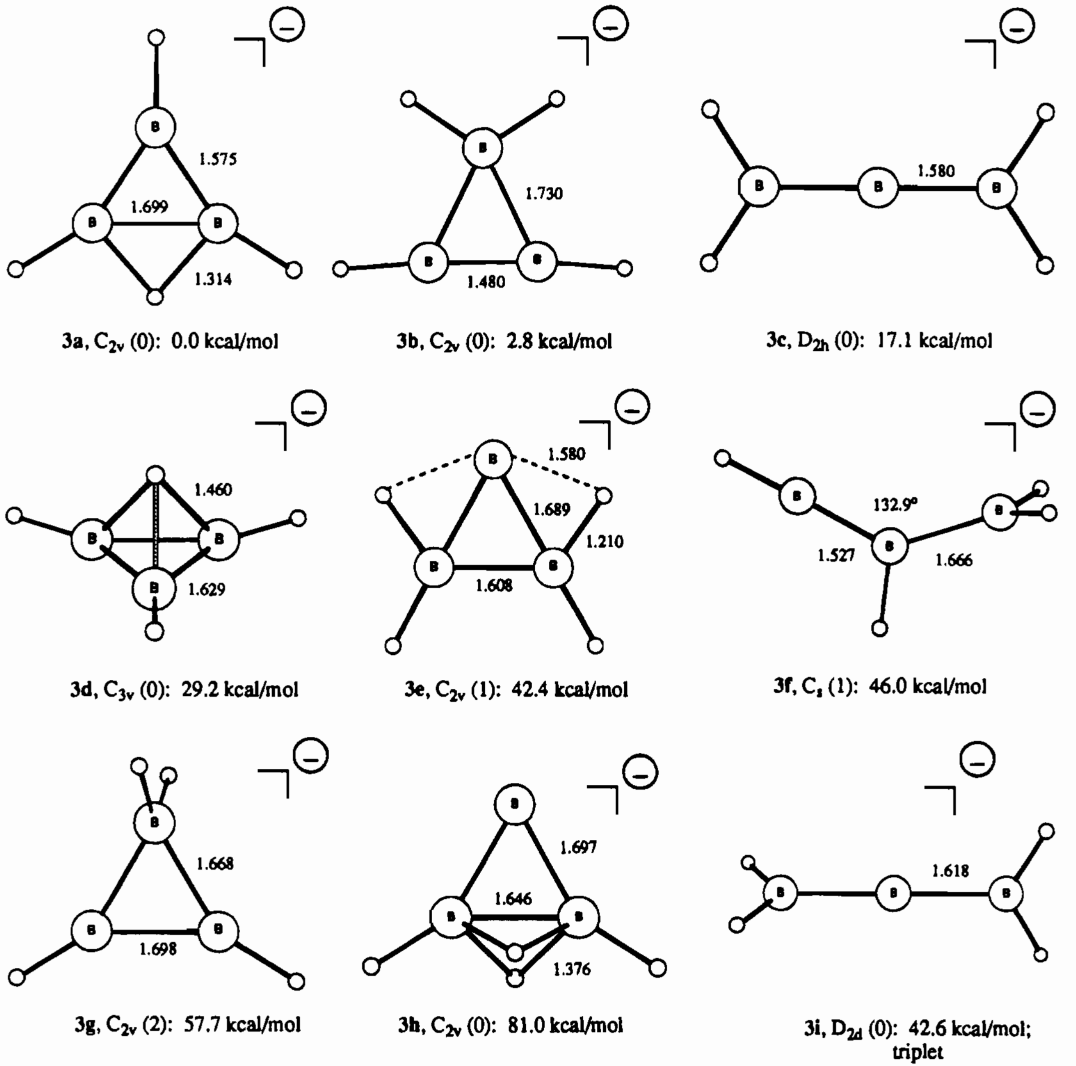
[21] (a) The strain energy and σ aromaticity (see ref 20c) should also be taken into account. (b) The magnetic criteria of aromaticity (see ref 20a-c) will be considered separately for the species studied here.



3a, C_{2v} (0): 0.0 kcal/mol

3b, C_{2v} (0): 2.8 kcal/mol

3c, D_{2h} (0): 17.1 kcal/mol

3d, C_{3v} (0): 29.2 kcal/mol

3e, C_{2v} (1): 42.4 kcal/mol

3f, C_s (1): 46.0 kcal/mol

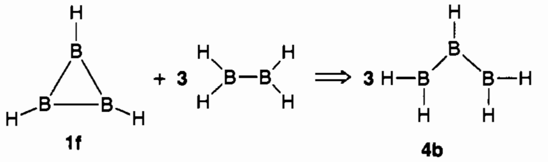
3g, C_{2v} (2): 57.7 kcal/mol

3h, C_{2v} (0): 81.0 kcal/mol

3i, D_{2d} (0): 42.6 kcal/mol; triplet

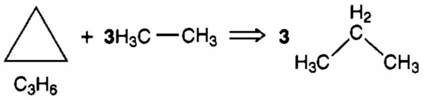
Figure 3. $B_3H_4^-$ structures. The number of imaginary frequencies is given in parentheses.

from eq 7, is higher than the corresponding value in cyclopropane defined from eq 8 (for earlier estimates, see ref 22). All structures chosen in eq 7 are planar and have no π electrons.



1f **4b** (7)

ΔE = 38.7 kcal/mol

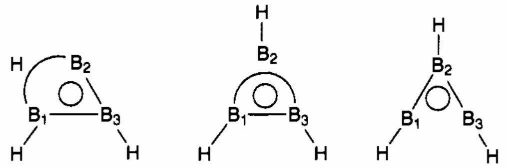


C_3H_6 (8)

ΔE = 26.2 kcal/mol

The BB distances in **1f** (1.726 Å), in the D_{2h} structure of B_2H_4 (1.744 Å), and in C_{2v} **4b** (1.742 Å) may be considered as "standard" boron–boron single bond lengths, since they are not influenced by conjugation or by hyperconjugation (compare with BB = 1.652 Å in the D_{2d} structure of B_2H_4, which benefits from double hyperconjugation[23]).

Three lowest energy structures of B_3H_3 (**1a–c**; see Figure 1 for the geometries) have delocalized 3c–2e π bonds; i.e., a pair of electrons is moved from the σ framework to a π orbital (MPP for **1a**: B^1, −0.74; B^2, −0.77; B^3, −0.49. MPP for **1b**: B^1 (B^3), −0.61; B^2, −0.78. MPP for **1c**: B^1 (B^3), −0.80; B^2, −0.60). The global minimum **1a** has unsymmetric B–H–B bonding without direct bonding overlap between the bridged boron atoms (WBI [MBP] (B^1B^2) = 1.321 [−0.811]). The two C_{2v} minima, **1b** and **1c**, arise from the first-order Jahn–Teller distortions of the D_{3h} symmetrical structure with two electrons in a degenerate e′ orbital lying in the ring plane. Structure **1b** has one localized BB and one three-center BBB



1a **1b** **1c**

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(22) (a) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467–7476. (b) Schoeller, W. W.; Dabisch, T. *Inorg. Chem.* **1987**, *26*, 1081. (c) Boatz, J. A.; Gordon, M. S.; Hilderbrandt, R. L. *J. Am. Chem. Soc.* **1988**, *110*, 352–358. (d) Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, 3408–3414.

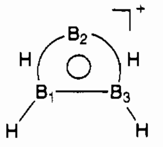
(23) (a) Vincent, M. A.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1981**, *103*, 5677. (b) Mohr, R. R.; Lipscomb, W. M. *Inorg. Chem.* **1986**, *25*, 1053. (c) Sana, M.; Leroy, G. *J. Mol. Struct. THEOCHEM* **1986**, *151*, 1053. (d) Kaufmann, E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3987. (e) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *90*, 4364. (f) Somogyi, A.; Gomory, A. *Chem. Phys. Lett.* **1992**, *192*, 221.

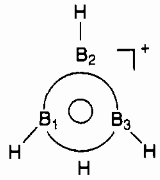
bond, while **1c** has two symmetrical σ bonds. There is no σ electron bonding between B^1 and B^3 atoms in **1c** (MBP = −0.230). Nevertheless B^1 and B^3 are bound by a $p_\pi-p_\pi$ interaction (WBI = 0.626). The B^1B^3 separation of 1.922 Å is too short to be a nonbonded distance.

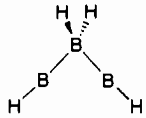
The open-chain isomer HB=B−BH$_2$ (**1d**) (the lowest energy minimum located in an earlier *ab initio* study[3a]) is substantially higher in energy than structures **1a−c**. While the B^1B^2 (1.554 Å) and the B^2B^3 (1.586 Å) bond lengths do not differ considerably in **1d**, there is no appreciable delocalization of π electrons into the B^3 p_π orbital (MPP = 0.10). The relative energies of **1b−d** (with respect to the global minimum **1a**) are similar at QCI (**1b** = 5.3 kcal/mol, **1c** = 7.5 kcal/mol, and **1d** = 28.8 kcal/mol), as at MP2 (see Figure 1). The other structures, **1e−h**, have higher energies and are not minima.

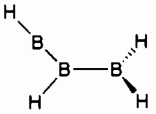
Two triplet structures considered, D_{3h} **1j** and C_{2v} **1k** (see Figure 1), have lower energies than singlet forms **1f** and **1d**, respectively. Structure **1j** (NIMAG = 2) has two unpaired electrons in the σ framework and an electron pair in a π MO. The singlet−triplet energy difference between **1d** and **1k** (8.2 kcal/mol) is lower than the corresponding HB=BH S−T value (23 kcal/mol; see also ref 23). This decrease in the S−T energy separation is due to more effective delocalization of two π electrons by the p_π orbital of the BH$_2$ group in **1d** than corresponding delocalization of one electron in **1k**. The double BB bond (1.554 Å) is longer and the single BB bond (1.586 Å) is shorter in **1d** than the corresponding separations in **1k** (1.527 and 1.651 Å). The decreased number of σ electrons and the cyclic π bonding lead to shorter BB bonds (1.599 Å) in **1j** than in **1f** (1.726 Å).

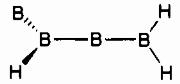
$B_3H_4^+$ (Figure 2). The two lowest energy C_{2v} structures **2a** and **2b** arise from the protonation of the BB bonds in **1a** and in **1b**, respectively. But **2b** is not a minimum (NIMAG = 2) and collapses to **2a** if the C_{2v} symmetry constraint is removed. Both **2a** and **2b** have cyclic delocalized 3c−2e π orbitals (MPP for **2a**: B^1 (B^3) = 0.55; B^2 = 0.90. MPP for **2b**: B^1 (B^3) = 0.71; B^2 = 0.58), while the B^1B^3 bond length in **2a** (1.729 Å) is close to the BB distance in **1f**.


2a


2b

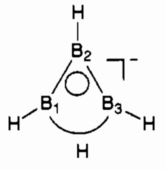

2c

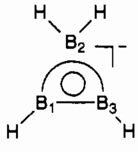

2e

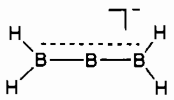

2f

All other open-chain (**2c−g**) and cyclic (**2h−j**) structures have higher energies. Single point energy computations on **2a−c** and **2e,f** at QCI show their energies to be closer to **2a** than those at MP2, but the relative order does not change (in kcal/mol): **2a** (0.0), **2b** (3.2), **2c** (4.7), **2e** (14.8), and **2f** (15.8). The highest energy structure **2j** is employed below in eq 10 as the reference species in the ASE estimate for $B_3H_4^-$. There are two localized and one H-bridged BB bonds in **2j** and no π electrons.

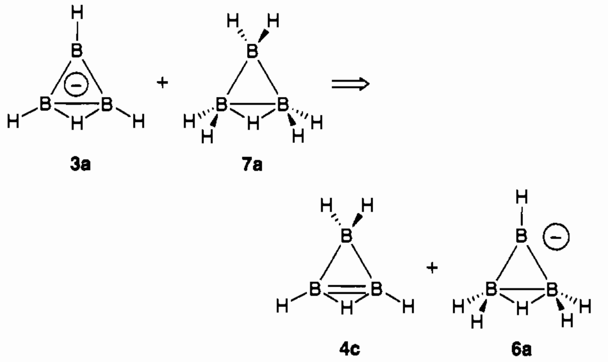
$B_3H_4^-$ (Figure 3). $B_3H_4^-$ is isoelectronic with aromatic CB_2H_4[3a,4,13d,24] and has a similar global minimum structure (**3a**) with a delocalized 3c−2e π bond (MPP: B^1 (B^3), −0.75; B^2, 0.50). Another C_{2v} structure (**3b**) with a 3c−2e π bond (MPP: B^1 (B^3), −0.68; B^2, 0.62) is only 2.8 kcal/mol higher in energy. Both **3a** and **3b** are lower in energy than the open-chain D_{2h} structure (**3c**), which has a linear 3c−2e π bond. The relative QCI energies are as follows: **3a**, 0.0 kcal/mol; **3b**, 2.1 kcal/mol; **3c**, 11.2 kcal/mol.


3a


3b

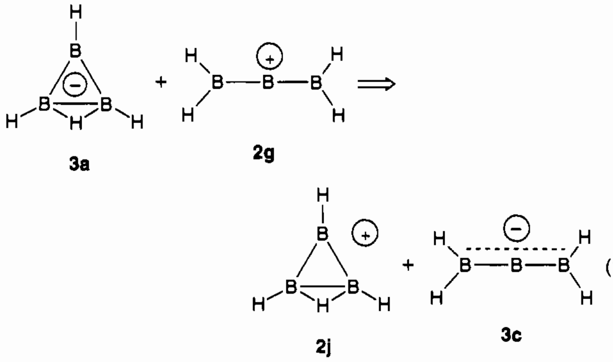

3c

While the SE in **3a**, estimated from eq 9 (44.5 kcal/mol), is smaller than the SE of **14** (64.1 kcal/mol, eq 1), the ASE



(9)

ΔE = 44.5 kcal/mol

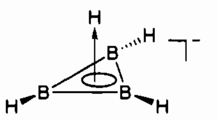


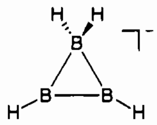
(10)

ΔE = 38.7 kcal/mol

estimates for **3a** (eq 10, 38.7 kcal/mol) and for **14** (eq 2, 35.7 kcal/mol) are similar. Because the reference structures in eqs 9 and 10 are so different from their counterparts in eqs 1 and 2, such comparisons are only qualitative.

Remarkably, the C_{3v} structure **3d** is also a minimum, although its energy is quite high. It can be regarded as a 4c−2e π


3d


3g

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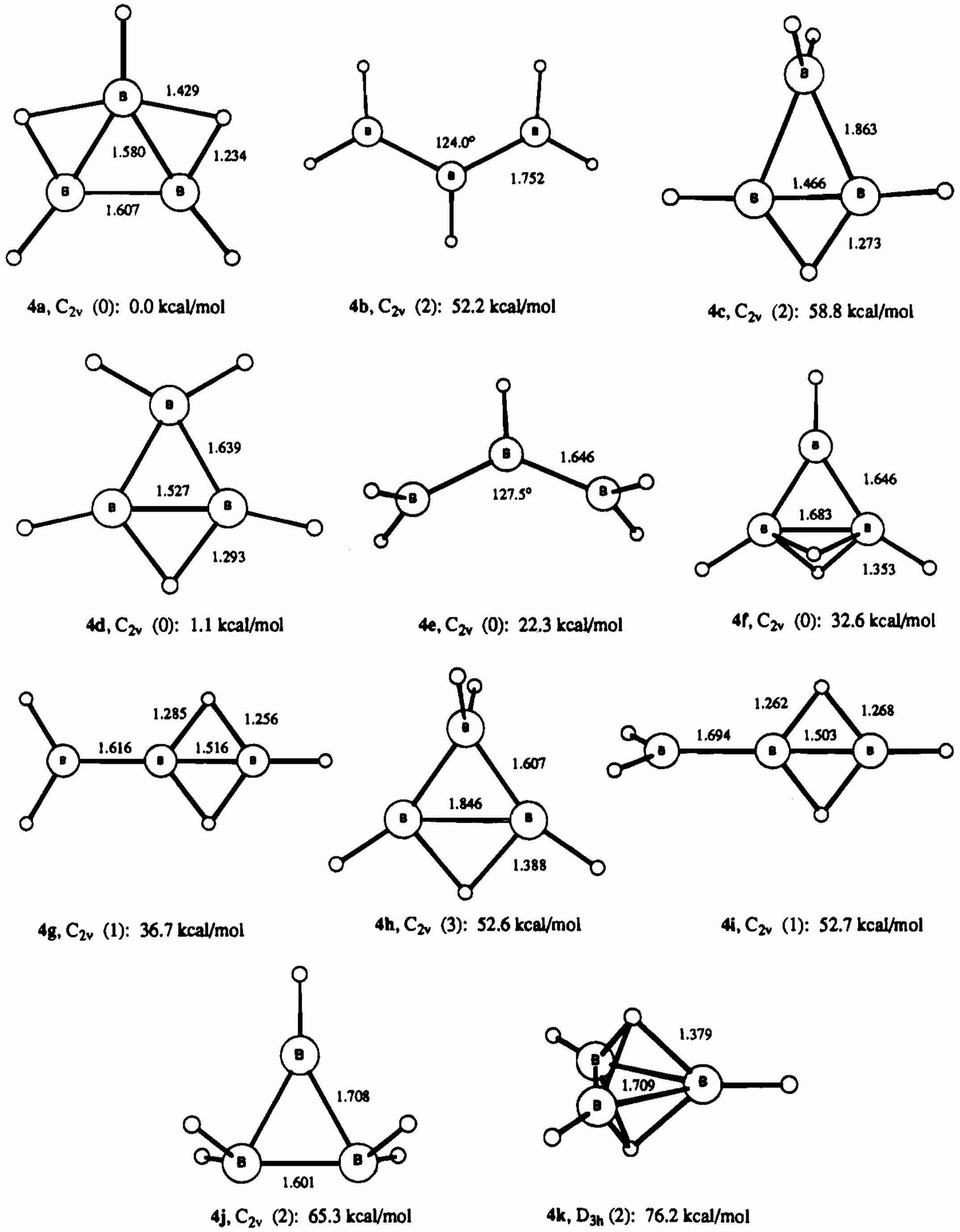
[24] (a) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419. (b) Krogh-Jespersen, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J. *J. Am. Chem. Soc.* **1979**, *101*, 4843. (c) Farras, J.; Olivella, S.; Sole, A.; Vilarrasa, J. *J. Comput. Chem.* **1986**, *7*, 428. (d) Budzelaar, P. H. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 3967.



4a, C_{2v} (0): 0.0 kcal/mol
4b, C_{2v} (2): 52.2 kcal/mol
4c, C_{2v} (2): 58.8 kcal/mol
4d, C_{2v} (0): 1.1 kcal/mol
4e, C_{2v} (0): 22.3 kcal/mol
4f, C_{2v} (0): 32.6 kcal/mol
4g, C_{2v} (1): 36.7 kcal/mol
4h, C_{2v} (3): 52.6 kcal/mol
4i, C_{2v} (1): 52.7 kcal/mol
4j, C_{2v} (2): 65.3 kcal/mol
4k, D_{3h} (2): 76.2 kcal/mol

Figure 4. B_3H_5 structures. The number of imaginary frequencies is given in parentheses.

complex (nonplanar 2π aromatic) of the aromatic dianion $B_3H_3^{2-}$ (**11**), which is isoelectronic with **14**.[13d,25a] Four other computed structures (**3e**–**h**) have higher energies. The C_{2v} form (**3g**), with a tetrahedral boron atom, was not a minimum; the same is true for the isoelectronic and isostructural CB_2H_4.[13d,24]

The triplet D_{2d} minimum, **3i** (see Figure 3), is considerably less stable at MP2 (42.6 kcal/mol) than the global minimum **3a**.

B_3H_5 (Figure 4). The lowest energy minima **4a**,**d**,**e** have already been examined by *ab initio* methods.[3a,4] Our data agree well with those of Jemmis et al.[4] at MP2/6-31G*. Structures **4b** (localized σ bonds and no π electrons) and **4c** (H and BH_2 bridges and π bond between B^1 and B^3) were employed as the reference species in eqs 7 and 9, respectively. Structure **4d** arises from the rotation of the bridging BH_2 group in **4c** to the ring plane, which leads to the cyclic delocalization of the π electrons into the B^2 $p\pi$ orbital. The B^1B^2 and B^2B^3 (1.639 Å) bonds are shorter and the B^1B^3 (1.527 Å) bond is longer in **4d** compared to **4c** ($B^1B^3 = B^2B^3 = 1.863$ Å and $B^1B^3 = 1.466$ Å). The cyclic C_{2v} structures **4a**,**d**, with π electron delocalization (MPP for **4a**: B^1 (B^3) = 0.59; B^2 = 0.82. MPP for **4d**: B^1 (B^3) = 0.76; B^2 = 0.48), have very similar energies: **4a** is

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(25) (a) Sundaralingam, A. M.; Jensen, L. H. *J. Am. Chem. Soc.* **1966**, *88*, 198. (b) Breslow, R. *Pure Appl. Chem.* **1971**, *28*, 111. (c) Ku, A. T.; Sundaralingam, M. *J. Am. Chem. Soc.* **1972**, *94*, 1688. (d) Radom, L.; Hariharan, J. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 10. (e) Krishnan, R.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (f) Allen, F. H. *Tetrahedron* **1982**, *38*, 645. (g) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl. No. 1* **1988**, *17*, 109. (h) Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 6976. (i) Lammertsma, K.; Gruner, O. F.; Thibodeaux, A. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 8995. (j) Lammertsma, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 7935. (k) Li, W.-K.; Riggs, N. V. *J. Mol. Struct. THEOCHEM* **1992**, *257*, 189.

Table 1. Total Energies (in au) and Zero Point Energies (in kcal/mol) of B_3H_n and Related Species

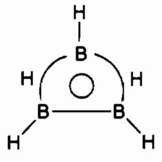
molecule	no. (PG)	HF/6-31+G*//6-31+G*	MP2(fu)/6-31+G*//MP2(full)/6-31+G*[a]	ZPE (NIMAG)[b]
B_3H_3	**1a** (C_s)	−75.65095	−75.92043 (−75.99361)	23.2 (0)
	1b (C_{2v})	−75.64855	−75.90701 (−75.98278)	21.5 (0)
	1c (C_{2v})	−75.64904	−75.90170 (−75.97939)	21.6 (0)
	1d (C_{2v})	−75.64065	−75.86026	21.1 (0)
	1e (C_{2v})	−75.50054	−75.82153	19.4 (2)
	1f (D_{3h})	−75.59733	−75.81057	20.3 (2)
	1g (C_{2v})	−75.53162	−75.79942	22.1 (1)
	1h (C_{2v})	−75.53905	−75.78365	21.8 (1)
	1i (C_{2v})	−75.47369	−75.77750	21.0 (3)
	1j (D_{3h})[c]	−75.64759	−75.87651	22.0 (2) [20.2 (2)]
	1k (C_{2v})[c]	−75.67327	−75.87311	22.0 (0)
$B_3H_4^+$	**2a** (C_{2v})	−75.96408	−76.22031 (−76.29735)	29.1 (0)
	2b (C_{2v})	−75.96110	−76.21206 (−76.29058)	27.9 (2) [26.3 (3)]
	2c (C_{2v})	−75.98556	−76.20388 (−76.28858)	27.5 (0)
	2d (C_{2v})	−75.94895	−76.18950	28.8 (1)
	2e (C_s)	−75.98856	−76.18820	27.9 (0)
	2f (D_{2d})	−75.99081	−76.18508	27.7 (0)
	2g (D_{2h})	−75.98976	−76.18321	27.7 (1)
	2h (C_{2v})	−75.95785	−76.17003	27.2 (1)
	2i (C_{2v})	−75.95029	−76.15570	27.5 (2)
	2j (C_{2v})	−75.94389	−76.14787	26.4 (2)
$B_3H_4^-$	**3a** (C_{2v})	−76.30113	−76.58819 (−76.67796)	28.9 (0)
	3b (C_{2v})	−76.29788	−76.58287 (−76.67383)	28.4 (0)
	3c (D_{2h})	−76.30336	−76.55869 (−76.65783)	27.4 (0)
	3d (C_{3v})	−76.25626	−76.53569	24.8 (0)
	3e (C_{2v})	−76.22527	−76.51830	27.2 (1)
	3f (C_s)	−76.25675	−76.51073	26.0 (1)
	3g (C_{2v})	−76.23229	−76.49386	25.0 (2)
	3h (C_{2v})	−76.17939	−76.45597	26.6 (0)
	3i (D_{2d})[c]	−76.29792	−76.51752	27.0 (0)
B_3H_5	**4a** (C_{2v})	−76.86764	−77.15293 (−77.24644)	36.4 (0)
	4b (C_{2v})	−76.84567	−77.06562	33.5 (2)
	4c (C_{2v})	−76.78743	−77.05915	34.8 (2)
	4d (C_{2v})	−76.86979	−77.15140 (−77.24569)	36.0 (0)
	4e (C_{2v})	−76.88406	−77.11363 (−77.21499)	33.8 (0)
	4f (C_{2v})	−76.83863	−77.10021	35.7 (0)
	4g (C_{2v})	−76.82550	−77.09391	36.1 (1)
	4h (C_{2v})	−76.80453	−77.06890	35.6 (3)
	4i (C_{2v})	−76.80374	−77.06239	31.7 (1)
	4j (C_{2v})	−76.78211	−77.04261	32.0 (2)
	4k (D_{3h})	−76.75321	−77.03099	33.3 (2)
$B_3H_6^+$	**5a** (C_{3v})	−77.19371	−77.46114	44.7 (0)
	5b (D_{3h})	−77.09315	−77.39189	43.0 (1)
	5c (C_{2v})	−77.18634	−77.44066	43.3 (0)
	5d (C_s)	−77.18871	−77.43642	43.4 (0)
	5e (C_{2v})	−77.17713	−77.42906	42.7 (1)
	5f (C_s)	−77.17022	−77.41435	41.7 (1)
	5g (C_{2v})	−77.16890	−77.41344	41.6 (1)
	5h (C_{2v})	−77.17515	−77.40920	42.2 (0)
	5i (C_s)	−77.16142	−77.39916	41.2 (1)
	5j (C_{2v})	−77.13362	−77.38286	41.0 (2)
	5k (D_{3h})	−77.09618	−77.32273	39.1 (3)
$B_3H_6^-$	**6a** (C_{2v})	−77.47375	−77.75846	39.8 (0)
	6b (C_{2v})	−77.42320	−77.72522	40.9 (0)
	6c (C_1)	−77.47909	−77.76711	39.8 (0)
	6d (D_{3d})	−77.47550	−77.75002	37.5 (0)
	6e (C_{2v})	−77.46591	−77.73980	37.9 (0)
	6f (C_s)	−77.46361	−77.73861	37.5 (1)
	6g (C_{2v})	−77.45859	−77.73846	38.5 (1)
	6h (C_{2v})	−77.45355	−77.73265	38.1 (2)
	6i (C_{2v})	−77.43565	−77.73425	40.2 (0)
	6j (C_{2v})	−77.46010	−77.72528	38.8 (2)
	6k (C_{2v})	−77.42865	−77.71894	41.2 (0)
	6l (D_{3h})	−77.39876	−77.69742	40.7 (2)
B_3H_7	**7a** (C_{2v})	−78.03119	−78.30321	48.5 (2)
	7b (C_{2v})	−77.99930	−78.28913	46.7 (3)
	7c (C_{2v})	−77.90036	−78.21423	49.5 (2)
	7d (C_s)	−78.03422	−78.31884	48.5 (1)
	7e (C_s)	−78.04901	−78.33388	50.1 (0)
	7f (C_{2v})	−78.05125	−78.32637	49.6 (0)
	7g (C_s)	−78.05119	−78.31724	49.4 (0)
	7h (C_s)	−77.98289	−78.26416	47.5 (1)

Table 1 (Continued)

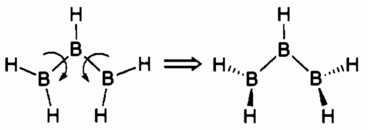
molecule	no. (PG)	HF/6-31+G*//6-31+G*	MP2(fu)/6-31+G*//MP2(full)/6-31+G*[a]	ZPE (NIMAG)[b]
$B_3H_8^+$	**8a** (C_{2v})	−78.29852	−78.55263	50.5 (2)
	8b (C_s)	−78.30012	−78.57945	52.1 (1)
	8c (D_{2d})	−78.35062	−78.61987	57.7 (0)
	8d (C_{2v})	−78.33445	−78.61282	58.1 (0)
	8e (C_s)	−78.32649	−78.58875	55.5 (1)
	8f (C_{2v})	−78.31619	−78.55880	53.2 (2)
	8g (C_{2v})	−78.30845	−78.54956	52.0 (2)
$B_3H_8^-$	**9a** (C_{2v})	−78.66539	−78.98121 (−79.1243)	43.4 (1) [53.4 (0)]
	9b (C_s)	−78.66638	−78.97815 (−79.12068)	54.2 (0) [53.0 (1)]
	9c (C_s)	−78.64485	−78.94451	53.0 (0)
B_3H_9	**10a** (D_{3h})	−79.18196	−79.47914	62.0 (3) [61.4 (3)]
	10b (C_{3v})	−79.18471	−79.48849	63.5 (0)
	10c (C_2)	−79.18004	−79.48207	62.5 (1) [61.7 (0)]
$B_3H_3^{2-}$	**11** (D_{3h})	−75.51083	−75.80995	21.4 (0)
$B_3H_5^{2-}$	(C_{2v})	−76.71714	−77.00324	31.8 (0)
$B_3H_3Li^-$	**12a** (C_{2v})	−83.14662	−83.44967	22.4 (0)
	12b (C_{3v})	−83.13853	−83.44494	22.7 (0)
$B_3H_3Li_2$	**13a** (C_{2v})	−90.63788	−90.94594	24.6 (0)
	13b (D_{3h})	−90.60960	−90.91733	23.5 (2)
$B_3H_5Li_2$	(C_{2v})	−91.80815	−92.12102	35.6 (1)

[a] Values in parentheses are at QCISDT/6-311+G**//MP2(FULL)/6-31+G*. [b] Not scaled; at HF/6-31+G* [MP2(FC)/6-31+G*]. [c] In the triplet state.

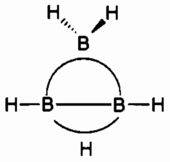
more stable at MP2 (see Table 1). Both **4a** and **4d** may be regarded as protonated forms of the lowest energy C_{2v} $B_3H_4^-$structures **3a**,**b**, respectively.



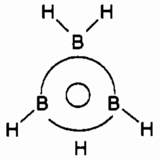
4a



4b **4e**



4c

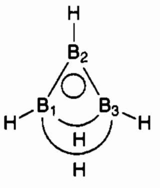


4d

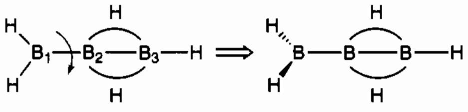
The "classical" open structure **4e** is the global minimum at HF (in agreement with earlier *ab initio* findings[3a]) but less stable than **4a** at MP2. The QCI energies, relative to **4a**, are 0.3 kcal/mol (**4d**) and 17.4 kcal/mol (**4e**). Structure **4e** arises from the rotation of two BH_2 groups in **4b** leading to the planar C_{2v} structure. The shorter BB distances in **4e** (1.646 Å) than in **4b** (1.752 Å) are due to hyperconjugation between the BH bonds and the empty p orbitals of neighboring B atoms. A similar variation is found in the BB bond lengths of the planar D_{2h} (1.744 Å) and the rotated D_{2d} (1.653 Å) B_2H_4 structures.[23] The 30 kcal/mol **4b** → **4e** energy difference is about twice the D_{2d} → D_{2h} rotation value in B_2H_4 (13 kcal/mol).

Our highest energy minimum **4f**, with its doubly H-bridged bond (a protonated form of **3h**), has not been considered previously. The strongly negative B^1B^3 MBP (−0.552) indicates the absence of direct bonding. All other structures we examined, **4g**−**k**, have higher energies and are not minima.

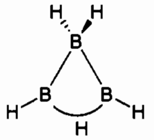
The C_{2v} planar **4g** is 16 kcal/mol lower in energy than the isostructural **4i**. This energy difference can be attributed to the delocalization of π electrons to B^1 p_π orbital in planar **4g**. Structure **4h** (no π electrons) is the analog of **3g** with an additional B−H−B bridged bond. The relative energies of **3g** and **4h** are similar to those of global minima, **3a** and **4a**, respectively. Isomer **4j** originates from a different distribution of two σ electron pairs bonding three boron atoms than in **4e**. There are two localized BB bonds in **4e** and one localized and one bridged BB bond in **4j**.



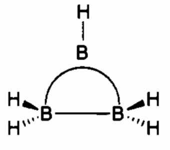
4f



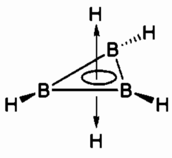
4g **4i**



4h



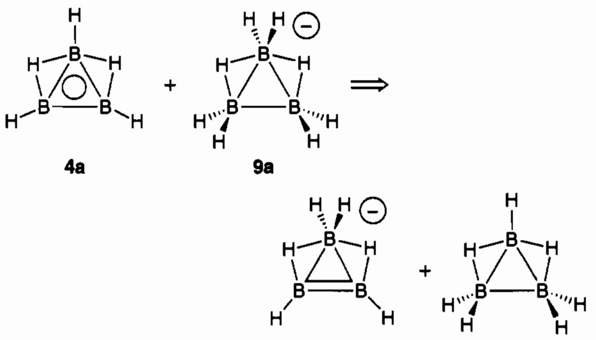
4j



4k

We have considered the high energy D_{3h} structure **4k** because of its potential three-dimensional aromaticity:[4,26] **4k** is the doubly protonated form of the aromatic dianion, **11**. However, **4k** is not a minimum and has a high energy.

Isodesmic eq 11 gives an estimate of the SE of **4a**, which is similar to the SE of the cyclopropenium cation, **14** (eq 1).[27] All species in eq 11 are isoelectronic with their corresponding counterparts in eq 1.



(11)

ΔE = 73.2 kcal/mol

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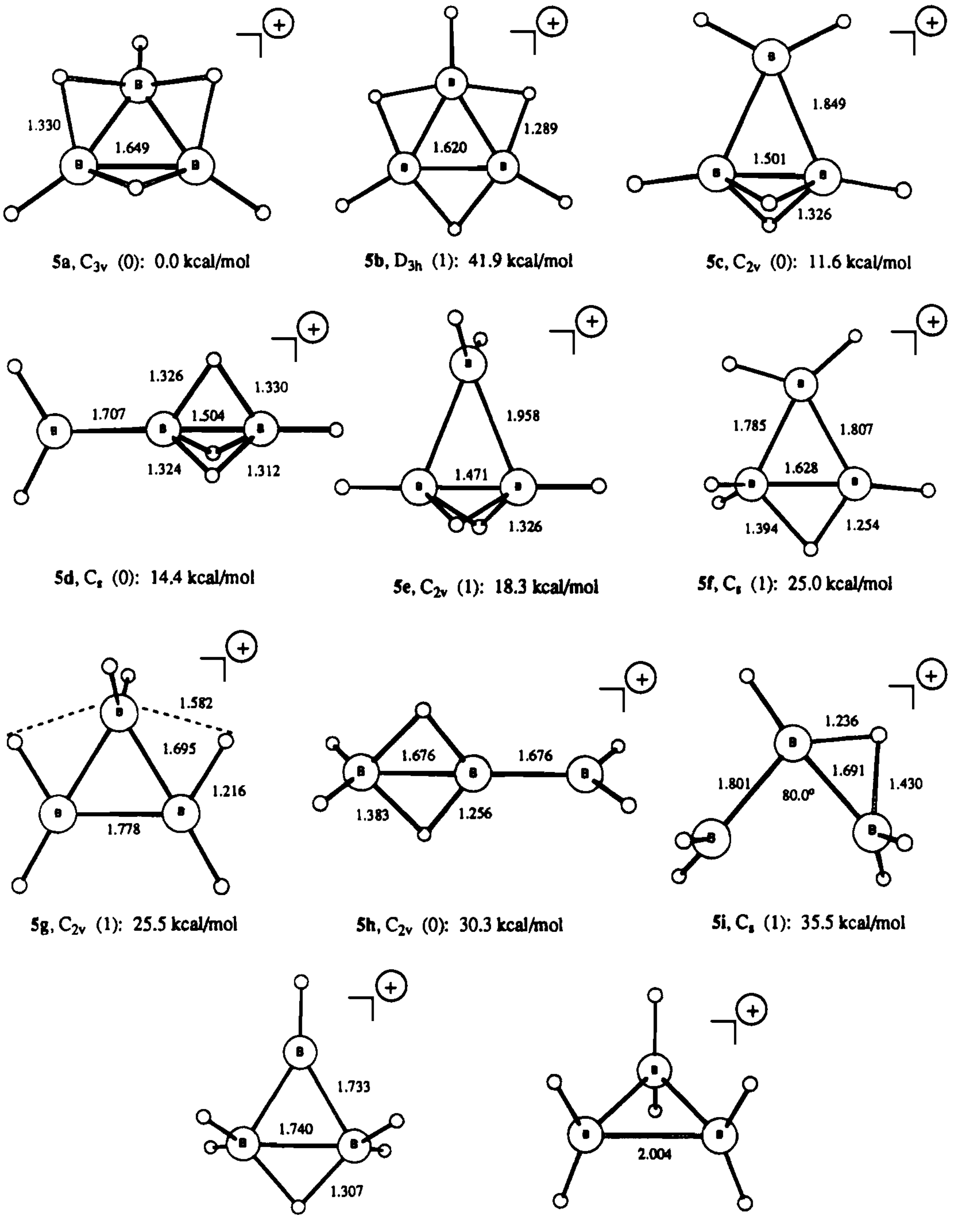
(26) (a) Krogh-Jespersen, K.; Schleyer, P. v. R.; Pople, J. A.; Cremer, D. *J. Am. Chem. Soc.* **1978**, *100*, 4301. (b) Chandrasekhar, J.; Schleyer, P. v. R.; Krogh-Jespersen, K. *J. Comput. Chem.* **1981**, *2*, 356.



5a, C_{3v} (0): 0.0 kcal/mol

5b, D_{3h} (1): 41.9 kcal/mol

5c, C_{2v} (0): 11.6 kcal/mol

5d, C_s (0): 14.4 kcal/mol

5e, C_{2v} (1): 18.3 kcal/mol

5f, C_s (1): 25.0 kcal/mol

5g, C_{2v} (1): 25.5 kcal/mol

5h, C_{2v} (0): 30.3 kcal/mol

5i, C_s (1): 35.5 kcal/mol

5j, C_{2v} (2): 45.8 kcal/mol

5k, D_{3h} (3): 81.9 kcal/mol

Figure 5. $B_3H_6^+$ structures. The number of imaginary frequencies is given in parentheses.

While **6b** is not the lowest energy $B_3H_6^-$ minimum and **7b** is not a minimum at all (NIMAG = 3), we believe that these reference structures are the most appropriate for the comparative SE estimation of **14** with **4a**. This assumption is based on an isoelectronic and isostructural analogy between corresponding structures in eq 1 and eq 11. The bonding patern is similar in the carbon and boron counterparts in eqs 1 and 11, respectively, while two localized bonds in the three-membered carbon cycles are replaced by 3c−2e H-bridged bonds in the boron rings. Thus, differences between counterparts in eqs 1 and 11 are counterbalanced in the left and right sides of the equations, and aromatic stabilization is emphasized. Similar approach was been employed, for example, in a comparative analysis of cyclic strain energies.[15d]

$B_3H_6^+$ (Figure 5). We have examined many $B_3H_6^+$ isomers (**5a**−**k**) and have estimated the isodesmic SEs in **5a**,**b** in order to compare the aromatic stabilization of $B_3H_6^+$ with $C_3H_3^+$. The 42 kcal/mol stabilization with respect to the planar D_{3h} structure **5b** results (as suggested in ref 4) from electron delocalization, as well as from the hydrogen atoms. The bridging and the terminal hydrogens are out of the ring plane by 0.678 and 0.385 Å, respectively, and BB bond distances are elongated by 0.03 Å in **5a** compared to those in D_{3h} **5b**.

The higher energy **5c**,**d** minima also have three bridged bonds. The bridging BH_2 group in **5c** is replaced by a bridging hydrogen in **5d**. The latter structure is an analog of the

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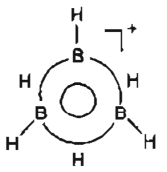
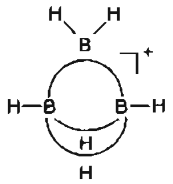
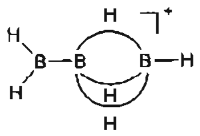
(27) Our later 64.1 kcal/mol SE estimate of $C_3H_3^+$ at MP2/6-31+G* + ZPE is closer to the earlier 69.5 kcal/mol value from ref 15a than to 78 kcal/mol value from ref 14b.



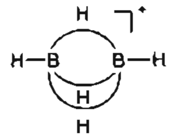
5a (5b)



5c



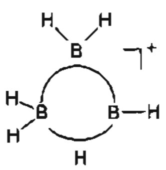
5d



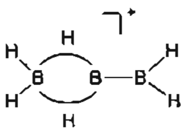
19

propargyl cation, H_2C-CCH^+, with a triply H-bridged BB arrangement instead of the triple CC bond. The energy difference between the cyclopropenium ion, **14**, and the propargyl cation (25−34 kcal/mol[24,27]) is about twice as large as between **5a** and **5d** (14.4 kcal/mol). Both **5c** and **5d** can also be related to the triply H-bridged $B_2H_5^+$ D_{3h} structure **19**, studied earlier by *ab initio* methods.[28]

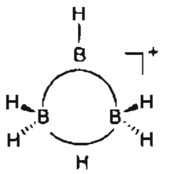
The transition structure C_{2v} **5e** is similar to **5c** but with the BH_2 group rotated. Both transition structures C_s **5f** and C_{2v} **5g** optimize to the global minimum **5a**, if the symmetry constraints are eliminated. In C_{2v} **5h**, the bond lengths of B^1B^2 (WBI = 0.700; MBP = 0.306) doubly H-bridged and B^2B^3 (WBI = 1.006; MBP = 0.248) localized single BB bonds are equal despite the difference in their bonding character. Nevertheless, WBIs (0.700 and 1.006) and MBPs (0.306 and 0.248) are also similar for B^1B^2 and B^2B^3 bonds. Like **5c,d**, the **5h** minimum and the **5f** transition structure are related through the exchange of a bridging hydrogen (e.g., in **5h**) with a bridging BH_2 group (in **5f**). The greater stability of **5c**, relative to **5d** (2.8 kcal/mol), as well as of **5f**, relative to **5h** (5.3 kcal/mol), reflects the better electron and charge delocalization in cyclic rather than open structures.



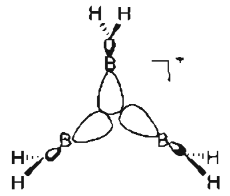
5f



5h



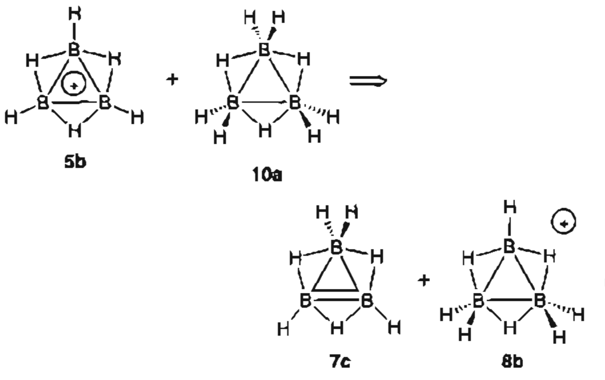
5j



5k

The other $B_3H_6^+$ structures we considered (**5i−k**) are higher in energy and are not minima. Structure **5j** is a protonated form of **4j** and also has two imaginary frequencies. The D_{3h} structure **5k**, with a single 3c−2e symmetric σ bond between the three boron atoms, has very high energy.

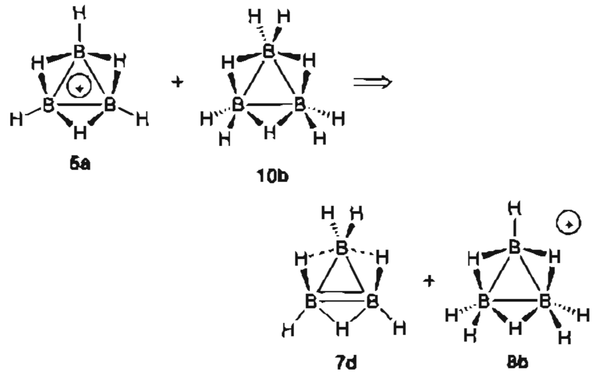
Planar **5b** has the same D_{3h} symmetry as the aromatic cyclopropenium ion, **14**. We suggest the isodesmic eq 12 for the estimation of the SE in **5b**. As in eq 11, all reference structures in eq 12 are isoelectronic with the corresponding structures in eq 1. The SE of **5b**, despite its higher symmetry, is smaller than that of **4a**. The BB bond lengths are longer in **5b** than in **4a**, due to the greater repulsion of nonbonded hydrogens in **5b**.



5b **10a** **7c** **8b** (12)

ΔE = 59.9 kcal/mol

The SEs of the D_{3h} symmetric **14** (eq 1) and **5b** (eq 12) are similar and are quite large. Nevertheless, the energy of nonplanar C_{3v} **5a** is 42 kcal/mol *lower* than **5b**. Is this due to increase of aromaticity in **5a**? In an attempt to elucidate this question, we have estimated the SE of **5a** from isodesmic eq 13. The structures in eq 13 (C_{3v} **5a** and C_s **7d**, **8b**, and **10b**) have lower symmetry than the corresponding structures in eq 12 (D_{3h} **5b** and C_{2v} **7c**, **8a**, and **10a**) as the bridging hydrogens are out of the boron ring plane.



5a **10b** **7d** **8b** (13)

ΔE = 24.6 kcal/mol

The species in eq 13 are more stable than the corresponding forms in eq 12 by 41.9 kcal/mol (**5a** vs **5b**), 4.6 kcal/mol (**10a** vs **10b**), 66.7 kcal/mol (**7d** vs **7c**), and 15.4 kcal/mol (**8b** vs **8c**). The sum of these energy differences due to symmetry reduction are higher for the reference species in the right side of eq 13. As a consequence, the SE of **5a** (24.6 kcal/mol, deduced from eq 13) is less than the SE of **5b** (59.9 kcal/mol, eq 12) despite the lower energy of **5a** than **5b**. This demonstrates how strongly the choice of reference species can influence SEs. While the bridging hydrogens are located more or less symmetrically in all species employed in eq 12, as well as in **5a** and in **10b** in eq 13, it is not true for **7d** and **8b**. The unsymmetrical H-bridging in B^1-H-B^2 and B^2-H-B^3 bonds of **7d** and **8b** complicates the comparison of the SEs estimated from eqs 12 and 13 (despite their formal correspondence), as hydrogen−hydrogen repulsion may not be properly counterbalanced in the left and right sides of eq 13. Nevertheless, we

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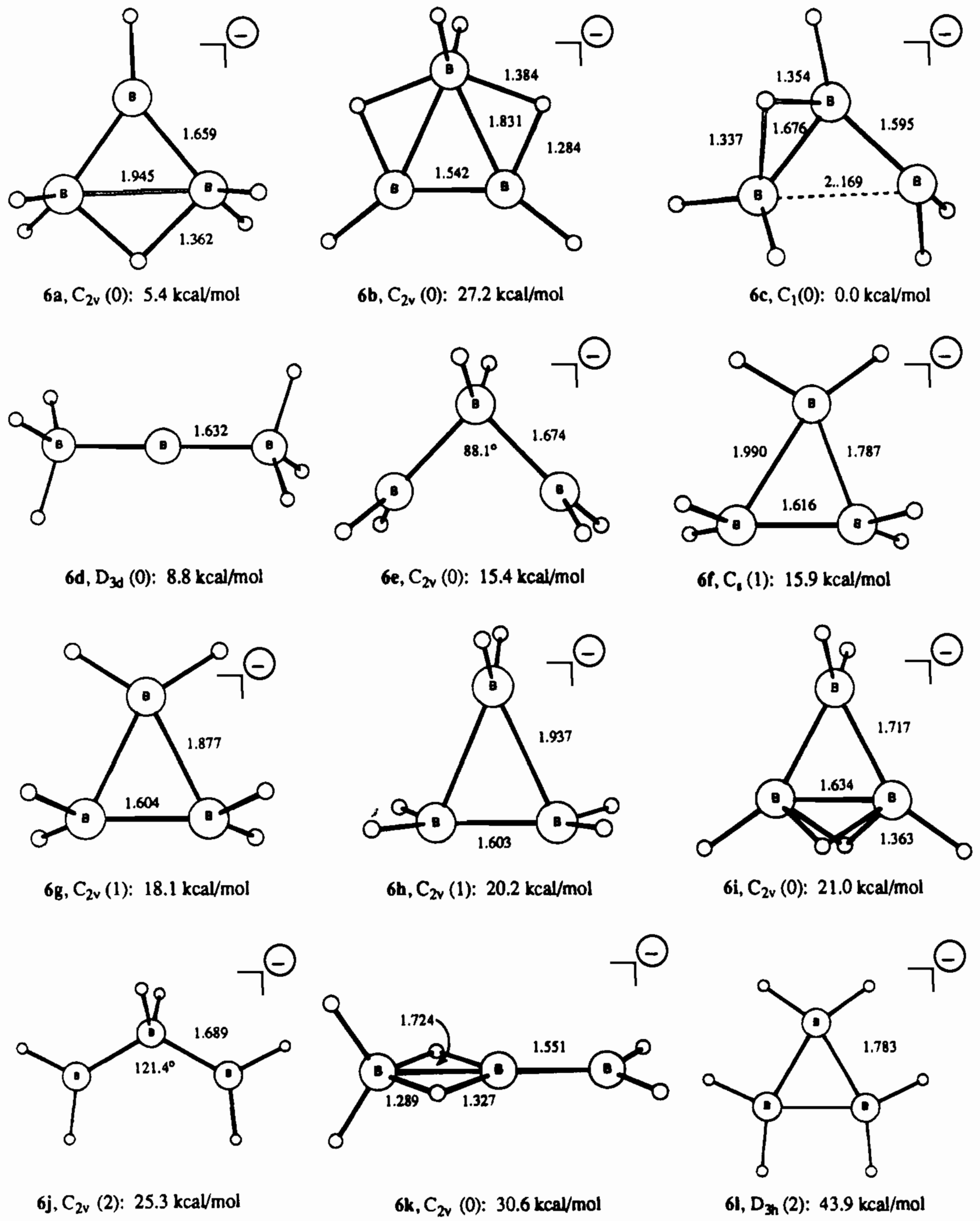
[28] (a) Rastogi, R.; Ray, N. K. *Int. J. Quantum Chem.* **1977**, *11*, 435. (b) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1985**, *24*, 762. (c) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1988**, *89*, 4875. (d) Olah, G. A.; Aniszfeld, R.; Surya Prakash, G. K.; Williams, R. E.; Lammertsma, K.; Guner, O. F. *J. Am. Chem. Soc.* **1988**, *110*, 7885. (e) Sana, M.; Leroy, G.; Henriet C. H. *J. Mol. Struct. THEOCHEM* **1989**, *187*, 233. (f) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *91*, 4189.



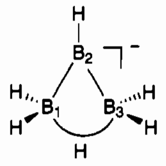
6a, C_{2v} (0): 5.4 kcal/mol
6b, C_{2v} (0): 27.2 kcal/mol
6c, C_1(0): 0.0 kcal/mol
6d, D_{3d} (0): 8.8 kcal/mol
6e, C_{2v} (0): 15.4 kcal/mol
6f, C_s (1): 15.9 kcal/mol
6g, C_{2v} (1): 18.1 kcal/mol
6h, C_{2v} (1): 20.2 kcal/mol
6i, C_{2v} (0): 21.0 kcal/mol
6j, C_{2v} (2): 25.3 kcal/mol
6k, C_{2v} (0): 30.6 kcal/mol
6l, D_{3h} (2): 43.9 kcal/mol

Figure 6. $B_3H_6^-$ structures. The number of imaginary frequencies is given in parentheses.

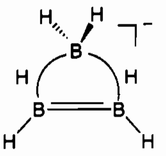
doubt that lower energy of nonplanar **5a** with respect to planar **5b** is due to an increase of aromaticity. Delocalization of this MO from the boron p_π orbitals to the bridging hydrogens (allowed by C_{3v} symmetry of the nonplanar **5a**) is not a convincing explanation; the same is true for the MO energy splitting.[4] The structure **7d** (eq 13), which does not involve aromaticity, is 67 kcal/mol lower in energy than **7c** (eq 12). We suggest that the cyclic delocalized π MO in **5b**, symmetrical with regard to the ring plane, corresponds to the cyclic 3c–2e bond in **5a** which also binds three borons and that the BHB three-center bonding is more favorable in **5a** than in **5b**. The central symmetric B–B–B bridge in **5a** can be depicted by ring line, similar to the cyclic π bond in **5b**.

$B_3H_6^-$ (Figure 6). The singly (**6a**) and doubly H-bridged (**6b**) minimum energy structures (both C_{2v}) were employed as the reference species in eqs 9 and 11, respectively. The singly bridged **6a** is only 5.4 kcal/mol higher in energy than the global $B_3H_6^-$ minimum **6c** (C_1), while the doubly bridged isomer is 27.2 kcal/mol less stable than **6c**. Two localized BB bonds and one H-bridged bond comprise the three-membered ring in **6a**: B^1 and B^3 share the negative charge ($q(B^1) = q(B^3) = -0.476$; $q(B^2) = 0.186$).

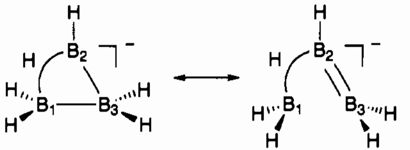
The asymmetric H-bridged open-chain structure **6c** is the global minimum both at HF and MP2. The negative charge in **6c** is substantially delocalized: $q(B^1) = -0.206$, $q(B^2) = -0.331$, and $q(B^3) = -0.158$. Some bonding exists between B^1 and B^3 (WBI = 0.326, MBP = 0.071) in spite of the long B^1B^3 separation (2.169 Å). The B^1–H–B^2 bridged bond (WBI = 0.944; MBP = −0.107) has no direct bonding between the boron atoms, but the B^2B^3 bond in **6c** (WBI = 1.304; MBP = 0.372) has partial double bond character. This is apparent from the short bond length, as well as from the population analysis. The two resonance contributors depict the bonding in **6c**.



6a

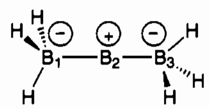


6b

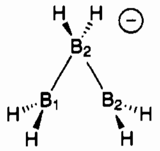


6c

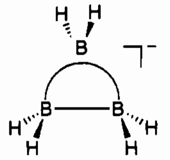
Two open-chain minimum energy structures with localized single bonds (D_{3d} **6d** and C_{2v} **6e**) have alternating charges. The central boron atom in **6d** is positively charged ($q(B^2) = 1.087$), whereas the terminal borons have negative charges ($q(B^1) = q(B^3) = -0.965$). In **6e** B^2 is negatively charged ($q(B^2) = -0.892$; $q(B^1) = q(B^3) = 0.283$). The small BBB bond angle (88.1°) and positive bond population between B^1 and B^3 atoms (WBI = 0.169; MBP = 0.091) indicates hyperconjugation between the σ^{BB} bonds and the empty p orbitals of B^1 and B^3.



6d



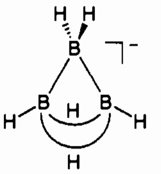
6e



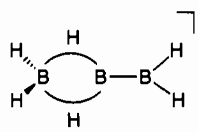
6h

The bonding is similar in transition structures **6f–h**: all three have a bridging BH_2 group. If the C_{2v} symmetry constraint of **6g** is reduced to C_s, the lower energy **6f** results upon further optimization. Both **6e** and **16h** both result from first-order Jahn–Teller distortions of the D_{3h} symmetrical structure with two σ electron pairs in the three-boron plane.

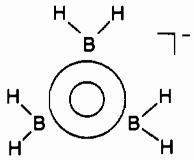
The C_{2v} minimum **6i** is another cyclopropene analog with doubly H-bridged ring B^1B^3 bond. This structure is 6.2 kcal/mol more stable than **6b**. The bridging in planar C_{2v} **6j** is similar to that in **6e**. However, the empty p orbitals of the terminal boron atoms in **6j** are perpendicular to the three-boron plane (hyperconjugation with BH instead of BB bonds) and the $B^1B^2B^3$ bond angle is widened (121.4°). Our highest energy minimum, **6k**, is an analog of allene with doubly H-bridged bond. While allene is 20–22 kcal/mol more stable than cyclopropene,[25g,29] cyclic **6i** is 9.6 kcal/mol more stable than the open-chain **6k**. The D_{3h} ring of **6l** is constructed from one σ and one π 3c–2e bond.



6l

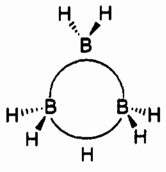


6k

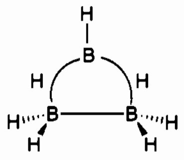


6l

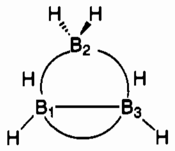
B_3H_7 (Figure 7). B_3H_7 isomers have been studied *ab initio* many times.[3,5–8] None of the four reference structures **7a–d** employed in the isodesmic eqs 9 and 11–13 are minima. The C_s global minimum, **7e**, with two bridged hydrogens, arises from the optimization of **7b**, when the C_{2v} symmetry constraint is removed.[5,6]



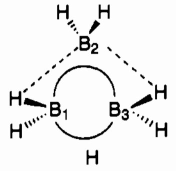
7a



7b



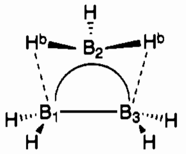
7c



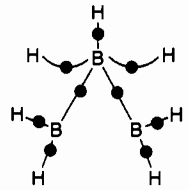
7d

While **7d** (with the H's bridges out of the ring plane) was considered in eq 13 as an analog of the triply in-plane H-bridged **7c**, the bonding and energy of **7d** is closer to those of singly H-bridged **7a**. Despite the long B^2H^b distance in **7d** (1.719 Å), bonding between each of the two bridging hydrogens and B^2 is indicated by $WBI(B^2H^b) = 0.167$ (compare with $WBI(B^2H^b) = 0.429$ in **7b**). The B^1B^3 separation in **7d** (1.613 Å) is closer to that in **7c** (1.595 Å) than in **7a** (1.703 Å). However, the WBI in **7d** (0.903) approaches the **7a** value (0.780) closer than that of **7c** (1.458). The shorter B^1B^2 and B^2B^3 bond lengths in **7d** (1.787 Å), compared to the corresponding bond distances in **7a** (1.905 Å) and in **7c** (1.922 Å), are a consequence of the diminished $H^b\cdots H^t$ repulsion in **7d**.

The electronic structure of **7e** has been analyzed recently[8g] in terms of Bader's theory of atoms in molecule (AIM).[30] No bond lines and critical points were found between the bridging hydrogens and the two equivalent borons, B^1 and B^3. AIM analysis also shows no bonding between B^1 and B^3. Instead, direct B^1B^2 and B^2B^3 bonding was demonstrated (**7e′**). The electron densities at the critical points (ϱ) on B^2H^t and on B^2H^b are 0.189 and 0.145, respectively. Our population analysis agrees qualitatively but does not exclude bridging $B^1H^bB^2$ and $B^2H^bB^3$ (WBI = 0.393; MBP = 0.081) and cyclic bonding B^1B^3 (WBI = 0.381; MBP = 0.061). B^2H^t (WBI = 0.973; MBP = 0.445) and B^2H^b (WBI = 0.555; MBP = 0.215) bond populations differ more that their ϱ values.[8g] We believe that **7e** provides the more satisfactory qualitative presentation of the bonding in B_3H_7 global structure.

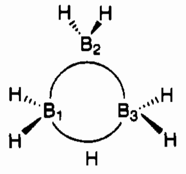


7e

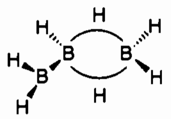


7e′

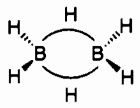
The two energy minima, **7f,g**, are related to diborane **20** since bridging (**7f**) or terminal (**7g**) hydrogens are substituted by a BH_2 group. In agreement with an earlier study,[6] **7f** is the most



7f



7g



20

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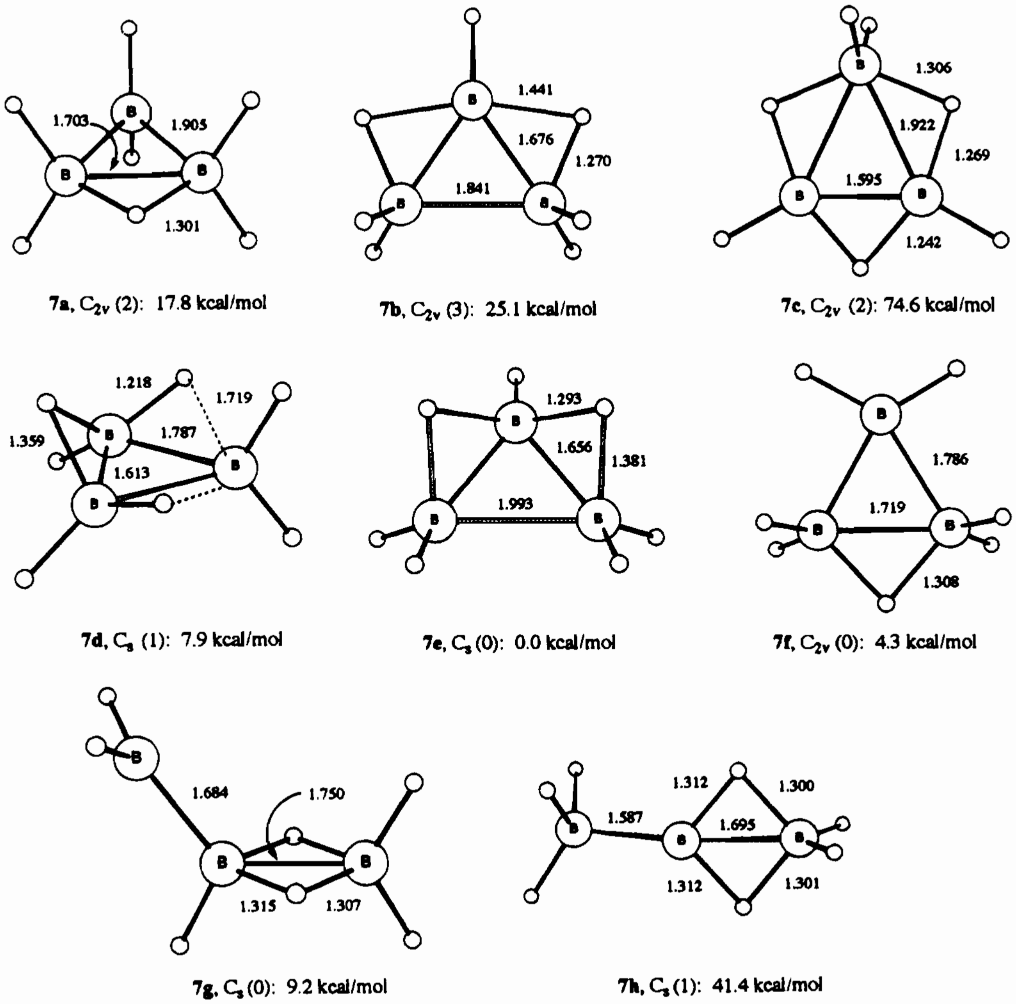
(29) Yoshmine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 4198.

(30) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, U.K., 1990.



7a, C_{2v} (2): 17.8 kcal/mol **7b**, C_{2v} (3): 25.1 kcal/mol **7c**, C_{2v} (2): 74.6 kcal/mol

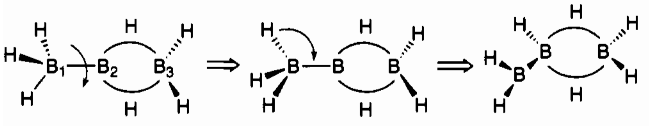
7d, C_s (1): 7.9 kcal/mol **7e**, C_s (0): 0.0 kcal/mol **7f**, C_{2v} (0): 4.3 kcal/mol

7g, C_s (0): 9.2 kcal/mol **7h**, C_s (1): 41.4 kcal/mol

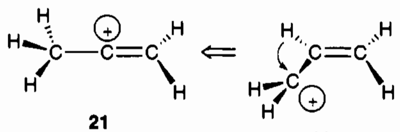
Figure 7. B_3H_7 structures. The number of imaginary frequencies is given in parentheses.

stable structure at HF, but electron correlations favors **7e**. Perpendicular (90°) rotation of the B^2H_2 group in **7f** out of ring plane leads to the higher energy structure **7a**.

The highest energy B_3H_7 isomer (**7h**) is the structural analog of the 1-methylvinyl cation **21**. Another rotamer **7h′** collapses to **7g** (an analog of $H_2C{=}CH{-}CH_2^+$ (**22**)) upon optimization. This contrasts with the conversion of the nonplanar allyl cation (**22**) into **21**.[31] The B^1B^2 bond in **7h** is unusually short (1.587 Å), is strongly polar ($q(B^1) = -0.793$; $q(B^1H_3) = -0.696$), and has partial double bonding character (WBI = 1.189).

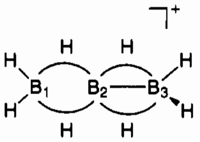


7h **7h′** **7g**

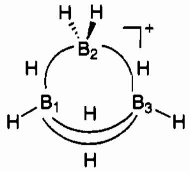


21 **22**

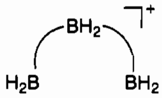
$B_3H_8^+$ (Figure 8). Neither $B_3H_8^+$ structure **8a** nor **8b** employed in eqs 12 and 13 is a minima. These two structures are related to **7b** and **7e** with an additional H-bridged bond between B^1 and B^3 in **8a** and **8b**. The two minima, **8c,d**, can be regarded as H-bridged analogs of allene and cyclopropene, respectively. The BB separation in doubly H-bridged cyclic **8d** (B^1B^3 = 1.625 Å) is shorter than in the open-chain **8c** (B^1B^2 = B^2B^3 = 1.717 Å). The double bond in cyclopropene (1.296 Å) is also shorter than the cumulated C=C bonds in allene (1.308 Å).[32] The BB bond population indices are similar for doubly bridged bonds in **8c** (WBI = 0.650; MBP = 0.171) and **8d** (WBI = 0.791; MBP = 0.174).



8c



8d



8e-g

Open-chain $B_3H_8^+$ isomers with three BH_2 groups held together by H-bridges also might be expected. However, none of our three structures with this bonding pattern, **8e–g**, were minima. Reduction of symmetry in **8f** or **8g** gave **8d** directly (C_2 rotation of the terminal BH_2 groups) or the C_s structure **8e**. A similar situation was encounted in the open-chain H-bridged $H_2B{-}H{-}BH_2^+$ cation.[28]

$B_3H_8^-$ (Figure 9). The C_{2v} structure **9a**, employed in eq 11 as an analog of cyclopropane (eq 1), is the lowest energy

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(31) Foresman, J. B.; Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2220–2226.

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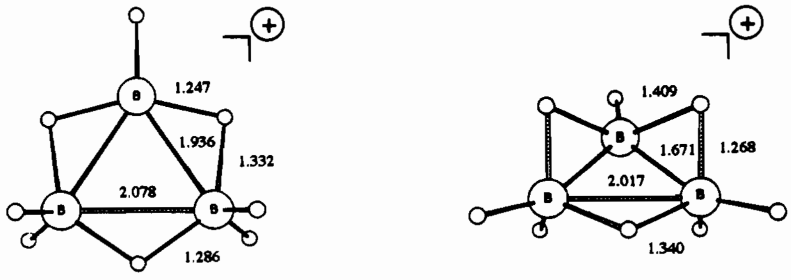
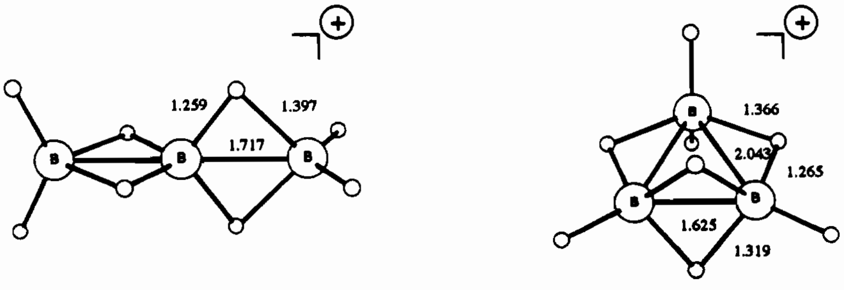


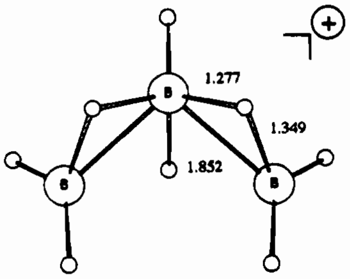
8a, C_{2v} (2): 35.7 kcal/mol

8b, C_s (1): 20.3 kcal/mol

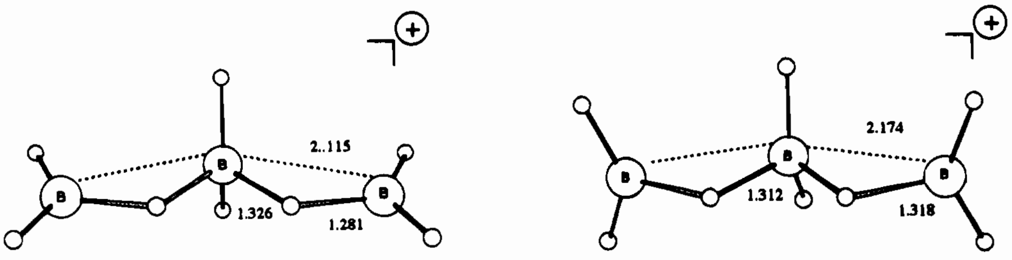


8c, D_{2d} (0): 0.0 kcal/mol

8d, C_{2v} (0): 4.8 kcal/mol



8e, C_s (1): 17.5 kcal/mol

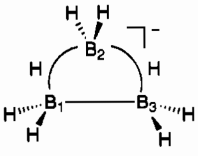


8f, C_{2v} (2): 35.2 kcal/mol

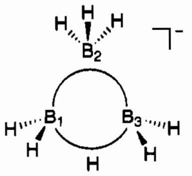
8g, C_{2v} (2): 39.0 kcal/mol

Figure 8. $B_3H_8^+$ structures. The number of imaginary frequencies is given in parentheses.

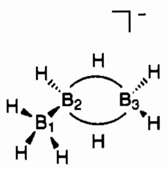
minimum at MP2; transition structure **9b** is 1.5 kcal/mol higher in energy (1.2 kcal/mol at QCI; for earlier *ab initio* studies of $B_3H_8^-$, see refs 5, 9, and 10). In contrast, **9b** is a minimum at HF, but **9b** is a TS (see Table 1). The negative charge in **9a** is



9a



9b

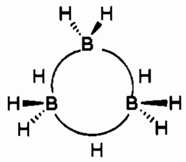


9c

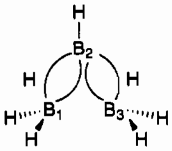
delocalized over the boron atoms ($q(B^1) = q(B^3) = -0.389$, $q(B^2) = -0.172$). The B^2H_3 group in **9b** bridges B^1 and B^3 atoms. The negative charge is distributed equally between the BH_3 group ($q(B^2) = -0.500$; $q(B^2H_3) = -0.550$) and the remainder of the anion.

Isomer **9c**, related to **7g** with H^- attached to the terminal BH_2 group, is 22.7 kcal/mol less stable than **9a**. The negative charge in **9c** is concentrated on the terminal B^1H_3 group ($q(B^1) = -0.603$; $q(B^1H_3) = -0.906$).

B_3H_9 (Figure 9). (For earlier *ab initio* studies of B_3H_9, see refs 5, 8, 11, and 12). The B_3H_9 D_{3h} form **10a** was used in eq

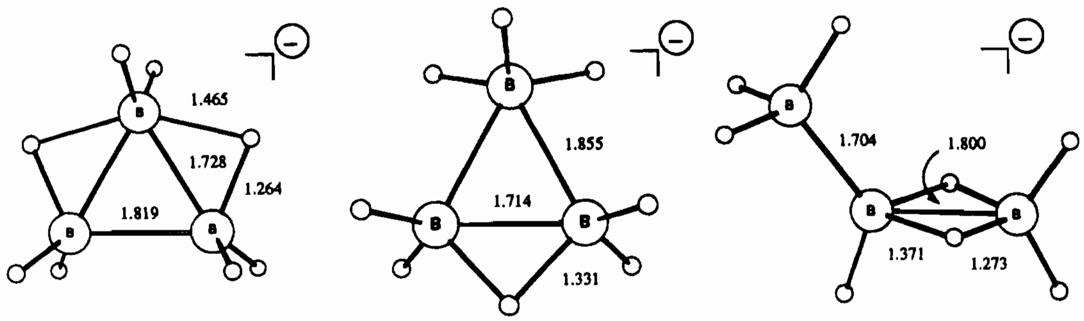


10a (10b)

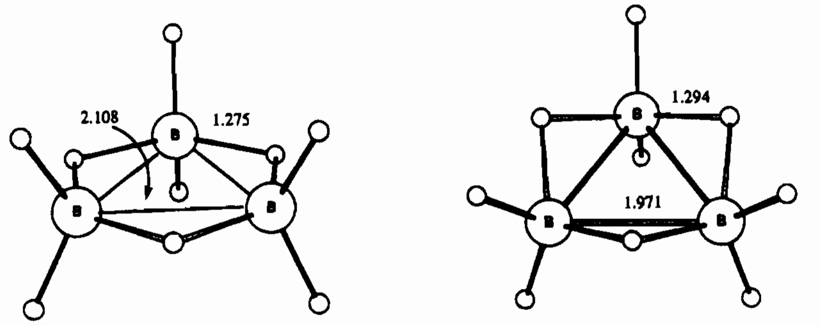


10c

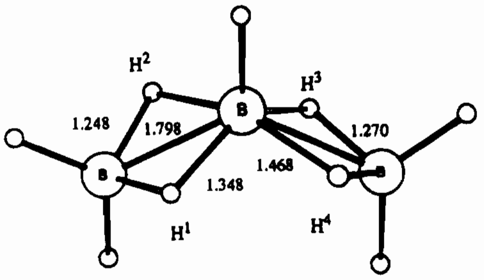
12 and the C_{3v} form **10b** was used in eq 13 as the best isostructural analogs of cyclopropane (eq 1). Triborane **10b** is less stable than diborane ($2B_3H_9 \rightarrow 3B_2H_6$; $\Delta E = 24.5$ kcal/



9a, C_{2v} (0): 0.0 kcal/mol **9b**, C_s (1): 1.5 kcal/mol **9c**, C_s (0): 22.7 kcal/mol



10a, D_{3h} (3): 4.6 kcal/mol **10b**, C_{3v} (0): 0.0 kcal/mol



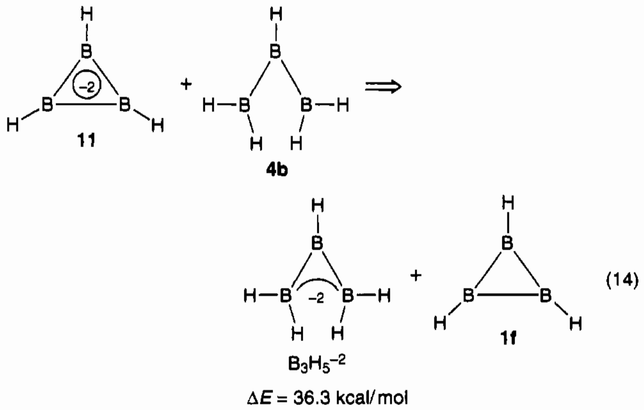
10c, C_2 (0): 3.7 kcal/mol

Figure 9. $B_3H_8^-$ and B_3H_9 structures. The number of imaginary frequencies is given in parentheses.

mol; see also refs 8d and 12). The energies of **10a** and **10b** differ by only 4.6 kcal/mol despite of the substantial differences in geometry. The nature of the bonding in **10b**, discussed[8f] recently in terms of AIM theory,[30] is characterized by six terminal BH bonds and three BHB bridged bonds without direct bonding interaction of BB atoms.

We have also considered the C_2 structure **10c**, which has recently been discussed in relation with the heavier analogs, Al_3H_9 and Ga_3H_9, as well as in diborane pyrolysis.[12] The 3.7 kcal/mol energy difference between **10b** and **10c** agrees with the CCSD/DZP value of 3.5 kcal/mol reported in ref 12. We also find **10c** to be a minimum but only when correlation is included[12,33] (see Table 1). The C_2 structure **10c** has a five-coordinated B^2 atom in the center of a distorted trigonal bipyramid. The bond angles at B^2 with the axial and the equatorial bridging hydrogens are 160.8° ($H^2B^2H^4$) and 122.2° ($H^1B^2H^3$), respectively (see Figure 9). As expected for a bipyramidal structure, the axial B^2H^2 and B^2H^4 bond distances are longer (1.468 Å) than equatorial B^2H^1 and B^2H^3 separations (1.348 Å). The five-coordinated boron atom is negatively charged ($q(B^1) = -0.173$), while the other two borons possess a substantial positive charge ($q(B^1) = q(B^3) = 0.614$).

$B_3H_3^{2-}$, $B_3H_3Li^-$, and $B_3H_3Li_2$. The D_{3h} dianion **11** is the most direct boron analog of the isoelectronic aromatic cyclopropenium ion, **14**. The remarkable similarity between ASEs of D_{3h} $C_3H_3^+$ and of **11** is evident from eqs 2 and 14.



ΔE = 36.3 kcal/mol

(14)

Lithium has a substantially lower ionization potential (5.4 eV) than hydrogen (13.6 eV)[34] and is expected to be a suitable counterion for **11**. Comparison of the ASEs given by eqs 2, 14, and 15 shows that two Li^+ bridges effectively stabilize the aromatic dianion **11**.

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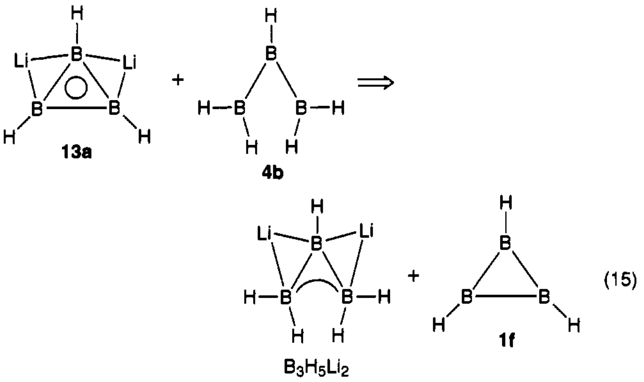
(33) Duke, B. J. Private communication.

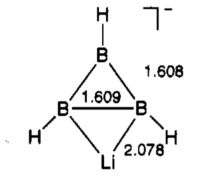
(34) *CRC Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1993.



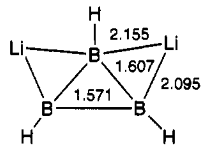
(15)

$\Delta E = 50.9$ kcal/mol

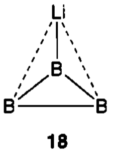
The replacement of the bridging hydrogens in **3a,d** and **4a,l** by lithiums diminishes the relative energy between planar (**12a** and **13a**) and nonplanar (**12b** and **13b**) structures substantially. The C_{2v} planar structure **12a** is only 3.3 kcal/mol more stable than C_{3v} **12b**. Both **12a** and **12b** are minima. The 13 kcal/mol preference of the C_{3v} pyramidal B_3Li **18** over the planar C_{2v} **23** isomer, noted by Hernandez and Simons,[13a] agrees with our 15 kcal/mol estimation.



12a, C_{2v} (0): 0.0 kcal/mol



13a, C_{2v} (0): 0.0 kcal/mol



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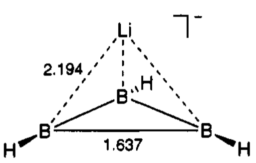
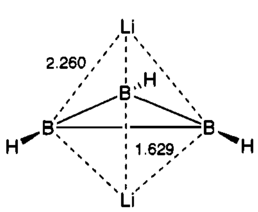
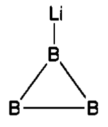


12b, D_{3v} (0): 3.3 kcal/mol



13b, D_{3h} (2): 17.0 kcal/mol



23

These lithium-containing aromatic structures are complexes of Li^+ cations, as the charge on lithiums is nearly one.[13c,35] Relative to the BB distance in **11** (1.624 Å), the BB bonds are shorter in the planar Li^+ complexes (**12a** and **13a**) but longer in the nonplanar structures (**12b** and **13b**).

Conclusions

Our results show that aromaticity (cyclic 3c−2e π delocalization) is important in the structural chemistry of three-membered boron cycles. While it is difficult to define aromaticity uniquely,[20,21] a combined study of energies, structures, and electron distribution help to clarify the nature of bonding in cyclic boron hydrides.

The cyclic aromatic B_3H_3 (**1a**), $B_3H_4^+$ (**2a**), $B_3H_4^-$ (**3a**), B_3H_5 (**4a**), and $B_3H_6^+$ (**5a**) structures are the global minima for each composition. The isodesmic stabilization energies of **3a**, **4a**, *planar* **5b**, **11**, and **13a** approach the substantial value of the cyclopropenium ion. However, we suggest that 42 kcal/mol higher stability of the *nonplanar* **5a** is not a consequence of an "extra" aromaticity but rather of the more favorable hydrogen placements in **5a** compared to those in **5b**. Lithium countercations can stabilize the aromatic anions **3a** and **11** and their cyclic electron delocalization.

Electron correlation contributes importantly to the relative stability of the three-boron hydride isomers and favors cyclic delocalized structures. While **5a** is the global minimum both at HF and MP2, open-chain isomers C_{2v} $HBBBH_2$ (**1k**, triplet), C_{2v} $H_2B(BH)_2^+$ (**2c**), D_{2h} $H_2BBBH_2^-$ (**3c**), and C_{2v} $HB(BH_2)_2$ (**4e**) are more stable than aromatic cycles at HF. The BB and BH separations in bridged bonds vary considerably depending on the bond character and non-bonding interactions.

Isoelectronic and isostructural analogies between boron and carbon species guide the search for new ionic and neutral boron hydrides.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Stiftung Volkswagenwerk, the Convex Computer Corp., and the Alexander von Humboldt Foundation (Fellowship to A.A.K.). We thank Prof. K. Jug and Prof. E. D. Jemmis for the valuable discussions. A.A.K. thanks Prof. K. Schaffner for the friendly personal support.

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(35) NBO charges on Li at HF/6-31+G* are 0.932 (**12a**), 0.766 (**12b**), 0.966 (**13a**), and 0.953 (**13b**).