Inorg. Chem. **1995,** *34,* 6559−6561

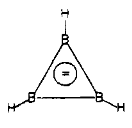
$B_3H_3X_3^+$ (X = H, F, and Li): Ab Initio MO Study

Eluvathingal D. Jemmis* and G. Subramanian

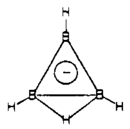
School of Chemistry, University of Hyderabad,
Hyderabad 500 046, India

Received June 8, 1995

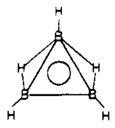
Isoelectronic borocyclic analogs of cyclopropenyl cation,[1] $B_3H_3^{2-}$ (**I**), $B_3(\mu\text{-H})H_3^-$ (**II**), and $B_3(\mu\text{-H})_2H_3$ (**III**), have been predicted to be planar 2π Huckel aromatics.[2−4] However, the cationic species $B_3(\mu\text{-H})_3H_3^+$ (**1a**) with a planar structure was characterized to be a transition state.[2,4] The nonplanar C_{3v} symmetric structure **1b** was predicted to be the minimum. The aromatic stabilization energy (ASE) deduced from an isodesmic equation suggests a value of 24.6 kcal/mol as a consequence of π-delocalization (eq 1).[2] In this paper, the effect of substituents in controlling the nonplanarity of $B_3(\mu\text{-H})_3H_3^+$ (**1b**) is discussed. A recent study on R_2BLi (R = H, CH_3, NH_2, OH, and F) by Wagner *et al.*[5] suggested lithioboranes to be moderately polar molecules with significant covalent character for the B−Li bond. The effects of π-substituents such as the halogens on lithioboranes were also studied in detail.[5] It occurred to us that fluorine and lithium substitution could have a large influence on the structure and stability (in particular the ASE) of the three-membered borocyclic ring. Theoretical studies using *ab initio* MO calculations on $B_3(\mu\text{-H})_3X_3^+$ for X = H, F, and Li (**1**−**3**) and $B_3(\mu\text{-Li})_3H_3^+$ (**4**) were performed to this end. A trilithiated derivative of $B_3H_6^+$ (**4a**) is found to prefer a planar structure.



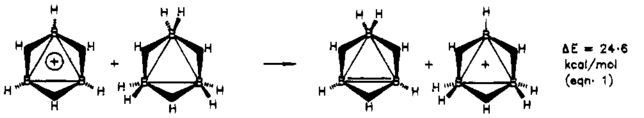
I



II



III



Method of Calculation

All the structures shown in Figure 1 were optimized both at the HF/6-31G*[6] and MP2(FC)/6-31G*[7] levels of computation using the Gaussian 92 program package.[8] Analytical derivatives characterizing the nature of the stationary point were obtained at the HF and MP2 levels. The total, relative, and zero point energies are given in Table 1 along with the number of imaginary frequencies. In calculating the relative energies, the zero point energies (ZPE's) are scaled by a factor of 0.89 and 0.95 for the HF and MP2 results.[9] The geometric parameters (as shown in Figure 1; distances in Å) and the energy comparisons (in kcal/mol) are at the MP2 level unless otherwise specified. Atomic charges and natural atomic orbital (NAO) bond orders (Figure 2) were calculated using the natural population analysis (NPA) and natural bond orbital (NBO) methods implemented in the Gaussian 92 package.[10]

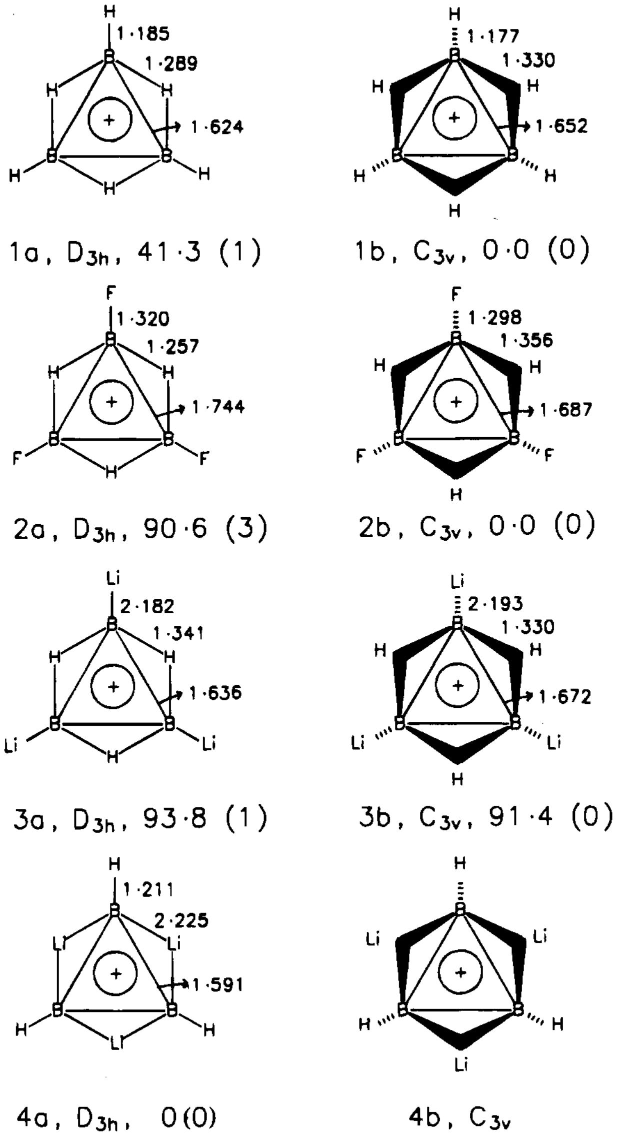


Figure 1. MP2/6-31G*-optimized geometries (distance in Å), relative energies (in kcal/mol), and the number of imaginary frequencies (in parentheses) for **1**−**4**.

Results and Discussion

The planar D_{3h} symmetric structure of $B_3(\mu\text{-H})_3X_3^+$ (X = H, F, and Li) is characterized to be a transition state for X = H (**1a**) and X = Li (**3a**) and a higher order stationary point for X

---

(1) (a) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986. (b) Minkin, V.; Glukhovtsev, M.; Simkin, E. *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*; Wiley Interscience: New York, 1994.

(2) Korkin, A. A.; Schleyer, P. v. R.; McKee, M. L. *Inorg. Chem.* **1995**, *34*, 961 and references cited therein.

(3) (a) Bigot, B.; Lequan, R. M.; Devaquet, A. *Nouv. J. Chem.* **1978**, *2*, 449. (b) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1878. (c) Krempp, M.; Damrauer, R.; DePuy, C. H.; Keheyan, Y. *J. Am. Chem. Soc.* **1994**, *116*, 3629.

(4) Jemmis, E. D.; Subramanian, G.; Srinivas, G. N. *J. Am. Chem. Soc.* **1992**, *114*, 7939.

(5) Wagner, M.; van Eikema Hommes, N. J. R.; Nöth, H.; Schleyer, P.v.R. *Inorg. Chem.* **1995**, *34*, 607.

(6) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Francl, M. M.; Pietoro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(7) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(8) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. J.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

(9) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular orbital Theory*; Wiley: New York, 1986.

(10) (a) Reed, A. E.; Weinhold, F. J. *J. Chem. Phys.* **1985**, *83*, 1736. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (c) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

0020-1669/95/1334-6559$09.00/0

Table 1. Total (hartrees), Relative (kcal/mol) and Zero Point Energies (ZPE; kcal/mol) Obtained at the HF/6-31G* and MP2/G-31G* Levels for **1**−**4**

		total energy		relative energy		ZPE (NIF)[a]	
molecule	symmetry	HF/6-31G*	MP2/6-31G*	HF/6-31G*[b]	MP2/6-31G*[c]	HF/6-31G*	MP2/6-31G*
1a	D_{3h}	−77.092 89	−77.374 92	61.7	41.3	43.1 (1)	41.0 (1)
1b	C_{3v}	−77.193 51	−77.444 85	0.0	0.0	44.7 (0)	43.7 (0)
2a	D_{3h}	−373.735 74	−374.518 70	102.7	90.6	33.1 (3)	31.4 (3)
2b	C_{3v}	−373.899 83	−374.664 80	0.0	0.0	33.4 (0)	32.5 (0)
3a	D_{3h}	−97.797 68	−98.120 24	114.5	93.8	21.8 (3)	22.2 (1)
3b	C_{3v}	−97.834 87	−98.128 59	95.1	91.4	26.2 (0)	25.2 (0)
4a	D_{3h}	−97.986 59	−98.274 43	0.0	0.0	26.3 (0)	25.3 (0)
4b	C_{3v}	does not correspond to a stationary point					

[a] Number of imaginary frequencies (NIF) in parentheses. [b] Includes zero point energy scaled by a factor of 0.89. [c] Includes zero point energy scaled by a factor of 0.95.

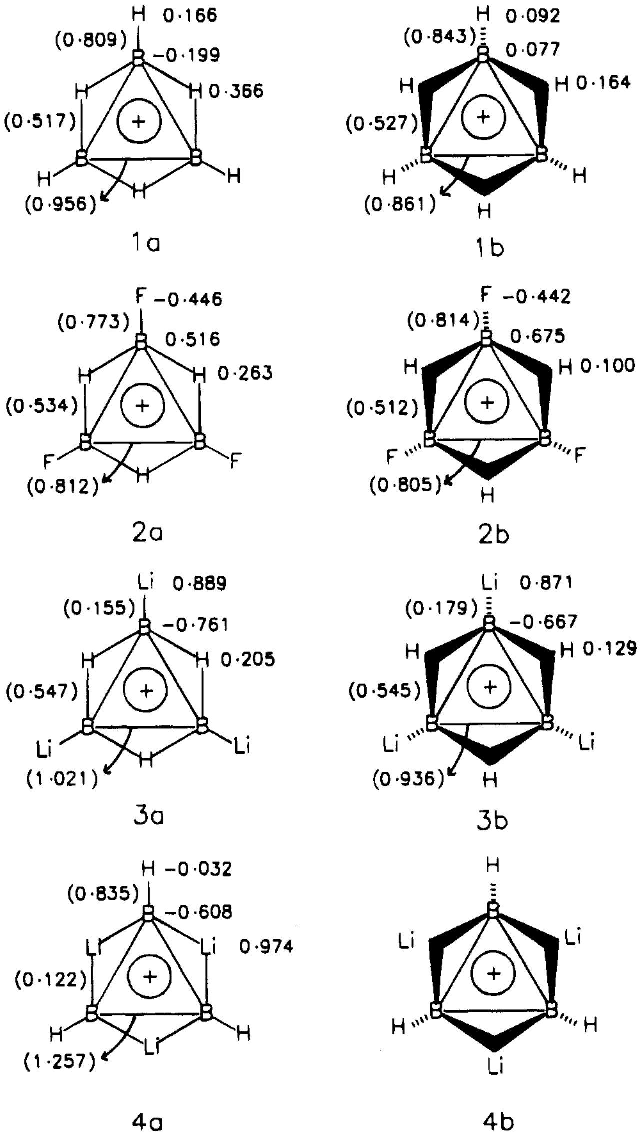
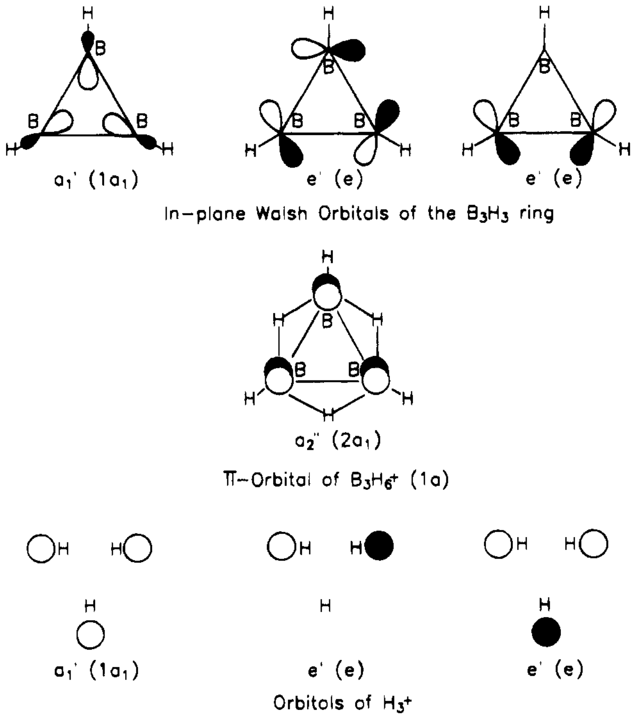


Figure 2. NPA charges and NAO bond orders (in parentheses) for **1**−**4** obtained at the MP2/6-31G* level.

Chart 1



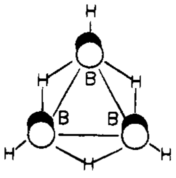
= F (**2a**). However, the nonplanar C_{3v} symmetric structure (**1b**−**3b**; Figure 1) is calculated to be a minimum (Table 1). The B−B distance increases on going from the D_{3h} to the C_{3v} symmetric structure for X = H (**1a** → **1b**) and X = Li (**3a** → **3b**), while it decreases for X = F (**2a** → **2b**). Further, the B−B distance in **2a** is significantly longer compared to that in **1a** and **3a** (Figure 1). This arises due to the strong electron-withdrawing tendency of the fluorine, which removes the electron density on boron, thereby leading to an increase in the B−B distance in **2a**. This is supported by the NPA charges, which indicate the negative charge to reside on boron in **1a** and **3a** but a positive charge in the case of **2a** (Figure 2). The NPA charges further reveal the charge separation between boron and hydrogen to be small in **1a** and **1b** (Figure 2). On the other hand, the charge separations between the boron and lithium atoms in both **3a** and **3b** are large (Figure 2). The NAO bond order, which provides a measure of the covalent character, suggests a bond order of 0.843 for the B−H bonds in **1b**, 0.814 for the B−F bonds in **2b**, and 0.179 for the B−Li bonds in **3b** (Figure 2). This clearly reflects the weak covalency of the B−Li bond in **3b** similar to that in $H_2B{-}Li$.[5]

By intuition the planar 2π Huckel aromatics, **1a**−**3a**, are expected to be more stable than the nonplanar C_{3v} symmetric structures, **1b**−**3b**. But calculations predict the contrary. The details of the electronic structure of $B_3(\mu\text{-}H)_3H_3^+$ (**1a** and **1b**) provide an explanation. The molecular orbitals (MO's) of **1a** can be constructed from the B_3H_3 and H_3^+ fragment MO's. The three in-plane Walsh orbitals of the B_3H_3 ring (a_1' and e') and the three MO's of the H_3^+ (a_1' and e') are shown in Chart 1 along with the π-orbital (a_2'') of the borocyclic ring.[11] The

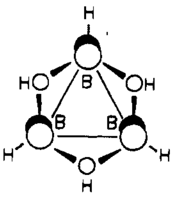
---

[11] The symmetry labels given in parentheses in Chart 1 correspond to the C_{3v} symmetric point group.

degenerate e′ orbital of both the B_3H_3 ring and H_3^+ leads to a stabilizing interaction. On the other hand, the a_1' orbitals of the fragments do not interact strongly. This is because the a_1' orbitals of B_3H_3 and H_3^+ are not directional in nature (Chart 1). Similarly, the π-orbitals (a_2'' symmetry; Chart 1) of the borocyclic ring and the a_1' orbital of H_3^+ (which lies in the nodal plane of the π-orbital) cannot interact due to their symmetry mismatch. A correlation diagram between the MO's of **1a** and **1b** reveals the dramatic changes in the bonding interaction as a result of the geometric distortion. In the C_{3v} symmetry (**1b**), the e′, a_1', and a_2'' orbitals of **1a** transform to e, $1a_1$, and $2a_1$ orbitals, respectively. While the e′ orbitals are destabilized marginally (e in C_{3v} symmetry), there is a substantial stabilization of the a_2'' orbital ($2a_1$ in C_{3v} symmetry).[4] This arises because the three bridging hydrogens (H_b) which were in the molecular plane in **1a** lie 0.678 Å above the B_3 ring plane in **1b** (0.809 and 0.499 Å in the case of **2b** and **3b**, respectively).[12] Now the $1a_1$ orbital of H_3^+ (in C_{3v} symmetry) has the right symmetry to interact with the π-orbital ($2a_1$ in C_{3v} symmetry) of the B_3H_3 ring. Thus, the two electrons which were delocalized over the p_π-orbital of the three boron atoms in **1a** are now delocalized over six orbitals (the additional three being the s-orbitals of the bridging hydrogens) in **1b**, as shown below.



1a, D_{3h}



1b, C_{3v}

The effects of substituents on the bonding interaction in **2b,b** and **3a,b** are seen to parallel those of **1a,b** and hence are not discussed further. However, the magnitude of the stabilization of the $2a_1$ orbital in **2b** and **3b** with respect to the a_2'' orbital in **2a** and **3a** shows a significant variation. This difference in the a_2'' and $2a_1$ orbitals is 0.87 eV for the structural distortion from **3a** → **3b** and 3.18 eV for **2a** → **2b**. The stabilization associated with the parent system **1a** → **1b** falls in between them (2.88 eV). This is also reflected in the variation of the relative energies for **1**–**3** (Table 1). The diminished antibonding interaction between the p_π orbital on boron and the p_π orbital on fluorine in **2b** accounts for the larger stabilization of the $2a_1$ orbital compared to the a_2'' orbital in **2a**.

A quantitative estimate of the substituent effect in **1b** is obtained from the energetics of the following isodesmic equations. The destabilizing effect of the fluorine substitution and the stabilization as a result of lithiation in **1b** are borne out in the exothermicities of the reactions

$$\underset{\mathbf{1b}}{B_3(\mu\text{-}H)_3H_3^+} + B_3F_3 \rightarrow \underset{\mathbf{2b}}{B_3(\mu\text{-}H)_3F_3^+} + B_3H_3 \qquad \Delta E = 49.4 \text{ kcal/mol}$$

$$\underset{\mathbf{1b}}{B_3(\mu\text{-}H)_3H_3^+} + B_3Li_3 \rightarrow \underset{\mathbf{3b}}{B_3(\mu\text{-}H)_3Li_3^+} + B_3H_3 \qquad \Delta E = -24.0 \text{ kcal/mol}$$

The tendency of Li to prefer a bridging position as in $C_3(\mu\text{-}Li)_3^+$,[13] $B_3(\mu\text{-}Li)H_3^-$, and $B_3(\mu\text{-}Li)_2H_3$[2] prompted us to look at the alternative structural arrangement $B_3(\mu\text{-}Li)_3H_3^+$ (**4a,b**) of $B_3(\mu\text{-}H)_3Li_3^+$ (**3a,b**). In contrast to **1a**–**3a**, the planar D_{3h} symmetric structure **4a** is characterized to be a minimum (Table 1). The nonplanar C_{3v} symmetric structure **4b**, upon optimization, collapses back to **4a**. Furthermore, **4a** is 91.4 kcal/mol more stable than its isomer **3b**, showing the remarkable stability of the B–Li–B bridging compared to the B–H–B bridging. The lower ionization potential of lithium (5.4 eV) in comparison to that of hydrogen (13.6 eV)[14] has been offered as an explanation for the stability of $B_3(\mu\text{-}Li)_2H_3$.[2] A similar explanation should be reasonable for **4a** as well.

The B–B distance in **4a** (1.591 Å) is much shorter than the B–B distance in **1a**–**3a** (Figure 1) and that in $B_3H_3^{2-}$ (1.612 Å). The NPA charges on boron and lithium (Figure 2) describe **4a** as an ionic species, $B_3H_3^{2-}(\mu\text{-}Li)_3^{3+}$, which is further supported by the B–Li bond order (0.122). A comparison of the electronic structure of **1a** and **4a** also reveals that the interaction between the fragments, B_3H_3 and Li_3^+, is mostly electrostatic. Thus, the bridging lithiums in **4a** act as counterions enhancing the stability of the aromatic dianion $B_3H_3^{2-}$.

Conclusions

The electronic structure of $B_3(\mu\text{-}H)_3X_3^+$ (X = H, F, and Li) explains the extra stability of the nonplanar C_{3v} symmetric structure (**1b**–**3b**) in comparison to the planar D_{3h} symmetric form (**1a**–**3a**). While fluorination (**2b**) destabilizes the aromatic π-delocalization in **1b**, lithiation (**3b**) acts to the opposite. In contrast to **1b**–**3b**, $B_3(\mu\text{-}Li)_3H_3^+$ (**4a**) is predicted to be stable in the planar form and 91.4 kcal/mol lower in energy than **3b**. The electronic structure, atomic charges, and bond order indicate the Li–B interactions in **4a** to be mostly electrostatic.

Acknowledgment. E.D.J. and G.S. thank the Department of Science and Technology and the Council of Scientific and Industrial Research, respectively, for financial support. The authors also thank the Computer Center, University of Hyderabad for providing computational facilities.

IC950721C

---

[12] The out-of-plane bending of the B–X bonds from the B_3 ring plane is calculated to be 19.1° for **1b**, 23.6° for **2b**, and 10.3° for **3b** at the MP2(FC)/6-31G* level of theory.

[13] $C_3(\mu\text{-}Li)_3^+$ in D_{3h} symmetry lies 10.9 kcal/mol lower in energy than $C_3Li_3^+$ (D_{3h} symmetry) at the MP2(FC)/6-31G* level of theory.

[14] *CRC Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1993.