

Nonplanarity at Tri-coordinated Aluminum and Gallium: Cyclic Structures for $X_3H_n^m$ ($X = B, Al, Ga$)

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Abstract: Structures and energies of $X_3H_3^{2-}$, $X_3H_4^-$, X_3H_5 , and $X_3H_6^+$ ($X = B, Al$ and Ga) were investigated theoretically at B3LYP/6-311G(d) level. The global minimum structures of B are not found to be global minima for Al and Ga. The hydrides of the heavier elements Al and Ga have shown a total of seven, six and eight minima for $X_3H_3^{2-}$, $X_3H_4^-$, and X_3H_5 , respectively. However, $X_3H_6^+$ has three and four minima for Al and Ga, respectively. The nonplanar arrangements of hydrogens with respect to X_3 ring is found to be very common for Al and Ga species. Similarly, species with lone pairs on heavy atoms dominate the potential energy surfaces of Al and Ga three-ring systems. The first example of a structure with tri-coordinate pyramidal arrangement at Al and Ga is found in $X_3H_4^-$ (**2g**), contrary to the conventional wisdom of $C_3H_3^+$, B_3H_3 , etc. The influence of π -delocalization in stabilizing the structures decreases from $X_3H_3^{2-}$ to $X_3H_6^+$ for heavier elements Al and Ga. In general, minimum energy structures of $X_3H_4^-$, X_3H_5 , and $X_3H_6^+$ may be arrived at by protonating the minimum energy structures sequentially starting from $X_3H_3^{2-}$. The resonance stabilization energy (RSE) for the global minimum structures (or nearest structures to global minimum which contains π -delocalization) is computed using isodesmic equations.

Introduction

Structural properties of the smallest 2π aromatic, cyclopropenyl cation and its boron analogues have been studied in detail. Numerous experimental reports are available on three-membered boron ring clusters.^{1–3} The importance of aromaticity in these three-membered boron ring hydrides is well documented.^{4–8}

Theoretical studies have revealed that the global minimum structures of $X_3H_3^{2-}$ (Scheme 1, **1a**),^{4,5} $X_3H_4^-$ (Scheme 2, **2a**),^{4–6} X_3H_5 (Scheme 3, **3a**)^{4,5,7,8} and $X_3H_6^+$ (Scheme 4, **4b**)^{4,8} ($X = B$, the all boron analogues of $C_3H_3^+$) contain cyclic π -delocalization. Although decreased in aromaticity, these are comparable in many ways to the smallest aromatic species $C_3H_3^+$. Heavier analogues of the cyclopropenyl cation have been

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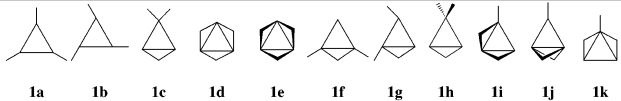
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studied in detail; especially well established are the differences between carbon and silicon chemistry. However, extremely little is known for heavier homologues of boron, the alanes, and the galanes. Only one example involving a group 13 congener ($\text{Ga}_3\text{H}_3^{2-}$) has been studied theoretically⁹ and a substituted analogue has been prepared by utilizing the extraordinary bulky ligand 2,6-Mes₂C₆H₃.^{9,10} The structural analyses of $\text{Na}_2[\text{Ga}_3\text{R}_3]$ (**5**, R = 2,6-Mes₂C₆H₃) and $\text{K}_2[\text{Ga}_3\text{R}_3]$ (**6**) have shown that the Ga_3R_3 ring is also π -delocalized.^{9,10} Stable aromatic four-membered ring structures stabilized by metal ions, have been observed recently as MX_4^- (**7**)¹¹ and M_2X_4 (**8**),¹² where M = Li, Na, Cu, and X = Al, Ga, In. Despite these developments, no systematic study exists for the related three-membered 2 π -electron structures composed of Al or Ga. We explore here in a comprehensive manner such structures with the molecular formulas $\text{X}_3\text{H}_3^{2-}$ (**1**), X_3H_4^- (**2**), X_3H_5 (**3**), and X_3H_6^+ (**4**); X = B, Al, Ga.

Generally, compounds containing elements from the second or higher row exhibit structural properties that differ from those of the first row elements.^{13–29} There are numerous reports highlighting such differences between hydrocarbons and the

heavier analogues in group 14. For example, (a) the four substituents of the alkene homologues no longer lie in a plane with the double-bonded atoms (D_{2h} symmetry), but rather show a trans-bent orientation,¹⁴ (b) the stability of H-bridged structures increases in C_3H_3^+ homologues,¹⁵ and (c) unlike allene, trisilaallene is shown to be nonlinear.¹⁶ But very few such comparisons of multiple bonds between more electropositive heavier elements are known in group 13. One example is the nonlinearity of the two substituents in galyne ($\text{Na}_2\text{Ga}_2\text{R}_2$, R = 2,4,6-ⁱPr₃C₆H₂) with the Ga–Ga bond.^{17,20} These structural differences of heavier analogues are attributed among others to the decrease in sp-hybridization caused by different radial extension of s and p valence orbitals and their energy differences in heavier elements starting from the second row.^{13,30} It is of interest to establish how these effects influence the aromatic three-membered ring structures composed of Al and Ga in comparison to those of boron. Of the many differences we found between

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Scheme 1. Structures **1a–k**, Relative Energies (kcal/mol, B3LYP/6-31 g(d)) and Number of Imaginary Frequencies (in parentheses) for $X_3H_3^{2-}$; X=B, Al, Ga^a


	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
B	0.0(0)	--	58.12(0)	88.29(3)	88.25(2)	37.87(1)	--	73.75(3)	--	91.64(2)	57.68(1)
Al	0.0(0)	--	-1.80(0)	11.17(1)	6.13(0)	-1.16(0)	1.82(0)	13.26(2)	3.76(0)	19.82(1)	2.04(0)
Ga	0.0(1)	0.18(0)	-6.82(0)	4.21(1)	0.20(0)	-2.70(0)	-2.14(0)	19.37(1)	-1.55(0)	14.54(1)	0.38(0)

^a C₃ symmetry.

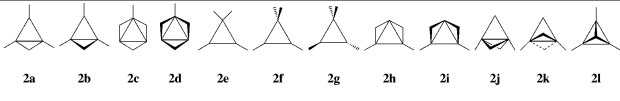
the B, Al, and Ga aromatic systems, the most intriguing structures are those containing pyramidal tricoordinated Al and Ga atoms.

Computational Methods

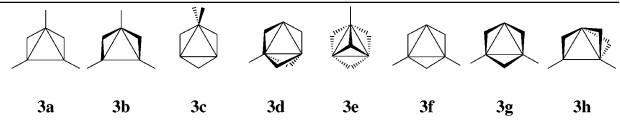
The geometries of structures **1**, **2**, **3**, **4** and all of the reference molecules were optimized using the Hartree–Fock (HF) and the hybrid Hartree–Fock/DFT (B3LYP) methods.^{31,32} The B3LYP method uses a combination of the three-parameter Becke exchange functional with the Lee–Yang–Parr nonlocal correlation functionals. The 6-311G(d) basis set was used for all the calculations.³¹ The nature of the stationary points was determined by evaluating the second derivatives of the energy (Hessian matrix).³³ All of the computations were done using the Gaussian 98 program package.³⁴ All total and Zero Point energies of the optimized structures of $X_3H_3^{2-}$, $X_3H_4^-$, X_3H_5 , and $X_3H_6^+$ are given in the Supporting Information. Fragment Molecular Orbital (FMO) and Natural Bond Orbital (NBO) methods were used to analyze the bonding in a given structure.^{35,36}

Results and Discussion

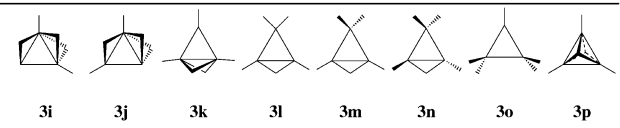
The structures considered in this article are obtained in a systematic way starting with the classical D_{3h} geometry with three terminal X–H bonds. Various arrangements are arrived at by considering three terminal X–H bonds, two terminal and one bridging X–H bonds, two bridging and one terminal X–H bonds, three bridging X–H bonds, one XH_2 group and an X–H–X bridge as indicated in Scheme 1 for $X_3H_3^{2-}$. Similarly, Schemes 2, 3, and 4 represent the variety of structures considered for $X_3H_4^-$, X_3H_5 , and $X_3H_6^+$ respectively. The

Scheme 2. Structures **2a–l**, Relative Energies (kcal/mol, B3LYP/6-31 g(d)) and Number of Imaginary Frequencies (in parentheses) for $X_3H_4^-$; X=B, Al, Ga


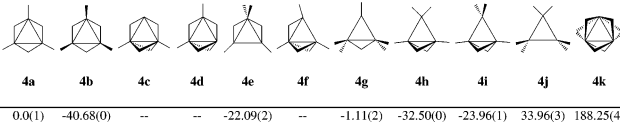
	2a	2b	2c	2d	2e	2f	2g	2h	2i	2j	2k	2l
B	0.0(0)	--	--	--	1.65(0)	47.29(2)	--	44.82(1)	--	81.37(2)	--	26.11(2)
Al	0.0(1)	-1.02(0)	--	4.34(0)	19.29(2)	21.27(2)	7.05(0)	6.48(2)	6.21(0)	8.41(1)	7.63(0)	9.48(0)
Ga	0.0(1)	-2.40(0)	20.26(1)	-4.04(0)	14.14(2)	17.93(3)	-0.97(0)	-1.79(2)	-0.53(0)	4.86(1)	3.90(0)	8.79(0) ^c

^c C₃ symmetry**Scheme 3.** Structures **3a–p**, Relative Energies (kcal/mol, B3LYP/6-31 g(d)) and Number of Imaginary Frequencies (in parentheses) for X_3H_5 ; X=B, Al, Ga


	3a	3b	3c	3d	3e	3f	3g	3h
B	0.0(0)	--	--	--	--	--	--	--
Al	0.0(2)	-18.64(0)	-12.21(1)	-17.14(0)	-16.08(0)	25.20(3)	-14.90(0)	-14.86(0)
Ga	0.0(2)	-23.97(0)	-31.20(1)	-33.88(0)	--	16.15(3)	-26.40(0)	-28.56(0)



	3i	3j	3k	3l	3m	3n	3o	3p
B	--	--	26.33(0)	0.15(0)	56.00(2)	--	56.34(2)	71.78(2)
Al	-15.52(0)	-12.83(0)	-18.49(0)	9.31(3)	-6.98(2)	-9.24(1)	1.02(2)	13.62(2)
Ga	-27.03(0)	-26.46(0)	-21.94(0)	4.90(2)	-19.70(1)	-18.66(0)	-14.66(2)	12.87(3)

Scheme 4. Structures **4a–k**, Relative Energies (kcal/mol, B3LYP/6-31 g(d)) and Number of imaginary frequencies (in parentheses) for $X_3H_6^+$; X=B, Al, Ga


	4a	4b	4c	4d	4e	4f	4g	4h	4i	4j	4k
B	0.0(1)	-40.68(0)	--	--	-22.09(2)	--	-1.11(2)	-32.50(0)	-23.96(1)	33.96(3)	188.25(4)
Al	0.0(3)	-58.79(0)	-73.69(0)	-59.92(1)	-57.54(1)	-67.99(0)	-46.93(1)	-45.83(1)	-42.51(2)	-18.54(3)	48.69(5)
Ga	0.0(3)	-60.47(0)	-85.79(0)	--	-68.56(0)	-72.58(0)	-63.58(1)	-52.41(2)	-48.81(3)	-38.80(3)	-11.64(3)

structures in the Schemes 1–4 are arranged so that the similarities between them can be discussed coherently, as seen in Schemes 7, 8, and 9. The relative energies and number of imaginary frequencies are also given in the Schemes 1–4. Figures 1–4 give the important geometric parameters of the minimum energy structures. Although only two of the eleven structures indicated are minima for $B_3H_3^{2-}$, as many as seven are minima for $Al_3H_3^{2-}$ and $Ga_3H_3^{2-}$, justifying the systematic approach. Throughout this paper, various structures in the text are represented by the structure number followed by the atomic symbol. For example the triangular structure **1a** for $B_3H_3^{2-}$ is represented by **1a-B**, $Al_3H_3^{2-}$ by **1a-Al**, $Ga_3H_3^{2-}$ by **1a-Ga**, etc. Similarly, individual atoms in a structure are identified by the atom number as superscript. For example **2b-Ga²** represents the gallium atom which is numbered 2 in **2b-Ga** (Figures 1–4).

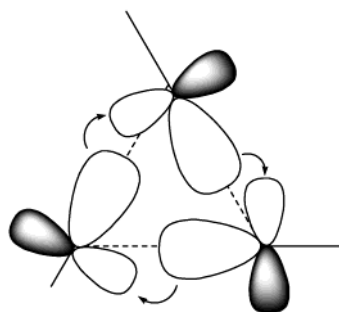
Several molecules are used as theoretical models for the idealized single, double, and H-bridged bonds for comparison. Table 1 gives the X–X bond distances in X_2H_4 (single bond),

- (31) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
- (32) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Vosko, S. H.; Wilk, L.; Nusair, M. *Can J. Phys.* **1980**, *58*, 1200.
- (33) Pople, J. A.; Raghavachari, K.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 255.
- (34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.
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- (36) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

Table 1. Calculated X–X Bond Distances in X_2H_4 , X_3H_3 , $X_2H_4^{2-}$, $X_3H_4^{3-}$, X_2H_6 , X_2H_2 at B3LYP/6-311G(d) Level of Theory^a

	$X_2H_4^b$	$X_3H_3^c$	$X_2H_4^{2-d}$	$X_3H_4^{3-e}$	$X_2H_6^f$	$X_2H_2^d$
B–B	1.744	1.727	1.596	1.557	1.767	
Al–Al	2.621	2.664	2.475	2.482	2.623	2.989
Ga–Ga	2.525	2.647	2.371	2.447	2.633	3.069

^a The reference below involves calculations at different levels. ^b Refs 22–24,7a. ^c Refs 9,29. ^d Refs 20,25. ^e Refs 26–28. ^f Refs 19–21.

Scheme 5

X_3H_3 (strained single bond), $X_2H_4^{2-}$ (double bond), $X_3H_4^{3-}$ (double bond in three-membered ring), X_2H_6 (doubly bridged structure as in B_2H_6 , and doubly bridged X_2H_2). Experimentally known Al and Ga compounds and their bond distances are used for comparison where appropriate.

Of all of these structures, we will elaborate only the most relevant ones to establish the major bonding features that distinguish the alanes and galanes from the boranes. Bonding principles are highlighted for selected cases, but the structural information of all of the isomers is contained in the Supporting Information. Some important geometric parameters are also given in Figures 1–4.

$X_3H_3^{2-}$. Total of seven minima were found for $Al_3H_3^{2-}$ and $Ga_3H_3^{2-}$, which contrasts the only two cyclic minima that were reported for $B_3H_3^{2-}$ (Scheme 1).⁵ Isomer **1a** with all terminal hydrogens, is the global minimum for $B_3H_3^{2-}$. However, H-bridged **1c** with its planar tetracoordinated heavy atom is the global minima for $Al_3H_3^{2-}$ and $Ga_3H_3^{2-}$. This isomer is 1.8 and 6.8 kcal/mol more stable than **1a** for Al and Ga, respectively. Although **1c** is a $B_3H_3^{2-}$ minimum, it is 58 kcal/mol higher in energy than **1a** which highlights the dramatic difference between B and its heavier analogues. It is interesting to note that an isomer similar to **1c** is the global minimum for the isoelectronic Si_2BH_3 .³⁷ **1a-Al** is also a minimum, but **1a-Ga** is a transition structure for the interconversion of C_{3h} structures (**1b-Ga**); the energy difference between **1a** and **1b** is negligible. A similar distortion from D_{3h} to C_{3h} is also seen in Pb_3H_6 .³⁸ The experimentally determined X-ray structures have C_{3h} symmetry.^{9,10} A general bonding picture of **1b-Ga** and **1a-Al,Ga** may be constructed from the X–H fragments in their singlet ground states with a σ lone pair and 2p orbitals in orthogonal planes. In Ga and to a lower extent in Al, the σ lone pair is found to be mostly of s character and does not prefer to form the traditional sp^2 hybrid orbitals commonly seen in carbon. The bonding then arises from donor acceptor interactions of the type indicated (Scheme 5). The extent of distortion depends on the differences in the s and p orbitals, the exact details of sp mixing, and the remaining bonds. Considering the

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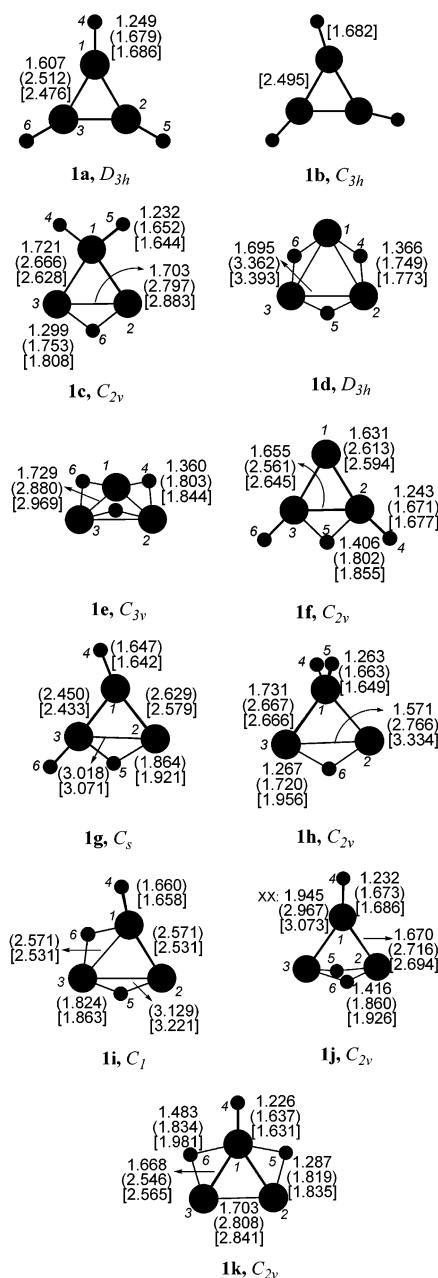


Figure 1. Optimized geometries and important bond distances for B, Al (in parentheses) and Ga (in brackets) isomers of $X_3H_3^{2-}$ at B3LYP/6-311G(d) level. Atoms are numbered in italics.

extremely small differences in energy between **1a-Ga** and **1b-Ga**, we do not attempt to correlate the s and p mixing and relative energies.

The Ga–Ga distance in **1b-Ga** is about 0.07 Å longer than those in the experimental structures **5** and **6**. We could not find any experimentally known three-membered Al dianion ring compound to compare to **1a-Al**, but the Al–Al distance in **1a** is between that of a single bond and a double bond length. A comparison can be made with the experimentally available Al_2R_4 (**9**, $R = Si^iBu_3$, $R = CH(SiMe_3)_2$ and $R = 2,4,6-(iPr)_3C_6H_2$).³⁹

(38) (a) Srinivas, G. N.; Kiran, B.; Jemmis, E. D. *J. Mol. Struct. (THEOCHEM)* **1996**, *361*, 205. (b) Nagase, S. *Polyhedron* **1991**, *10*, 1299.

(39) (a) Wiberg, N.; Amelunxen, K.; Blank, T.; Nöth, H.; Knizek, J. *Organometallics* **1998**, *17*, 5431. (b) Uhl, W. *Z. Naturforsch.* **1988**, *43B*, 1113. (c) Wehmschulte, R. J.; Ruhland-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983.

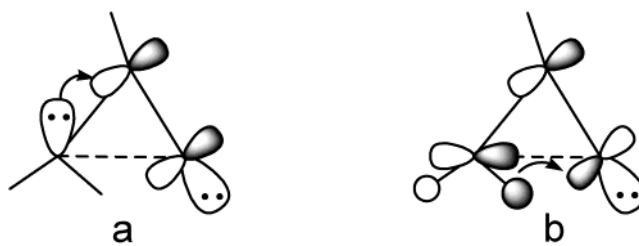
The Al–Al bond distances here are 2.751 Å, 2.660 Å and 2.647 Å respectively. These are indeed longer than the Al–Al distance in **1a-Al** (2.512 Å). A part of this shortening comes from the nature of the bent bonds. For example, the C–C distance in cyclopropane is considerably shorter than in ethane. Another contributor is the 2π electron delocalization. A similar comparison can also be made to the experimental structures of Ga₂R₄ (**10**, 2.541 Å, R = CH(SiMe₃)₂; 2.515 Å, R = 2,4,6-(ⁱPr)₃C₆H₂)⁴⁰ which also show shorter bond distances for **1b-Ga** (2.495 Å).

The Al–Al and Ga–Ga bond distances in **1c** (Figure 1, **1c-Al**¹–Al³: 2.666 Å, **1c-Ga**¹–Ga³: 2.628 Å) are similar to those of the single bonds of X₃H₃ (*D*_{3h}). This is the result of a weak sigma bond (in fact, a 3c–2e bond) and 2π -aromatic delocalization. The H-bridged Al–Al and Ga–Ga distances are longer than those of dialane(6) and digalane(6) but shorter than in the doubly H-bridged Al₂H₂ and Ga₂H₂. An MO analysis of **1c-Al,Ga** reveals that it has two 3c–2e bonds between X–H–X and X–X(H₂)–X, two 2c–2e X–H bonds, lone pairs on X² and X³, and a delocalized π orbital over the ring. This is a remarkable result. Though minimum energy structures with square planar boron atoms have been found experimentally and theoretically, there were always lower energy alternatives.⁴¹ Here, we find that **1c**, the lowest energy that we obtained, has a square planar Al. The unusual stability of the square planar arrangement is also seen with Ga. **1c-Ga** is the lowest energy isomer we considered.

The triply H-bridged planar isomer **1d**, which can display 2π delocalization, is a higher order stationary point for B and a transition structure for both Al and Ga. The imaginary frequency indicates a distortion to a *C*_{3v} nonplanar structure **1e**. This isomer is about 7–8 kcal/mol less stable than the global minimum **1c** for both Al and Ga. Structure **1b** with only terminal hydrogen and structure **1e** with only bridging hydrogens are nearly isoenergetic for Ga, but **1e** is 6 kcal/mol less stable than **1a** for Al. It is interesting to note that a Si₃H₃⁺ structure similar to **1e** is nearly 42 kcal/mol higher in energy than its **1a**-like global minimum at MP2/6-31G(d) level,¹⁵ whereas, **1e-B** is a higher order stationary point. The observed deformation of **1d** to **1e-Ga** may be understood from its molecular orbital description using a correlation diagram which depicts the interaction of π and σ orbitals on *C*_{3v} distortion (Figure 5).⁴² The HOMO in *D*_{3h} symmetry is the nondegenerate π -MO. The vacant 3a' orbital which is a bonding combination of the 1s orbitals of the hydrogen atoms, mix with the π MO when the symmetry is lowered to *C*_{3v}, leading to the stabilization of the π MO. Figure 5 shows the dramatic effect of this σ – π mixing.

Structure **1f** is a minimum for both Al and Ga, and a transition structure for B. Among all ring structures considered, **1f-Al** and **1f-Ga** are the second best structures. The energy differences between **1c** and **1f** increases from Al (0.6 kcal/mol) to Ga (4.1 kcal/mol). Both the X–X and H-bridged X–X bond distances in **1f** are shorter when compared to those in **1c**, with the

Scheme 6



exception of the X–H_b. An analysis of the MOs of **1f** reveals that there are two 2c–2e X–X bonds, two 2c–2e X–H bonds, one 3c–2e X–H–X bond, a lone pair on X¹, and a delocalized π MO. X¹–X² and X¹–X³ pairs in **1c** are bonded by two 3c–2e bonds (one σ and one π). On the other hand, **1f** has a 2c–2e σ -bond and a 3c–2e π -bond to bind X¹–X² and X¹–X³. Therefore, the X¹–X² and X¹–X³ bond distances in **1f** are shorter than in **1c** ($\Delta = 0.05$ Å for Al and 0.03 Å for Ga).

An unsymmetrical arrangement of hydrogens around the ring leads to isomer **1g** (*C*_s), which is also a minimum for both Al and Ga with an energy difference with **1c** of 3.6 and 4.7 kcal/mol, respectively. The H-bridged X–X bond distance is lengthened in **1g** (3.018 Å) compared to **1f** (2.561 Å) and **1c** (2.797 Å). An MO description of **1g-Al,Ga** that accounts for the long M–M distance is as follows. The structure can be visualized as a combination of H–Al–Al and AlH₂. The sigma lone pair of AlH₂ is donated to the in-plane bonding combination (π -MO) of p orbitals of H–Al–Al (Scheme 6a). The pseudo π (in-plane) AlH₂ MO is involved in weak interaction with the antibonding combination of the in-plane p orbitals (Scheme 6b). In addition, there is a delocalized 3-center π -MO that forms the HOMO-1. This explains the long Al²–Al³ distance as well as long Al²–H⁵ distance. The bonding in the Ga analogues is similar except that the order of HOMO and HOMO-1 are interchanged. A structure similar to **1g** is a minima for Si₂BH₃ and is 6.7 kcal/mol higher in energy than its global minima at QCISD(T)/6-31G(d) level.³⁷

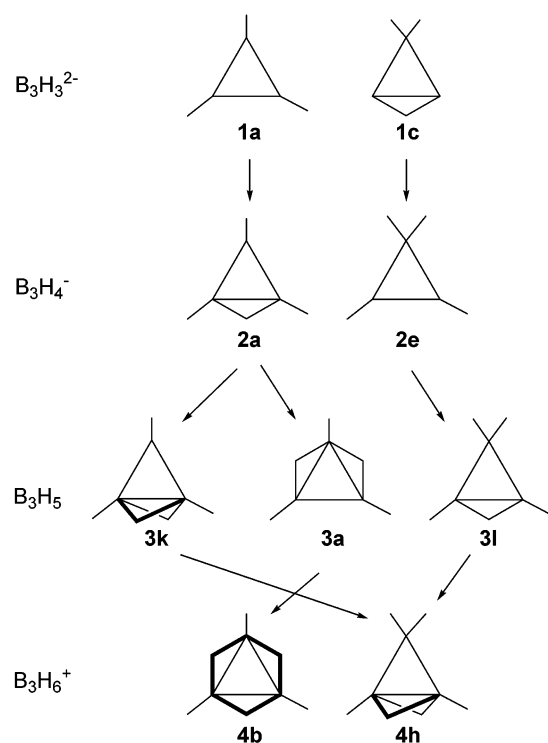
Nonplanar alternative **1h**, obtained by a twist of the XH₂ group in **1c**, is a higher order saddle point for B and Al, but a transition structure for Ga. The imaginary frequency of **1h-Ga** leads to the nonplanar doubly H-bridged isomer **1i**, which is ~5 kcal/mol higher in energy than global minimum **1c-Ga**. Isomer **1i** is also a minima for Al and is likewise ~5 kcal/mol higher in energy than **1c-Al**. The electronic structure of **1i** consists of 2c–2e X¹–X² and X–H bonds, two 3c–2e X–H–X bonds, and lone pairs on X² and X³. Its ring-delocalized π -orbital interacts with two bridged H's leading to a hybrid delocalized orbital similar to that in **1e**.

Isomer **1j**, which has two H-bridging X²–X³ bonds, is a transition structure for both Al and Ga. Optimization in the direction of the imaginary vector (without any symmetry constrains) leads to planar isomer **1k**, which is a minimum for both Al and Ga with an energy difference of 3.8 and 7.2 kcal/mol, respectively, with **1c**. We note that a similar structure is a minima for the iso-electronic Si₃H₃⁺ and a transition structure for Si₂BH₃.^{15,37} The electronic structure of **1k** also shows 2π electron delocalization over the ring along with two 3c–2e H-bridged X–X bonds, one 2c–2e X–X bond, and a 2c–2e X–H bond.

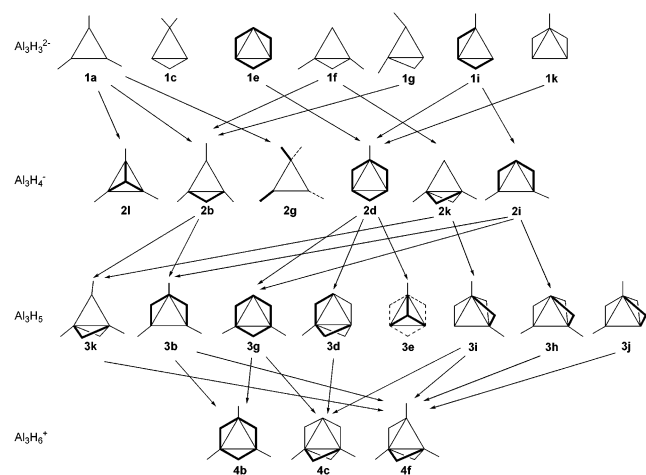
X₃H₄[–], X₃H₅, and X₃H₆⁺ Results on the studies of the isomers of X₃H₄[–], X₃H₅, and X₃H₆⁺ are summarized in Scheme

- (40) (a) Brothers, P. J.; Power, P. P. *Adv. Organomet. Chem.* **1996**, *39*, 1. (b) Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289. (c) He, X.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717.
- (41) (a) Präsang, C.; Młodzianowska, A.; Sahin, Y.; Hofmann, M.; Geiseler, G.; Massa, W.; Berndt, A. *Angew. Chem.* **2002**, *114*, 3529; *Angew. Chem., Int. Ed.* **2002**, *41*, 3380. (b) Präsang, C.; Hofmann, M.; Geiseler, G.; Massa, W.; Berndt, A. *Angew. Chem.* **2002**, *114*, 1597; *Angew. Chem., Int. Ed.* **2002**, *41*, 1526; (c) Maier, A.; Hofmann, M.; Pritzkow, H.; Siebert, W. *Angew. Chem.* **2002**, *114*, 1600; *Organic Chem., Int. Ed.* **2002**, *41*, 1529.
- (42) Jorgenson, W. L.; Salem, L. *The Organic Chemists Book of Orbitals*; Academic Press: New York, 1973.

Scheme 7

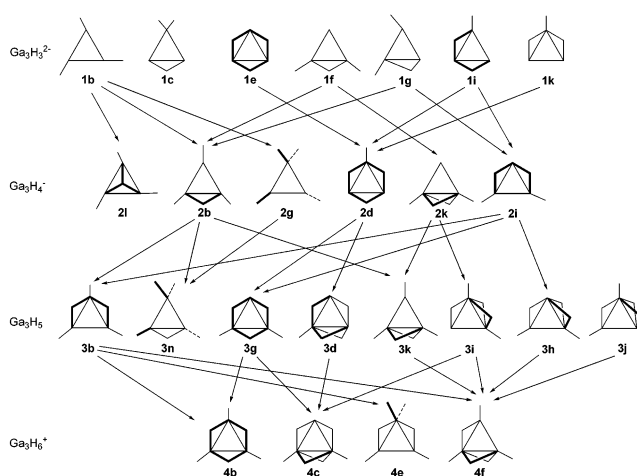


Scheme 8



2, 3, and 4, for X = B, Al, and Ga. Although each of these structural types may be discussed individually, a better understanding is obtained by considering the evolution of the isomers corresponding to $X_3H_4^-$, X_3H_5 , and $X_3H_6^+$ by sequential protonation from $X_3H_3^{2-}$ which is discussed above. These are done for B, Al, and Ga separately, starting with the minimum energy structures available for $X_3H_3^{2-}$ (Schemes 7, 8, and 9). Thus, Scheme 7 provides the minimum energy structures available starting from **1a** and **1c**, the only two minima on the $B_3H_3^{2-}$ PES with triangular B_3 arrangement. Arrows indicate the direct relationships that exist between structures via protonation. A comparison of Scheme 7 with the general Schemes 1–4 indicates that this formal protonation strategy includes all minimum energy structures. The basic structural preferences appear to be decided already in the isomers of $X_3H_3^{2-}$. The large number of transition states and other higher order stationary points calculated for $B_3H_3^{2-}$ do not lead to any

Scheme 9



minimum energy structures. There are two interesting points to be noted here. First is the preference for the planar tetracoordinate arrangement at boron seen in **1c-B**, **2e-B**, **3l-B**, and **4h-B**. In contrast, stabilization of planar tetracoordinate carbon is more difficult.⁴³ Differences in relative energies of $2c-2e$ and $3c-2e$ bonds involving carbon and boron atoms contribute to this trend. Carbon–carbon single bonds are considerably stronger than boron–boron single bonds. Still **1c-B** is higher in energy than **1a-B** by 58.12 kcal/mol. A second important aspect of the minimum energy structures is the nonplanar $B_3H_6^+$ structure. The interplay of $\sigma-\pi$ mixing mentioned earlier control the energetics here. However, the balance is delicate, as structures **2a-B**, **3a-B**, and **3l-B** prefer planar arrangements (see Figure 5 for analogous MOs). This is in contrast to the behavior of Al and Ga structures seen below.

The number of triangular structures calculated to be minimum in energy for Al_3H_n is considerably larger. Scheme 8 attempts to relate all structures to the isomers of $Al_3H_3^{2-}$. In addition to the propensity for square planar arrangements, there are several novel structural features seen in Al_3H_n that are not seen with B_3H_n . The most dramatic one is the unsymmetric terminal Al–H bonds as seen in **1g-Al**. This is exceptional because there is only one structure in the entire Al₃ set with this feature. As explained in Scheme 6, the structure is best considered as a combination of AlH_2 and $HAL-Al$. The bridging hydrogen-terminal hydrogen combination is seen in the structure of Si_2H_2 as well.^{14m,n} A symmetrical C_{3h} structure with three distorted terminal Al–H bonds (**1b-Al**) was not a stationary point. Protonation of **1g-Al** led to **2b-Al** with terminal Al–H bonds which are symmetrically placed.

The next unusual structural aspect in comparison to B_3H_n is the out-of-plane distortion of bridging hydrogens in $Al_3H_3^{2-}$, $Al_3H_4^-$, and Al_3H_5 . Structures with one bridging hydrogen is in the plane of the X_3 ring in **1c**, **1f**, and **1g**; but not so in **2b**. Similarly, the two bridging hydrogens are in the X_3 plane in **1k**, but out-of-the plane in **1i**. However protonation of **1i** and **1k** leads to the same triply bridged structure **2d** where all the

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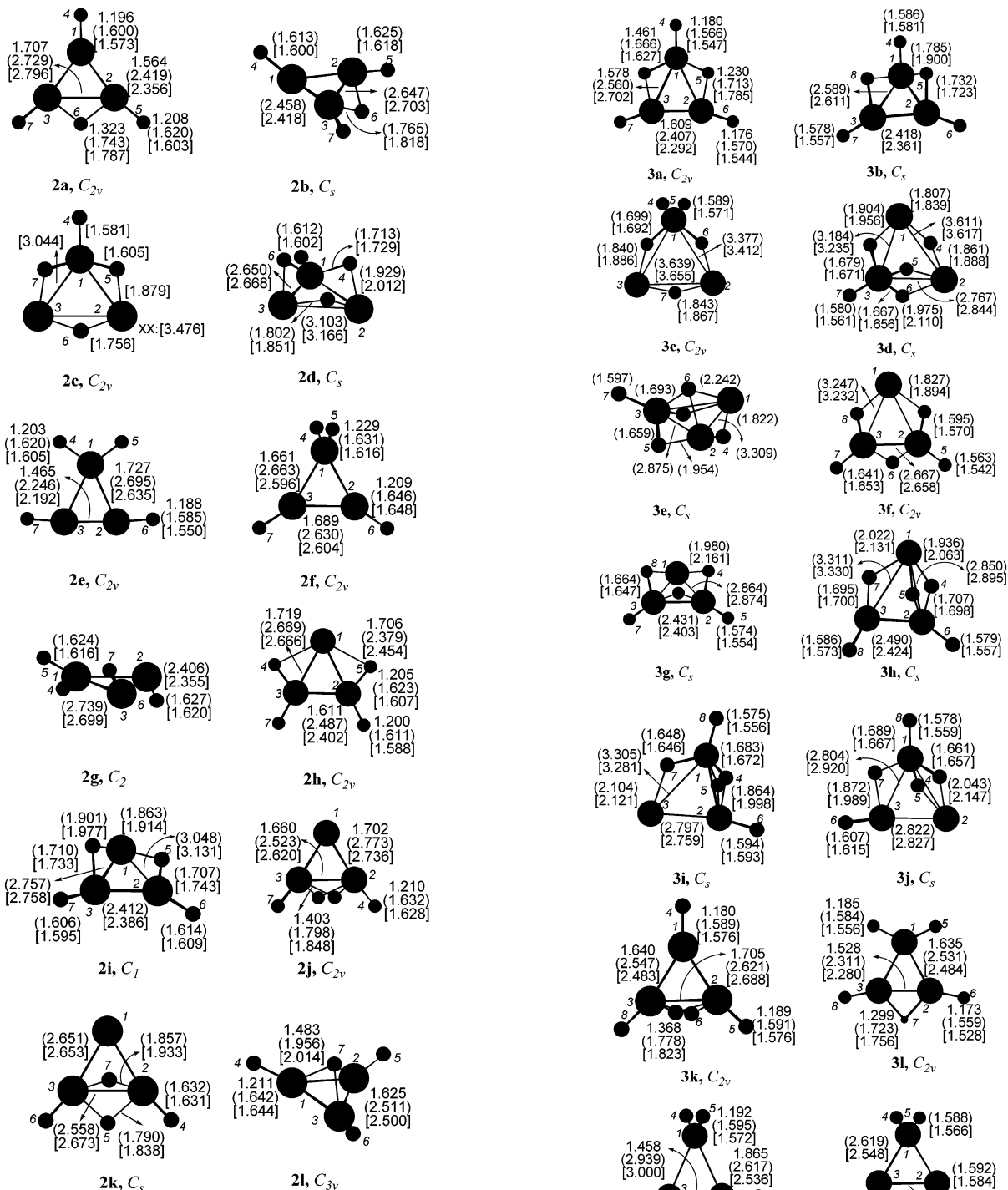


Figure 2. Optimized geometries and important bond distances for B, Al (in parentheses) and Ga (in brackets) isomers of $X_3H_4^-$ at B3LYP/6-311G(d) level. Atoms are numbered in italics.

three hydrogens are outside the X_3 plane. Three bridging hydrogens bring the same situations as has been observed in **1e** (Figure 5) and remain out of the Al_3 plane.

Another difference between boron and Al structures is the propensity of doubly H-bridged structures with Al. Thus **2k**, **3k**, **3d**, **3i**, **3h**, **4c**, and **4f** are all calculated to be minima. In contrast there are only two structures **3k-B** and **4h-B** with doubly H-bridged bonds among boron isomers. The decrease in bond energy of a regular $2c-2e$ X-H bond in going from $X = B$ to $X = Al$ perhaps explains this propensity for bridged structures.

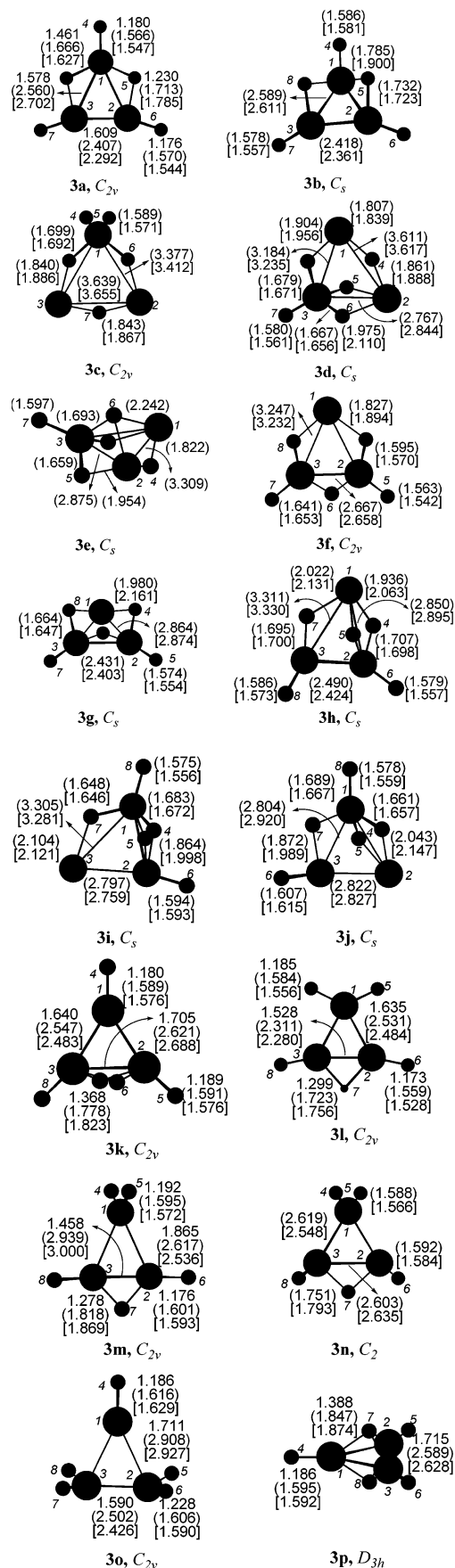


Figure 3. Optimized geometries and important bond distances for B, Al (in parentheses) and Ga (in brackets) isomers of X_3H_5 at B3LYP/6-311G(d) level. Atoms are numbered in italics.

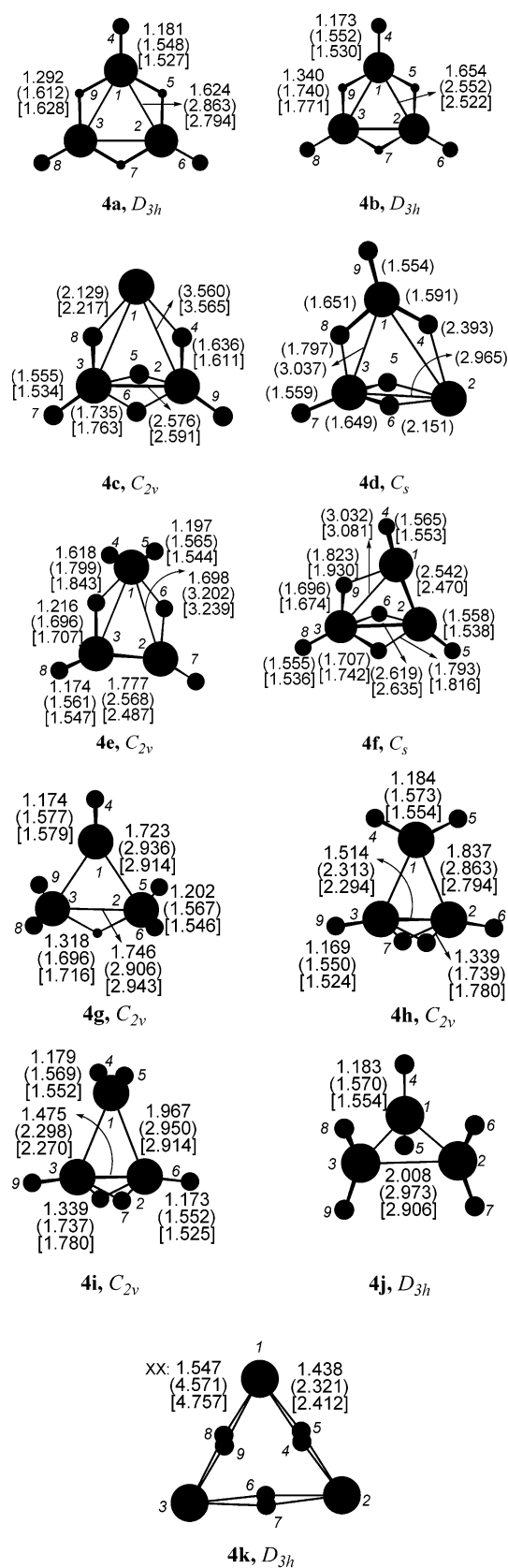
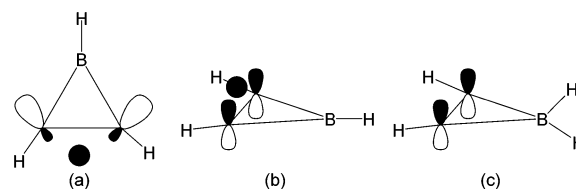


Figure 4. Optimized geometries and important bond distances for B, Al (in parentheses) and Ga (in brackets) isomers of $X_3H_6^+$ at B3LYP/6-311G(d) level. Atoms are numbered in italics.

Structures with H-capping the triangle, **2l-Al** and **3e-Al**, are also special to the Al_3 series. The interaction of the 1s orbitals

Scheme 10



of the capping hydrogens with the orbitals of the Al_3 is enhanced by the tilting of the $Al-H_i$ bonds toward the side of the capping hydrogens in **2l-Al**. The second such structure, **3e-Al**, is even more remarkable with three bridging hydrogens on the opposite side, but the lone terminal $Al-H$ bond tilted toward the capping hydrogen. These structural details are in tune with the idea of compatibility of orbitals in overlap that we have detailed elsewhere.^{44,46}

The gallium series brings in the unusual structural aspects found in Al structures in larger measure. The classical structure **1a-B** and **1a-Al** does not have a counterpart with Ga. The D_{3h} structure distorts to **1b-Ga** (C_{3h}). The bonding model (Scheme 5) which describe this structure is also suggested to explain similar C_{3h} structure of Group 14 compounds such as Pb_3R_6 and Sn_3R_6 .^{9,15c,38} The C_{3h} structure **1b-Ga** leads to the C_3 structure **2l-Ga**. However, similar distortion in **1g-Ga** is removed on protonation to **2b-Ga** or **2i-Ga**. Similarly the tendency for the out-of-plane distortion of the bridging hydrogens is enhanced in the structures of gallium compounds. The delicate balance between a planar bridged structure and out-of-plane tilting is also seen dramatically in the structures **2a-B**, **2b-Al**, and **2b-Ga**.

Isomer **2a** obtained by protonation of a $X-X$ bond of **1a**, is the global $B_3H_4^-$ minimum, but it is a transition structure for Al and Ga. The imaginary frequency leads to nonplanar structure **2b** (C_s). An MO explanation is provided below. We note that a similar distortion from the planar C_{2v} structure has been reported for SiB_2H_4 .⁴⁵ The energy difference between **2a** and **2b** is only 1.0 kcal/mol for Al and 2.4 kcal/mol for Ga. The X^2-X^3 bond distance is shortened and the X^1-X^2 distance is lengthened in **2b** as compared to **2a**. The electronic structure of **2a-B** consists of three $2c-2e$ $X-H$ bonds, two $2c-2e$ $X-X$ bonds, and a $3c-2e$ $X-H-X$ bond, and an occupied π -MO. The in-plane $3c-2e$ $X-H-X$ bond is weaker for Al and Ga, (as the $X-X$ bond gets longer) due to the less effective overlap of the bridging hydrogen with the bent Walsh orbitals. (Scheme 10a). Instead, on moving the bridging hydrogen out of plane, better overlap with the π -orbitals on X results (Scheme 10b). As a result, the bridging H contributes to the ring-delocalized π -orbital. The 1,2-shift in cyclic vinyl cations is another example where the bridging hydrogen is distorted from planarity.⁴⁶

C_{2v} structure **2e** with a planar tetracoordinated boron atom is a $B_3H_4^-$ minima due to the strong π -delocalization and is only 1.6 kcal/mol less stable than **2a**. Both the van't Hoff (**2f**) and anti-van't Hoff (**2e**) structures are higher order saddle points for Al but, the twisted nonplanar form **2g-Al** (C_2) is a minimum. The experimentally known neutral Al_3R_4 ($R = Si^tBu_3$) (**11**)

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radical is known to have such a nonplanar structure,⁴⁷ but that of Ga₃R₄ (**12**) reportedly has a van't Hoff structure.⁴⁸ The reduced species Ga₃R₄⁻ (**13**) (R = 'Bu) has, however, a completely different geometry, in which one of the substituent's methyl groups interacts with the Ga² atoms leading to a very long Ga¹-Ga² bond distance of 2.935 Å.⁴⁸ Of the two sets of X-X bonds in **2g**, one (Al: 2.406 Å; Ga: 2.355 Å) is shorter than a normal X-X double bond and the other (Al: 2.739 Å, Ga: 2.699 Å) is longer than a regular X-X single bond. The Al¹-Al² bond distance in **2g-Al** is similar in length to that in **11**, but the Al²-Al³ distance is nearly 0.3 Å shorter. These structures are also examples of pyramidal tricoordination which along with planar tetracoordination rewrite the structural basis of the main group chemistry. The tricoordinate planar geometry of CH₃⁺ and BH₃, are taken for granted. Recently, we had shown that pyramidal tricoordinate boron is a possibility.⁴⁹ Structures **2g-Al** and **2g-Ga** are the first such examples with nonplanar Al and Ga atoms. The electronic structure of **2g** can be best understood by comparing it with isomer **2f**, which has an empty π-LUMO, formed from the p_z (X²) and p_z (X³) atomic orbitals (Scheme 10c) and sp² hybridized X² and X³ atoms. Due to the decreased sp²-hybridization for the heavier elements Al and Ga,²⁹ their X²-X³ and X²-H⁶ (X³-H⁷) bonds are weak. This is compensated by moving the H⁶ and H⁷ atoms out of plane to enable them to interact with the empty p_z orbital (π-MO) resulting in nonplanarity of the structure and causing the XH₂ group to twist.

It is interesting to note that the imaginary frequency in **3c-Ga** led to **3d**, where as **3c-Al** led to **3e**! We also found that **3d-Al** is a minimum. However, on optimization **3e-Ga** (without any symmetry constraints) collapsed to **3d**. The singly H-bridged X¹-X² and X¹-X³ bonds in **3d** are longer than those in X₂H₆ and X₂H₂. The X³-H,⁸ X³-H⁶, and X³-H⁵ distances are very short compared to X¹-H,⁸ X²-H⁵, and X²-H⁶ respectively. For example, H⁵ is closer to X³ by 0.31 Å in Al₃H₅ and 0.45 Å in Ga₃H₅ than to X². This shows that the isomer **3d** can be viewed as an adduct formed by the interaction between X₂H⁺ (consists of X¹, X², and H⁴) and XH₄⁻ (consists of X³, H⁵, H⁶, H⁷, and H⁸). The NBO charges also support such an interpretation, the sum of the natural charges on Ga³ (0.72), H⁵ (-0.35), H⁶ (-0.35), H⁷ (-0.44) and H⁸ (-0.27) is -0.7e and the sum of the charges on Ga¹ (0.70), Ga² (0.60) and H⁴ (-0.60) is +0.7e. Similar results were found for **3d-Al**. Isomer **3e-Al** is very much close to **3d**, because the bridging hydrogen H⁶ is now interacting with both Al¹ and Al² in **3e** instead of only with Al² in **3d**. Alternatively isomer **3e** can be arrived by capping **2d** with a proton. The bond lengths in **3e** show trends similar to **3d** and the bonding features of **3e** are almost similar to that of **3d**. That is isomer **3e** can also be viewed as an adduct of AlH₄⁻ (Al³, H⁵⁻⁸) and Al₂H⁺ (Al¹, Al², and H⁴). The NBO charges also support the interpretation (Al¹: 0.62, Al³: 1.02, H⁴: -0.59, H⁵: -0.44, H⁶: -0.44, H⁷: -0.35). The energy difference between **3d-Al** and **3e-Al** is only 1.0 kcal/mol.

The potential energy surfaces of Al and Ga three-rings contrasts dramatically with that of B three-rings. The nonplanarity of hydrogens with respect to X₃ ring is found to be very

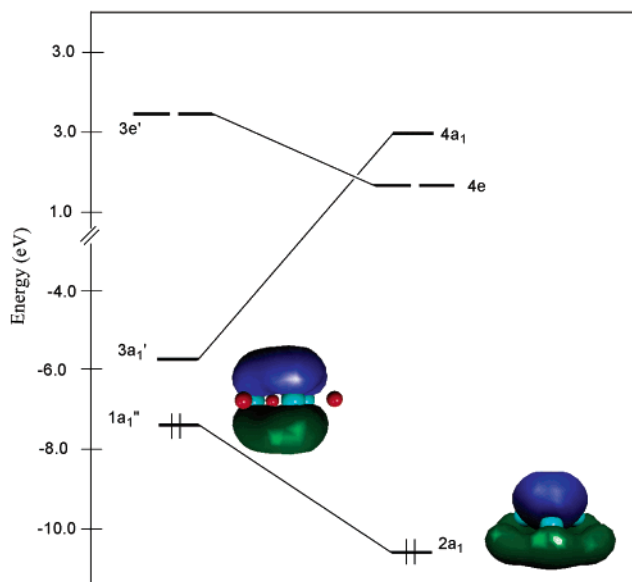


Figure 5. Correlation diagram between **1d** and **1e** showing the dramatic stabilization of the π orbital.

common for Al and Ga species. Similarly species with lone pairs on heavy atoms dominate the potential energy surfaces of Al and Ga three-ring systems. The global minimum structures of B are minima for Al and Ga only in case of X₃H₃²⁻ and X₃H₆⁺. Even here, Ga₃H₃⁻² has a distortion from D_{3h} to C_{3h}. On the potential energy surface of X₃H₄⁻ and X₃H₅, the global minimum structures of B are not even minima for Al and Ga. Similarly, the influence of π-delocalization in stabilizing the structures is decreased from X₃H₃²⁻ to X₃H₆⁺. For example, the global minimum structures of X₃H₃²⁻, X₃H₄⁻ have the 2π-delocalization for both Al and Ga. However, the global minima of X₃H₆⁺ does not have conventional 2π-electrons for both Al and Ga. In the case of X₃H₅, the global minima is aromatic for Al and not aromatic for Ga. The propensity of isomers with bridging hydrogens and para Al and Ga atoms calculated here is a reflection of the nature of structure and bonding observed in heavier elements of the main group. For example, the lowest energy isomer of Si₂H₂ has two bridging hydrogens.^{14m,n} The next isomer has one bridging hydrogen. In view of such experimental observations available in the literature, we are confident that the novel structures that are presented here will stand experimental scrutiny.

The resonance stabilization energy (RSE) for the global minimum structures (or nearest structures to global minimum which contains π-delocalization) is computed using the isodesmic eqs 1-6 (Scheme 11).⁴ We tried to maintain the nonplanarity of bridging hydrogens in the reference species (**14-19**) in accordance with isomers **2b**, **2d**, **3b**, **3g**, and **4b**. However, on optimization, all of the reference species **14-19** (except **16c**) collapsed to planar structures (Figure 6). Detailed explanations for the relative energies here are difficult because the RSE differences between different compounds or between Al and Ga are very small. There are many uncertainties in deriving these energies. For example (a), the selection of the reference molecules is not unambiguous, (b) even if we select some very good reference molecules, on optimization, planar or nonplanar arrangement of hydrogens may not be consistent with the molecule for which we are trying to get the RSE. For example,

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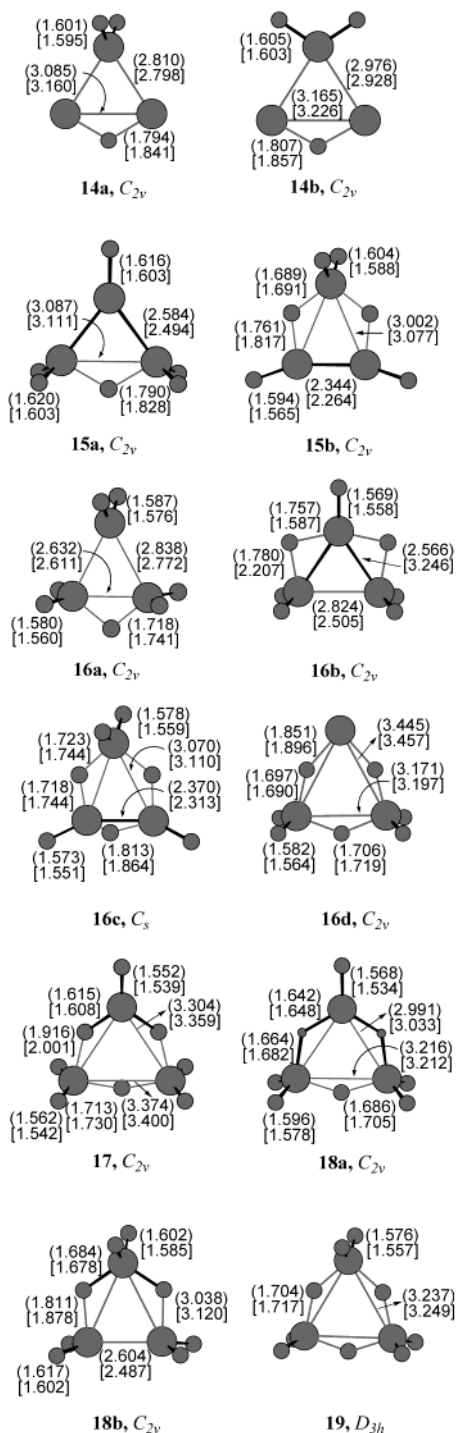
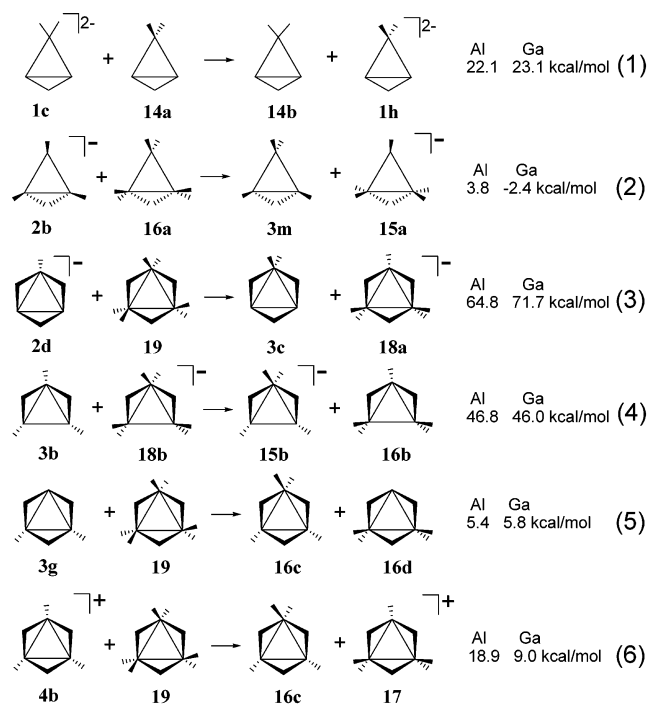


Figure 6. Optimized geometries of the reference species X_3H_3 (14), $X_3H_6^-$ (15), X_3H_7 (16), $X_3H_8^+$ (17), $X_3H_8^-$ (18), and X_3H_9 (19). The important bond distances for Al (in parentheses) and Ga (in brackets) are given at B3LYP/6-311G(d) level.

isomer **2b** has nonplanar arrangement of both terminal and bridging hydrogens whereas the reference molecules **16a**, **3m**, and **15a** all have planar bridging hydrogens. This will certainly have its effect on RSE because all the heavy atoms are not similar on both sides of the equation (at least in terms of hybridization). Therefore, we caution the reader that the best way to know whether a particular molecule has π -delocalization or not is to look at its electronic structure.

Scheme 11



Conclusions

Present computational study of the structures and energies of cyclic $X_3H_3^{2-}$, $X_3H_4^-$, X_3H_5 , and $X_3H_6^+$ ($X = B, Al,$ and Ga) reveals several characteristics. The diversity of structures that are minima is large for Al and Ga, and differs from those of B_3 hydrides. The most salient features are as follows: (1) $X_3H_3^{2-}$ has a total of seven minima for Al and Ga in contrast to only two cyclic minima available to B. The π -delocalized isomer with two lone pairs **1c** is the global minima for Al and Ga. (2) $X_3H_4^-$ has six minima for Al and Ga, whereas for B, there are only two cyclic minima known. Unlike $X_3H_3^{2-}$, the global minimum structure for Al and Ga are different for $X_3H_4^-$. The singly H-bridged nonplanar C_s isomer **2b** is the global minima and the triply H-bridged nonplanar C_s structure **2d** with two lone pairs is the second best structure for $Al_3H_4^-$. Contrarily, **2d** is the global minima and **2b** is the second best structure for $Ga_3H_4^-$. The energy difference between **2b** and **2d** is 5.4 and 1.6 kcal/mol for Al and Ga, respectively. A structure with tricoordinate pyramidal arrangement at Al and Ga is found in **2g**, contrary to the conventional wisdom of $C_3H_3^+$, B_3H_4 , etc. (3) The neutral species X_3H_5 has a total of eight minima for Al and Ga, whereas B has only three cyclic minima. Similar to that of $X_3H_4^-$, the global minimum structures of Al_3H_5 and Ga_3H_5 are different. The doubly H-bridged nonplanar structure **3b** is the global minima for Al_3H_5 , whereas the four H-bridged C_s isomer **3d** is the global minima for Ga_3H_5 . (4) The cationic species $X_3H_6^+$ has three and four minima for Al and Ga, respectively. In the case of $B_3H_6^+$, there are only two cyclic structures that are minima. The four H-bridged C_{2v} isomer **4c** with a lone pair is the global minima for Al and Ga. (5) The nonplanarity of hydrogens with respect to X_3 ring is found to be very common for Al and Ga species. (6) Structures with lone pair on heavy atoms dominate the potential energy surfaces of Al and Ga three ring systems. (7) The influence of π -delocalization in stabilizing the structures is decreased from

$X_3H_3^{2-}$ to $X_3H_6^+$. (8) The resonance stabilization energy (RSE) for the global minimum structures (or nearest structure to global minimum which contains π -delocalization), computed using the isodesmic equations, give quantitative trends, but cannot be used as a test of aromaticity.

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Supporting Information Available: Cartesian coordinates of the structures in Figures 1–4 and Tables of Total Energies

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