

Group 14 Analogs of the Cyclopropenium Ion: Do They Favor Classical Aromatic Structures?

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Despite the very high ring strain, the cyclopropenium ion (**1-C**) is highly stable since it benefits from the highest resonance stabilization energy of all Hückel $4n + 2C_nH_n$ annulenes.¹ Silyl and germyl cations, free from Lewis base interactions, are still elusive after much current effort.² Are D_{3h} structures like **1** also favorable for the heavier $A_3H_3^+$ ($A = Si, Ge, Sn, \text{ and } Pb$) cations? Seen from the perspective of the heavier elements, the structures of carbon compounds are unusual and often do not serve as general models for periodic behavior.³ How does Hückel aromaticity compete with the trend toward nonclassical geometries in going down group 14?⁴ We now compare "classical" (D_{3h} **1**) structures with hydrogen-bridged (C_{3v} **2**, D_{3h} **3** and **3'**) alternatives for the cyclic $A_3H_3^+$ cations of the set of group 14 elements: C, Si, Ge, Sn, and Pb (Figure 1).

The $A_3H_3^+$ cations and the reference species were computed using the Gaussian 92 program⁵ with density functional theory employing Becke's three-parameter exchange functional⁶ and the nonlocal correlation potential provided by Lee et al.⁷ (Becke3LYP). The $C_3H_3^+$ forms were treated in full-electron and the Ge–Pb species in valence-electron (pseudopotential

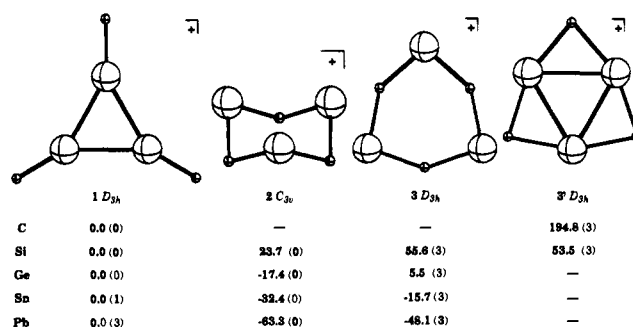


Figure 1. Schematic representation of $A_3H_3^+$ cation structures. Relative energies in kcal/mol, number of imaginary frequencies in parentheses.

approximations.⁸ Both full-electron and pseudopotential computations were carried out for $Si_3H_3^+$ structures. The 6-311++G-(2d,2p) basis set was employed for C, Si, and H.⁹ The TZ2P+ basis sets for the ns/np valence orbitals were combined with quasi-relativistic pseudopotentials for the core electrons of Ge, Sn, and Pb.⁷ The vibrational frequencies established the nature of the stationary points. The wave functions were characterized by the Wiberg bond indices (WBIs) and by the hybridizations given by natural bond orbital (NBO) analysis.¹⁰ The results from full-electron and pseudopotential approximations for $Si_3H_3^+$ are similar (see Table 1).

The relative stability of **1** vs bridged structures **2** and **3** decreases dramatically down the group (Figure 1). Structural and electronic population trends are in accord with the relative energies: e.g., the AA bond lengths and the WBIs in the heavier element cations progressively approach the $D_{3d} A_2H_6$ single bond values (computed at the same level, Table 1). The AA bond length in **1-Pb** (2.946 Å) is even longer than that in Pb_2H_6 (2.891 Å).

All C_{3v} bridged structures **2** are minima with the exception of $C_3H_3^+$: optimization gives D_{3h} planar **3'-C**, but this is a third-order saddle point. The three heaviest group 14 C_{3v} cations, **2-Ge**, **2-Sn**, and **2-Pb**, are more stable than the corresponding planar D_{3h} forms, **1-Ge**, **1-Sn**, and **1-Pb**. Neither **1-Sn** nor **1-Pb** is a minimum: **1-Sn** has one imaginary frequency, and **1-Pb** has three imaginary frequencies. Figure 1 summarizes this information.

The structural features and bonding patterns of the nonplanar C_{3v} bridged minima, **2-Si**, **2-Ge**, **2-Sn**, and **2-Pb**, are similar. Unlikely **1**, the calculated A–A single bond distances in the corresponding $D_{3d} A_2H_6$ molecules are shorter than those in the bridged C_{3v} isomers **2** (Table 1). The H–A–H bond angles are close to 90° in **2**. The NBO analysis confirms the almost nonhybridized p-character of the A–H bond AOs and the s-character of the nonbonding orbitals (lone pairs) in all bridged structures.

The reduced efficiency of π bonding in heavy atom species accounts only partially for the greater stability of the bridged C_{3v} structure **2** over the classical cyclopropenium cation form **1**. Aromatic stabilization in Hückel $(CH)_n$ annulenes is most

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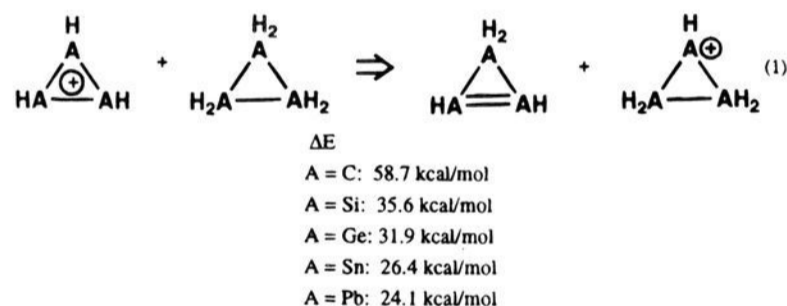
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Table 1. Selected Properties of the $A_3H_3^+$ Cations and Reference Species

	A				
	C	Si ^a	Ge	Sn	Pb
1 (D_{3h})					
$R(AA)^b$	1.359	2.203 [2.203]	2.361	2.746	2.946
$R(AH)^b$	1.079	1.477	1.542	1.716	1.781
WBI(AA)	1.428	1.400	1.324	1.263	1.065
2 (C_{3v})					
$R(AA)^b$		2.565 [2.203]	2.803	3.216	3.343
$R(AH)^b$		1.678 [1.684]	1.781	1.964	2.031
$R(A_3-H_3)^{b,c}$		0.825 [0.830]	0.858	0.911	0.920
$\angle HAH^d$		96.0	93.3	89.3	90.2
$\angle AHA^e$		99.6	103.8	109.9	110.8
WBI(AA)		0.639	0.596	0.553	0.550
WBI(AH)		0.439	0.430	0.397	0.405
% s-AO ^e		97	98	99	99
3' (D_{3h})/ 3 (D_{3h})					
$R(AA)^b$	1.471	2.303 [2.303]/ 3.030 [3.052]	3.227	3.637	3.739
$R(AH)^b$	1.288	1.723 [1.728]/ 1.597 [1.605]	1.695	1.885	1.946
$\angle HAH^d$	170.4	156.1/97.0	95.6	90.6	92.3
4 (D_{3h})					
$R(AA)^b$	1.422	2.345	2.530	2.908	3.032
WBI(AA)	1.522	1.476	1.471	1.460	1.445
% s-AO ^e	47	72	80	82	88
A_2H_6 (D_{3d})					
$R(AA)^b$	1.529	2.356	2.464	2.822	2.891
WBI(AA)	1.046	0.977	0.952	0.925	0.890

^a Pseudopotential data are given in square brackets. ^b In angstroms. ^c Distance between the A_3 and the H_3 planes. ^d In degrees. ^e Percentage of s-AO in lone pairs.

favorable energetically in 2π electron three-membered ring systems. This is shown by, e.g., the homodesmotic¹¹ and Hückel (topological)¹² stabilization energies (SEs); however, these decrease down group 14 (eq 1). This change is largest from

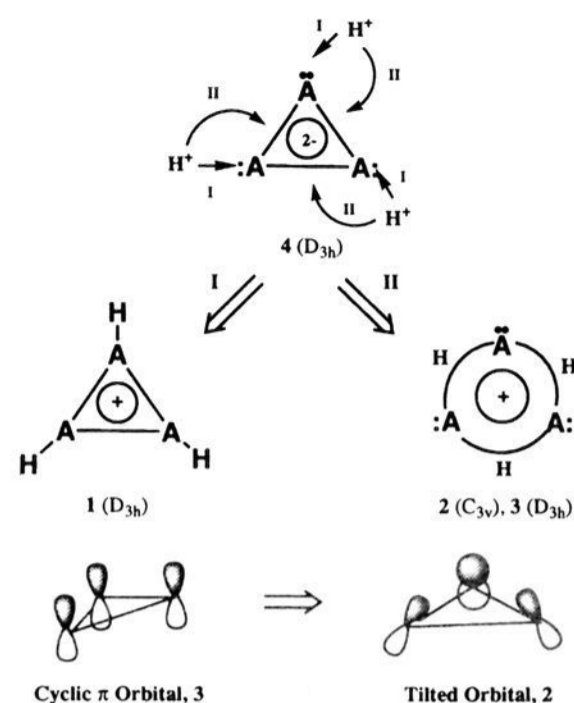


1-C to **1-Si** but then only gradual for the rest of the series. Like **1-C** (among its $C_3H_3^+$ isomers), **1-Si** is the global $Si_3H_3^+$ minimum. Likewise, **1-Ge** is a local minimum, although **1-Sn** is a first-order and **1-Pb** a third-order saddle point.

Instead of differences in π stabilization, the variations in the heavy element hybridization explain the increasing preferences of the bridged structures **2** versus classical structures **1** along the $A_3H_3^+$ series. Both **1** and **2** can be regarded as A_3^{2-} rings (**4**) triply protonated either at the lone pairs (which leads to the A-H bond formation in **1**) or at the A-A bonds (to give the A-H-A bridges in **2** and **3/3'**). While A-H localized bonds are more favorable for C and Si, the heavier elements tend to prefer divalent arrangements, and this increases down the group.¹³ The s orbital contributions in the A_3^{2-} lone pairs increase (Table 1), and the lone pairs become less effective as bonding sites in going from C to Pb.

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Scheme 1

However, due to the less effective 2π electron three-center bonding, the *nonplanar* C_{3v} structures **2** are preferred over *planar* D_{3h} structures **3** for the metal cations (Figure 1). As shown in Scheme 1, the π orbitals in **2** are tilted, resulting in better overlap. $C_3H_3^+$ is a special case: among the H-bridged possibilities, π bonding in the bridged planar D_{3h} **3'-C** is best because of the close approach of the carbon atoms. This precludes both the C_{3v} **2-C** and the "loose" (i.e., with greater A-A separations) **3-C** form. Both H-bridged D_{3h} $Si_3H_3^+$ isomers, *loose* **3-Si** and *"tight"* **3'-Si**, with nearly equal energies and the same electronic configurations $(1a_1')^2(2a_1')^2(1e')^4(2e')^4-(a_2'')^2$, were characterized, albeit as third-order saddle points. Only *loose* H-bridged D_{3h} stationary points, with large A-A distances and small H-A-H angles, are found for **3-Ge**, **3-Sn**, and **3-Pb**.

In summary, our calculations indicate that the relative stabilities of bridged structures, which do not exist for $C_3H_3^+$, increase down the group 14 $A_3H_3^+$ cations. The classical cyclopropenium cation structures are favored only for **1-C** and **1-Si**, whereas C_{3v} H-bridged forms can be expected for **3-Ge**, **3-Sn**, and **3-Pb**. These results provide another example of the quantitatively and even qualitatively exceptional behavior of the Li-Ne row elements. True periodic variations are observed only below the second period.³ Nevertheless, our $A_3H_3^+$ results suggest new opportunities for the experimental observation of free cations of the heavier group 14 elements.²

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