H-Bridged Structures for Tetrahedranes A_4H_4 (A = C, Si, Ge, Sn, and Pb)

Gantasala Naga Srinivas and Eluvathingal D. Jemmis*

Contribution from the School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

Received June 23, 1997. Revised Manuscript Received September 19, 1997[⊗]

Abstract: *Ab initio* MO studies at the HF, MP2, and Becke3LYP levels on H-bridged tetrahedranes of the group 14 elements (A_4H_4, A = C, Si, Ge, Sn, Pb) with the 6-31G* basis set for C and Si and LANL1DZ and quasirelativistic pseudopotential basis sets for Ge, Sn, and Pb are reported. As expected, the classical T_d structure **1** is more stable than all the other tetrahedrane alternatives for C_4H_4. The triply hydrogen bridged structure **2** (C_{3v}) is found to be more stable for Si, Ge, and Sn. Pb_4H_4 prefers the four H-bridged structure **8** (C_s). However, the calculations with the quasirelativistic pseudopotential basis set show the quadruply H-bridged D_{2d} structure **7** to be the most stable structure for Ge, Sn, and Pb. Thus the structures derived from the transition metal organometallic chemistry are competitive for heavier elements (Si to Pb). The periodic behavior begins only with the second period; Li to Ne, are the exceptions. Suggestions for the realization of these H-bridged structures for Pb from NaPb are discussed.

Introduction

The main group tetrahedranes are of interest from several viewpoints: in addition to their aesthetic appeal, bonding features, strain, and many possible applications are compelling reasons for their exploration.[1−4] The electronic structure of group 14 and 15 tetrahedranes is explained by 2c−2e bonding, whereas in group 13 multicenter surface bonding has to be invoked.[1,2] The first possible group 15 tetrahedrane N_4 has been predicted as a high energy density material in high specific inpulse fuels.[4] Theoretical studies at the CCSD(T) level show that N_4 (T_d) is a local minimum, 186 kcal/mol higher in energy than $2N_2$.[5] However, N_4 (T_d) is experimentally yet to be prepared. In contrast, the tetrahedral P_4 is well-known.[6] Various substituted B and Al tetrahedrane molecules are prepared experimentally (e.g., $B_4{}^tBu_4$, B_4Cl_4, and $Al_4(\eta^5\text{-}C_5\text{-}Me_5)_4$), and the role of substituents on the stability of B_4 and Al_4 cages is discussed in the literature.[2,7,8] The tetrahedrane structures of C and Si are known experimentally with sterically very bulky substituents.[9,10] In C_4R_4, the substituent R is the ^{t}Bu group, where as in Si_4R_4 the substituent R is the "super

silyl" group (Si^tBu_3). The parent C_4H_4, **1-C** (throughout this paper the structure number is followed by the symbol of the atom to specify the molecule) is theoretically predicted to be a "super base".[3] The structure of **1-C** is explained by the tetravalent carbon despite its high strain energy.[1] However, **1-Si** (tetrasilatetrahedrane) is calculated to be a second order saddle point at the MP2(FC)/6-31G* level on the potential energy surface of Si_4H_4.[11] Nagase et al. predicted that two SiSi bonds in **1-Si** can be broken without a barrier to form a four-membered ring isomer.[12] The triply H-bridged tetrahedrane for silicon (**2-Si**) is 20.7 kcal/mol lower in energy than the classical structure (**1-Si**) at the MP2(FC)/6-31G* level.[11] The H-bridged alternative structures are found to be competitive in stability with the classical structures for heavier analogs of cyclopropane and cyclobutane.[13,14] Similarly, the structural differences between ethylene and acetylene with their heavier analogs are well-known.[15,16] The contrasts between carbon and its heavier analogs are not restricted to the neutral species.[17−19] For example, the side-on complex is the most stable isomer for Sn and Pb in the AH_3^+ (A = C, Si, Ge, Sn, Pb) system.[18] The triply H-bridged C_{3v} structures of $A_3H_3^+$ are found to be

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

(1) (a) Minkin, V. I.; Minyaev, R. M.; Zholanov, Yu. A. *Nonclassical Structures of Organic Compounds*; Mir Publishers: Moscow, 1987. (b) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules;* Academic: New York, 1978. (c) Grimme, S. *J. Am. Chem. Soc.* **1996,** *118,* 1529. (d) Kollmar, H.; Carrian, F.; Dewar, M. J. S.; Bingham, R. J. *Am. Chem. Soc.* **1981,** *103,* 5292. (e) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975,** *97,* 6941.

(2) (a) McKee, M. L.; Buhl, M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1993,** *32,* 4549. (b) McKee, M. L. *J. Phys. Chem.* **1991,** *95,* 9273. (c) Swanton, D. J.; Ahlrichs, R. *Theor. Chim. Acta* **1989,** *75,* 163. (d) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1981,** *20,* 4452.

(3) Notario, R.; Elguero, J. *J. Chem. Soc., Chem. Commun.* **1995,** 1543.

(4) (a) Lauderdale, W. J.; Myers, M. J.; Bernhodt, D. E.; Stanton, J. F.; Bartlett, R. J. The search for Tetrahedral N_4. In *Proceedings of the High Energy Density Materials Contractors Conference*, AFOSR: Washington, DC, 1990. (b) Yorkony, D. R. *J. Am. Chem. Soc.* **1992,** *114,* 5406.

(5) Lee, T. J.; Rice, J. E. *J. Chem. Phys.* **1991,** *94,* 1215.

(6) (a) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins College Publishers: New York, 1993; p 785. (b) Edwards, H. G. M. *J. Mol. Struct.* **1993,** *295,* 95. (c) Balasubramanian, K. *J. Chem. Phys.* **1992,** *97,* 3437. (d) Bock, H.; Müller, H. *Inorg. Chem.* **1984,** *23,* 4365.

(7) (a) Mennekes, T.; Paetzold, P.; Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 173. (b) Lebreton, P. R.; Urano, S.; Shahbaz, M.; Emery, S. L.; Morrison, J. A. *J. Am. Chem. Soc.* **1986,** *108,* 3937. (c) Emery, S. L.; Marrison, J. A. *Inorg. Chem.* **1985,** *24,* 1612. (d) Aihara, J. *Bull. Chem. Soc. Jpn.* **1983,** *56,* 335. (e) Davan, T.; Marrison, J. A. *Inorg. Chem.* **1979,** *18,* 3194. (f) Atoji, M.; Lipscomb, W. N. *Acta. Crystallgr.* **1953,** *6,* 547.

(8) (a) Schneider, U.; Ahlrichs, R.; Horn, H.; Schäfer, A. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 353. (b) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 564. (c) Ahlrichs, R.; Ehrig, M.; Horn, H. *Chem. Phys. Lett.* **1991,** *183,* 227.

(9) (a) Maier, G.; Pfriem, S.; Schäfer, U.; Malsch, K.; Matusch, R. *Chem. Ber.* **1981,** *114,* 3965. (b) Maier, G.; Wolf, R.; Kalinowski, H.-O.; Boese, R. *Chem. Ber.* **1994,** *127,* 191. (c) Maier, G.; Pfriem, S.; Schäfer, U.; Matush, R. *Angew. Chem., Int. Ed. Engl.* **1978,** *17,* 520.

(10) Wiberg, N.; Finger, C. M. M.; Polborn, K. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 1054.

(11) Jemmis, E. D.; Srinivas, G. N. *J. Am. Chem. Soc.* **1996,** *118,* 3738.

(12) Nagase, S.; Nakano, M. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1081.

(13) (a) Srinivas, G. N.; Kiran, B.; Jemmis, E. D. *J. Mol. Struct. (THEOCHEM)* **1996,** *361,* 205. (b) Nagase, S.; Kobayashi, K.; Nagashima, M. *J. Chem. Soc., Chem. Commun.* **1992,** 1302.

(14) Srinivas, G. N. Ph.D. Thesis, University of Hyderabad, India, 1996.

(15) (a) Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1992,** *114,* 9559. (b) Curtiss, L. A.; Raghavachari, K.; Deutsch, P. W.; Pople, J. A. *J. Chem. Phys.* **1991,** *95,* 2433. (c) Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990,** *112,* 8559. (d) Schelyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988,** *110,* 2105. (e) Teramae, H. *J. Am. Chem. Soc.* **1987,** *109,* 4140. (f) Olbrich, G. *Chem. Phys. Lett.* **1986,** *130,* 115. (g) Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985,** *107,* 537. (h) Krogh-Jespersen, K. *J. Phys. Chem.* **1982,** *86,* 1492. (i) Grev, R. S.; Schaefer, H. F. III; Baines, K. M. *J. Am. Chem. Soc.* **1990,** *112,* 9458. (j) Trinquier, G. *J. Am. Chem. Soc.* **1990,** *112,* 2130. (k) Trinquier, G. *J. Am. Chem. Soc.* **1991,** *113,* 144. (l) Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1991,** *113,* 8634.

competitive to the classical D_{3h} 2π aromatic structures.[19] The heavier group 14 tetrahedranes should show equally dramatic contrast.

1   **2**
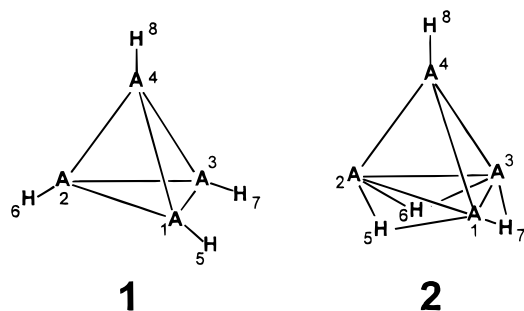
Transition metal tetrahedrane structures with four hydrogens exhibit a variety of topological arrangements. Wilson et al. reported that the structure of H$_4$Ru(CO)$_{12}$ contains face bridging hydrogens, **3**.[20] A D_{2d} structure (considering the M$_4$H$_4$ core alone), **4**, where the four hydrogens bridge four edges of the tetrahedrane, was also found for H$_4$Ru$_4$(CO)$_{12}$.[21] In this D_{2d} structure, the two unbridged Ru−Ru bonds are opposite to each other. The compounds H$_4$Os$_4$(CO)$_{11}$(CNMe), H$_4$-Ru$_4$(CO)$_{10}$(PPh$_3$)$_2$, H$_4$Ru$_4$(CO)$_{11}$[P(OMe)$_3$], and H$_4$Ru$_4$(CO)$_8$-[P(OMe)$_3$]$_4$ are also shown to have D_{2d} symmetry.[21−24] A C_s structure **5**, where the two unbridged Ru−Ru bonds are adjacent to each other, is reported for H$_4$Ru$_4$(CO)$_{10}$[μ{Ph$_2$P(CH$_2$)$_n$PPh$_2$}] (n = 1−4), H$_4$Ru$_4$(CO)$_{10}$[μ{Ph$_2$PCH$_2$CH(CH$_3$)PPh$_2$}], H$_4$-Ru$_4$(CO)$_{10}$[Ph$_2$PCH$_2$CH(CH$_3$)PPh$_2$], and H$_4$Ru$_4$(CO)$_{11}$(η^1-C=N(CH$_3$)CH$_2$CH$_2$CH$_2$).[25,26] The "isosynaptic" analogy connects the structural patterns of organometallic compounds with the main group compounds.[27] According to this analogy, Fe-(CO)$_3$ is very much like Si or Ge with a stereochemically inactive "ns-electron pair" (as represented below).

Fe(CO)$_3$ ⟶ Si, Ge

Further, it has been extended to Ru and Os complexes and

shown that Ru(CO)$_3$ and Os(CO)$_3$ are also isosynaptic to Si and Ge.[27] This relation can also be achieved by two isolobal replacements (depicted below).[28,29]

Fe(CO)$_3$ ⟷ BH ⟷ Si

Various H-bridged tetrahedranes of group 14 are derived from organometallics by using this isosynaptic analogy. Structure **2** (C_{3v}) is discussed previously for Si.[11] The transition metal structure with face-bridging hydrogens, **3**, suggests isomer **6**

3   **4**
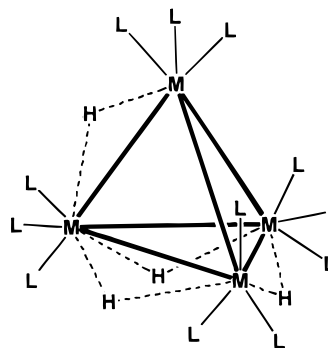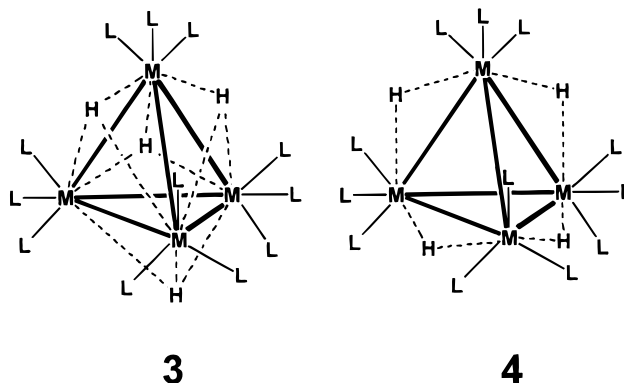
5

(T_d). Similarly, the structures having the edge-bridging hydrogens, **4** and **5**, lead to **7** (D_{2d}) and **8** (C_s), respectively. The triply hydrogen bridged structure, **9** (C_{3v}), is another candidate considered in the present study. The lowest energy structure suggested for Si$_4$H$_4$, **10** (C_s), is also included for comparison.[30] Thus the present study deals with the classical as well as the H-bridged tetrahedranes to see how the heavier analogs of tetrahedrane structures in group 14 (Si to Pb) behave. We expect that the H-bridged tetrahedranes discussed here for heavier elements can be prepared experimentally with use of

(16) (a) Grev, R. S.; Schaefer, H. F., III *J. Chem. Phys.* **1992**, *97,* 7990 and references therein. (b) Cordonnier, M.; Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Chem. Phys.* **1992**, *97,* 7984 and references therein. (c) Colegrove, B. T.; Schaefer, H. F., III *J. Phys. Chem.,* **1990,** *94,* 5593. (d) Palagyi, Z.; Schaefer, H. F., III; Kapuy, E. *J. Am. Chem. Soc.* **1993***, 115,* 6901. (e) Grev, R. S.; Deleeuw, B. J.; Schaefer, H. F., III *Chem. Phys. Lett.* **1990**, *165,* 257.

(17) (a) Nachtigall, P.; Jordan, K. D.; Smith, A.; Jónsson, H. *J. Chem. Phys.* **1996**, *104*, 148. (b) Archibong, E. F.; Schreiner, P. R.; Leszcynski, J.; Schleyer, P. v. R.; Schaefer, H. F.; Sullivan, R. *J. Chem. Phys.* **1995**, *102*, 3667. (c) Scheiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F. *J. Chem. Phys.* **1994**, *101*, 2141. (d) Su, M.-D.; Schegel, H. B. *J. Phys. Chem.* **1993**, *97*, 9981. (e) Katircioglu, S.; Erkoç, S. *Phys. Status Solidi B* **1993**, *117*, 373. (f) Raghavachari, K. *J. Chem. Phys.* **1992**, *96*, 4440. (g) Raghavachari, K. *J. Chem. Phys.* **1991**, *95*, 7373. (h) Gordon, M. S.; Gano, D. R.; Binkley, J. S.; Frisch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2191.

(18) Kapp, J.; Schreiner, P. R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *118*, 12154.

(19) (a) Jemmis, E. D.; Srinivas, G. N.; Leszcynski, J.; Kapp, J.; Korkin, A. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 11361. (b) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997**, *275*, 60.

(20) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4687.

(21) (a) Wilson, R. D.; Wu, S. M.; Love, R. A.; Bau, R. *Inorg. Chem.* **1978**, *17*, 1271. (b) Osella, D.; Nervi, C.; Ravera, M.; Fiedler, J.; Strelets, V. V. *Organometallics* **1995**, *14*, 2501.

(22) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1980**, *19*, 306.

(23) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4687.
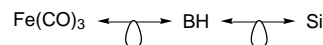
(24) Orpen, A. G.; McMullan, R. K. *J. Chem. Soc., Dalton Trans.* **1983**, 463.

(25) Puga, J.; Arce, A.; Braga, D.; Centritto, N.; Grepioni, F.; Castillo, R.; Ascanio, J. *Inorg. Chem.* **1987**, *26*, 867.

(26) Day, M. W.; Hajela, S.; Kabir, S. E.; Irving, M.; Mcphillips, T.; Wolf, E.; Hardcastle, K. I.; Rosenbe, R. G.; Milone, L.; Gobetto, R.; Osello, D. *Organometallics* **1991**, *10*, 2743.

(27) Epiotis, N. D. *Top. Curr. Chem.* **1989**, *150*, 47.

(28) (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711. (b) Wong, K. S.; Haller, K. J.; Dutta, T. K.; Chipman, D. M.; Fehlner, T. P. *Inorg. Chem.* **1982**, *21*, 3197.

(29) (a) Jemmis, E. D.; Prasad, B. V.; Prasad, P. V. A.; Tsuzuki, S.; Tanabe, K. *Proc. Ind. Acad. Sci. (Chem. Sci.)* **1990**, *102*, 107. (b) Jemmis, E. D.; Prasad, B. V.; Tsuzuki, S.; Tanabe, K. *J. Phys. Chem.* **1990**, *94*, 5530.

(30) (a) Clabo, D. A.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1986** *108*, 4344. (b) Sax, A. F.; Kalcher, J. *J. Chem. Soc., Chem. Commun.* **1987**, 809. (c) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60. (d) Yates, B. F.; Clabo, D. A.; Schaefer, H. F., III *Chem. Phys. Lett.* **1988**, *143*, 421. (e) Yates, B. F.; Schaefer, H. F., III *Chem. Phys. Lett.* **1989**, *155*, 563. (f) Sax; A. F.; Kalcher, J. *J. Comput. Chem.* **1989**, *10*, 309.

12970 *J. Am. Chem. Soc., Vol. 119, No. 52, 1997*

Srinivas and Jemmis

the known tetraanions A_4^{4-} (A = Si, Ge, Pb).[31,32] One such possibility for Pb_4H_4 is also discussed.

6   **7**   **8**

9   **10**
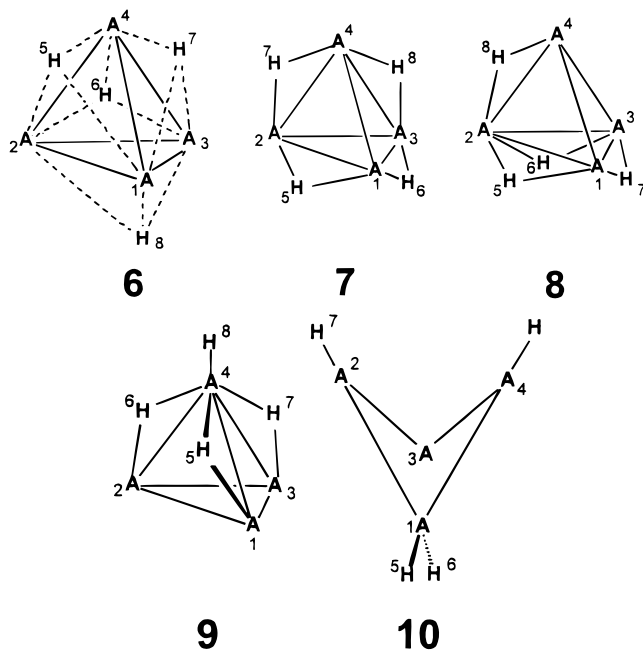
Computational Methods

The geometries of all the structures are optimized at HF and MP2 levels under the symmetry specified.[33,34] Density functional calculations at the Becke3LYP (B3LYP) level were also done for comparison of relative energies.[35] For C and Si, the 6-31G* basis set (as implemented in GAUSSIAN92) was used.[36] Molecules involving Ge, Sn, and Pb were optimized with the LANL1DZ basis set.[37] This basis set uses the valence double-ζ (DZ) basis on H and effective core potentials plus DZ on Ge, Sn, and Pb. The nature of the stationary points was determined by harmonic force constants and vibrational frequencies.[38] To see the relativistic effects on the stabilities of molecules with heavier atoms, calculations are performed at the B3LYP level with the TZ2P+ basis sets for the ns/np valence orbitals and the quasirelativistic pseudopotentials for core electrons of Ge, Sn, and Pb.[39] All the calculations were carried out with the GAUSSIAN92 program packages.[40] The energy comparisons are at the MP2/6-31G*//MP2/6-31G*+ZPE level for C and Si and at the MP2/LANL1DZ//MP2/

(31) (a) Marsh, R. E.; Shoemaker, D. P. *Acta Crystallogr.* **1953**, *6*, 197. (b) Hewaidy, I. F.; Busmann, E.; Klemm, W. *Z. Anorg. Allg. Chem.* **1964**, *328*, 283. (c) Corbett, J. D. *Struct. Bonding* **1997**, *87*, 157.

(32) Queneau, V.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1754.

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

(34) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(35) (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.

(36) (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(37) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

(38) Pople, J. A.; Raghavachari, K.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 255.

(39) (a) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431. (b) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245. (c) d-polarization functions from: Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis sets for Molecular Calculations*; Elsevier: New York, 1984.

(40) 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. S.; Gomperts, R.; Andres, J. L.; Raghavacharei, K.; Binkley, J. S.; Gonzalez, G.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92, Revision A, Gaussian, Inc.: Pittsburgh, PA, 1992.

Table 1. Relative Energies[a] (kcal/mol) of Calculated Structures at HF and MP2 and at B3LYP Levels Using the 6-31G* Basis Set for C and Si and the LANL1DZ Basis Set for Ge, Sn, and Pb

compd	HF	MP2	B3LYP	B3LYP/TZ2P+
1-C	0.0 (0)	0.0 (0)	0.0 (0)	
2-C	106.4 (2)	84.2 (2)	87.6 (2)	
6-C	359.7 (8)	275.0 (8)	295.3 (8)	
7-C	155.7 (4)	121.8 (4)	127.5 (4)	
8-C	collapsed			
9-C	collapsed to **1**			
10-C	−19.16 (0)	−9.5 (0)	−9.2 (0)	
1-Si	0.0 (2)	0.0 (2)	0.0 (0)	
2-Si	−12.4 (0)	−20.7 (0)	−27.2 (0)	
6-Si	102.1 (3)	49.6 (2)	50.6 (2)	
7-Si	7.9 (0)	−2.9 (0)	−14.1 (0)	
8-Si	collapsed to **2**			
9-Si	9.95 (0)	−2.2 (0)	−1.7 (2)	
10-Si	−48.6 (0)	−49.4 (0)	−47.0 (0)	
1-Ge	0.0 (3)	0.0 (0)	0.0 (3)	0.0
2-Ge	−54.0 (0)	−55.6 (0)	−57.6 (0)	−72.3
6-Ge	34.8 (3)	1.4 (0)	2.2 (0)	−24.6
7-Ge	−45.1 (0)	−46.8 (0)	−52.8 (0)	−78.0
8-Ge	−41.0 (0)	collapsed to **2**	−48.9 (0)	−72.4
9-Ge	collapsed to **11**			−38.4
10-Ge	−68.5 (0)	−68.3 (0)	−64.2 (0)	−72.3
11-Ge	−39.6 (0)	−18.8 (0)	−23.7 (0)	
1-Sn	0.0 (3)	0.0 (0)	0.0 (3)	0.0
2-Sn	−74.9 (0)	−69.3 (0)	−70.6 (0)	−74.1
6-Sn	−9.6 (3)	−32.3 (0)	−30.6 (0)	−37.7
7-Sn	−75.6 (0)	−66.0 (0)	−71.1 (0)	−82.2
8-Sn	−73.1 (0)	−66.1 (0)	−69.9 (0)	−77.1
9-Sn	collapsed to **11**			
10-Sn	−69.1 (0)	−66.0 (0)	−62.9 (0)	−67.1
11-Sn	−52.1 (0)	−31.3 (0)	−35.3 (0)	−37.1
1-Pb	0.0 (3)	0.0 (0)	0.0 (3)	0.0
2-Pb	−120.4 (0)	−111.4 (0)	−102.3 (0)	−104.7
6-Pb	−79.4 (3)	−92.9 (0)	−80.9 (0)	−77.4
7-Pb	−134.5 (0)	−119.8 (0)	−114.3 (0)	−122.9
8-Pb	−133.3 (0)	−121.7 (0)	−114.7 (0)	−117.8
9-Pb	collapsed to **11**			
10-Pb	−103.4 (0)	−93.4 (0)	−84.4 (0)	−92.8
11-Pb	−93.5 (0)	−72.0 (0)	−67.7 (0)	−74.1

[a] The relative energies are calculated after scaling the zero point energy by 0.9. [b] The last column is the relative energies of Ge, Sn, and Pb structures using the TZ2P+ basis set with relativestic psuedo-potentials at B3LYP level). The values in the parentheses are the number of imaginary frequencies.

LANL1DZ+ZPE level for Ge, Sn, and Pb. Zero-point energies were scaled by 0.9.[33] The natural bond orbital (NBO) analysis at the HF level and the geometries at the MP2 level are used in the discussion.[41]

Results and Discussions

There are many theoretical calculations available in the literature on **1-C** and **1-Si**.[1,30] Structure **1** is a minimum for C to Pb, except for Si, in which it is a second order saddle point (Table 1). However, the results at the HF and B3LYP levels are different. Structure **1** is a minimum for C and Si and a third-order saddle point for Ge to Pb at these levels. The A–A bond lengths are compared with the ethane-like structures (A_2H_6)[42] and 3-membered-ring structures.[13] The A–A distances in **1-C** and **1-Si** (Table 2) are found to be slightly shorter than those in A_2H_6 (C 1.542 Å; Si 2.342 Å) and cyclic A_3H_6 (C 1.504 Å; Si 2.332 Å). But for **1-Ge** to **1-Pb**, the A–A bond distances are elongated compared with A_2H_6 (Ge 2.499 Å; Sn 2.850 Å; Pb 3.012 Å) and cyclic A_3H_6 (Ge 2.496 Å; Sn 2.860 Å; Pb 2.954 Å). The bonding in **1** is found to be classical.

The triply H-bridged structure, **2**, is more stable than the classical structure **1** by 20.7, 55.6, 69.3, 111.4 kcal/mol for Si

(41) (a) Read, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*; Naaman, R., Vager, Z., Eds.; Plenum: New York, 1988; p 277.

(42) Schleyer, P. v. R.; Kaupp, M.; Hampel, F.; Bremer, M.; Mislow, K. *J. Am. Chem. Soc.* **1992**, *114*, 6791.

Table 2. Important Geometrical Parameters of the Optimized Structures at the MP2 Level (Distances in Å and Angles in Degrees)

compd	parameter	calcd value	compd	parameter	calcd value	compd	parameter	calcd value
1-C	C−C	1.477	**2−Ge**	Ge(1)−Ge(2)	3.162	**10−Sn**	Sn(1)−Sn(2)	2.870
	C−H	1.073		Ge(1)−Ge(4)	2.544		Sn(2)−Sn(3)	2.889
2-C	C(1)−C(2)	1.732		Ge(1)−H(5)	1.848		Sn(1)−H(5)	1.722
	C(1)−C(4)	1.465		Ge(4)−H(8)	1.529		Sn(1)−H(6)	1.727
	C(1)−H(5)	1.288		θ_1	28.79		Sn(2)−H(7)	1.742
	C(4)−H(8)	1.078	**6−Ge**	Ge(1)−Ge(2)	3.080		H(5)−Sn(1)−H(6)	107.74
	θ_1	29.23		Ge(1)−H(5)	1.964		Sn(2)−Sn(3)−Sn(1)−Sn(4)	163.04
6-C	C(1)−C(2)	1.736	**7−Ge**	Ge(1)−Ge(2)	3.152	**11-Sn**	Sn(1)−Sn(4)	2.927
	C(1)−H(5)	1.406		Ge(1)−Ge(4)	2.574		Sn(1)−Sn(2)	4.601
7-C	C(1)−C(2)	1.773		Ge(1)−H(5)	1.839		Sn(1)−H(5)	1.785
	C(1)−C(4)	1.448	**10−Ge**	Ge(1)−Ge(2)	2.505		Sn(4)−H(8)	1.733
	C(1)−H(5)	1.289		Ge(2)−Ge(3)	2.527		Sn(4)−H(5)	3.436
10-C	C(1)−C(2)	1.498		Ge(1)−H(5)	1.548	**1-Pb**	Pb-Pb	3.111
	C(2)−C(3)	1.432		Ge(2)−H(7)	1.565		Pb-H	1.782
	C(1)−H(5)	1.085		Ge(2)−Ge(3)−Ge(1)−Ge(4)	159.53	**2-Pb**	Pb(1)−Pb(2)	3.645
	C(2)−H(7)	1.089		H(5)−Ge(1)−H(6)	109.92		Pb(1)−Pb(4)	2.978
	C(2)−C(3)−C(1)−C(4)	143.66	**11-Ge**	Ge(1)−Ge(4)	2.572		Pb(1)−H(5)	2.067
	H(5)−C(1)−H(6)	113.84		Ge(1)−Ge(2)	3.981		Pb(4)−H(8)	1.739
1-Si	Si-Si	2.315		Ge(1)−H(5)	1.615		θ_1	27.64
	Si-H	1.478		Ge(4)−H(8)	1.557	**6-Pb**	Pb(1)−Pb(2)	3.460
2-Si	Si(1)−Si(2)	2.715		Ge(4)−H(5)	3.053		Pb(1)−H(5)	2.175
	Si(1)−Si(4)	2.283	**1-Sn**	Sn-Sn	2.927	**7-Pb**	Pb(1)−Pb(2)	3.691
	Si(1)−H(5)	1.695		Sn-H	1.719		Pb(1)−Pb(4)	3.013
	Si(4)−H(8)	1.469	**2-Sn**	Sn(1)−Sn(2)	3.555		Pb(1)−H(5)	2.066
	θ_1	30.0		Sn(1)−Sn(4)	2.908	**8-Pb**	Pb(1)−Pb(2)	3.632
6-Si	Si(1)−Si(2)	2.658		Sn(1)−H(5)	2.010		Pb(1)−Pb(3)	3.456
	Si(1)−H(5)	1.764		Sn(4)−H(8)	1.703		Pb(1)−Pb(4)	3.166
7-Si	Si(1)−Si(2)	2.764		θ_1	27.20		Pb(2)−Pb(4)	3.630
	Si(1)−Si(4)	2.257	**6-Sn**	Sn(1)−Sn(2)	3.398		Pb(1)−H(5)	2.046
	Si(1)−H(5)	1.711		Sn(1)−H(5)	2.126		Pb(1)−H(7)	2.070
9-Si	Si(1)−Si(2)	2.507	**7-Sn**	Sn(1)−Sn(2)	3.605		Pb(2)−H(8)	1.962
	Si(1)−Si(4)	2.324		Sn(1)−Sn(4)	2.943		Pb(4)−H(8)	2.072
	Si(1)−H(5)	1.604		Sn(1)−H(5)	2.010	**10-Pb**	Pb(1)−Pb(2)	2.985
	Si(4)−H(8)	1.473	**8-Sn**	Sn(1)−Sn(2)	3.573		Pb(2)−Pb(3)	3.035
10-Si	Si(1)−Si(2)	2.314		Sn(1)−Sn(3)	3.396		Pb(1)−H(5)	1.768
	Si(2)−Si(3)	2.283		Sn(1)−Sn(4)	3.091		Pb(1)−H(6)	1.769
	Si(1)−H(5)	1.483		Sn(2)−Sn(4)	3.580		Pb(2)−H(7)	1.822
	Si(2)−H(7)	1.494		Sn(1)−H(5)	2.002		H(5)−Pb(1)−H(6)	103.79
	Si(2)−Si(3)−Si(1)−Si(4)	154.72		Sn(1)−H(7)	2.015		Pb(2)−Pb(3)−Pb(1)−Pb(4)	170.97
	H(5)−Si(1)−H(6)	110.90		Sn(2)−H(8)	1.900	**11-Pb**	Pb(1)−Pb(4)	2.985
1-Ge	Ge-Ge	2.546		Sn(4)−H(8)	2.041		Pb(1)−Pb(2)	4.658
	Ge-H	1.542					Pb(1)−H(5)	1.834
							Pb(4)−H(8)	1.772
							Pb(4)−H(5)	3.500

to Pb, respectively (Table 1), and is a minimum. Structure **2-C** is a second-order saddle point and higher in energy than **1-C**. The A−A bridged bonds in **2-Si** to **2-Pb** are shortened to a large extent (Table 2) compared to the A−A bridged bonds in triply H-bridged cyclopropane analogs (Si 3.080 Å; Ge 3.417 Å; Sn 3.783 Å; Pb 3.889 Å).[13] However, the A−H$_b$ distance in **2** is slightly longer than the corresponding distance in triply H-bridged cyclopropane. The unbridged A−A distance is slightly shorter than the corresponding distance in the classical structure **1**. The nonplanarity of bridging hydrogens (that is the angle between the A$_3$ plane and the AHA plane, θ_1) is nearly constant (∼28.4°) for **2-Si** to **2-Pb**. The NBO analysis gives the following bonding in **2**: three 2c−2e classical A−A bonds, three 3c−2e H-bridged A−A bonds, and a lone pair on each divalent A.

The T_d structure, **6**, where the four hydrogens bridge the four faces of A$_4$, is a minimum for Ge, Sn, and Pb at the MP2 and B3LYP levels and a higher order stationery point at the HF level (Table 1). For C and Si, **6** is a higher order saddle point. **6-Sn** and **6-Pb** are 32.3 and 92.9 kcal/mol more stable than **1-Sn** and **1-Pb**. But **6-Ge** is 1.4 kcal/mol less stable than **1-Ge**. The A−A distance in **6** (Table 2) is calculated to be shorter than the H-bridged A−A distance in isomer **2** and triply H-bridged A$_3$H$_6$. However, the A−H distance is elongated in **6** compared to **2** and A$_3$H$_6$ (Table 2). The electronic structure of **6** can be analyzed better by the fragment molecular orbital (FMO) method[43] (since a localized picture cannot be attained

for **6** by the NBO method). The molecule is divided into A$_4$ (T_d) and H$_4$ (T_d) fragments. The interaction diagram between A$_4$ and H$_4$ leading to A$_4$H$_4$ (**6**) is shown in Figure 1. The 1a$_1$ orbital of A$_4$ is an all-symmetric combination of s orbitals and the 2a$_1$ is an sp-hybridized orbital on heavy atoms. Hence, these two MOs lead to the lone pair on A and an electron density at the centroid of the A$_4$ tetrahedrane.[44] The 1t$_2$ and 2t$_2$ MOs of A$_4$ mainly contribute to the formation of the A−A bonds and lone pair on A in A$_4$, and by the tetrahedral symmetry these lead to significant electron density at the center of the tetrahedral faces.[44] The 1a$_1$ and 1t$_2$ orbitals of H$_4$ interact with the 1a$_1$, 2a$_1$, 1t$_2$, and 2t$_2$ orbitals of A$_4$ leading to 1a$_1$, 2a$_1$, 1t$_2$, and 2t$_2$ in A$_4$H$_4$, respectively. Hence these orbitals contribute to the surface bonding of H$_4$ on the A$_4$ tetrahedrane. The 1e set of orbitals of A$_4$ lead to A−A bonds and by symmetry it has null density at the center of the tetrahedrane face, hence, no interaction with the H$_4$ fragment.

In Structures **7** and **8**, the four hydrogens bridge the edges of the A$_4$ cage. The main difference between **7** and **8** is that the unbridged A−A bonds in **7** are opposite to each other

(43) (a) Fujimoto, H.; Hoffmann, R. *J. Phys. Chem.* **1974**, *78*, 1167. (b) The interaction diagram in Figure 1 is drawn for **6-Sn**. The extended Huckel parameters for Sn [5s (−16.16, 2.32), 5p (−8.32, 1.94)] and H [1s (−13.6, 1.3)] are from the following: Tremel, W.; Hoffmann, R. *Inorg. Chem.* **1987**, *26*, 118. Jørgensen, K. A.; Wheeler, R. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1987**, *109*, 3240.

(44) Hoffmann, R.; Schilling, B. E. R.; Bau, R.; Kaesz, H. D.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1978**, *100*, 6088.
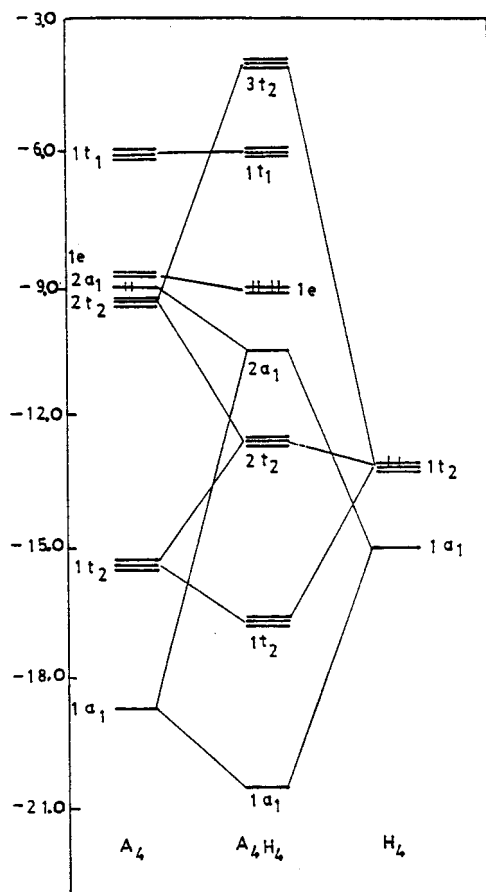
Figure 1. Interaction diagram between A_4 (T_d) and H_4 (T_d) leading to A_4H_4 (T_d). The HOMO of A_4 and A_4H_4 is $2a_1$ and $1e$, respectively. The HOMO of H_4 is a triply degenerate $1t_2$ with only two electrons in it.

whereas in **8** they are adjacent. **7** is a minimum for Si to Pb and is calculated to be more stable than the classical structure, **1**, by 2.9, 46.8, 66.0, and 119.8 kcal/mol for Si, Ge, Sn, and Pb, respectively. Structure **8** is a minimum for Sn and Pb and collapses to **2** on optimization for Si and Ge! However, **8** exists for Ge to Pb at both HF and B3LYP levels and it is a minimum (Table 1). On optimization, **8-C** gets dismantled by breaking the H-bridged C—C bonds. **8-Sn** and **7-Sn** are energetically degenerate, whereas **8-Pb** is 1.8 kcal/mol more stable than **7-Pb**. The H-bridged A—A bond distances for **7-Si** to **7-Pb** are very close to the corresponding distances in **2** (Table 2) and shorter compared to the triply H-bridged cyclic A_3H_6 structure.[13] However, these distances in **8-Sn** and **8-Pb** are slightly shorter compared to **7-Sn** and **7-Pb**, respectively (Table 2). The NBO analysis shows the following bonding in **7**: four 3c—2e H-bridged A—A bonds, two 2c—2e A—A bonds, and a lone pair on each A. A similar type of bonding was observed in **8-Sn** and **8-Pb** as well.

The second triply H-bridged structure, **9**, is minimum only for Si! For Ge to Pb, **9** collapses to **11** (C_{3v}) on optimization

11
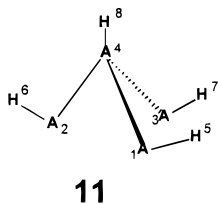
and for C it collapses to **1**. **9-Si** is 2.2 kcal/mol more stable than the classical structure **1**. The H-bridged Si—Si bonds

(2.314 Å) are much shorter than what is found in **2-Si** and **7-Si**. The unbridged Si—Si bonds (2.507 Å) in **9-Si** are longer than the unbridged Si—Si bonds in **2-Si** and **7-Si**. The NBO analysis has shown an interesting bonding feature for this isomer. There is a lone pair on each Si(1), Si(2), and Si(3). The Si(4)—H(8) bond is a classical 2c—2e type. The remaining bonds, Si(1)—H(5)—Si(4), Si(3)—H(7)—Si(4), Si(2)—H(6)—Si(4), Si(4)—Si(1)—Si(2), Si(4)—Si(1)—Si(3), and Si(4)—Si(2)—Si(3), are found to be 3c—2e bonds. This type of bonding picture should lead to longer Si(1)—Si(2), Si(1)—Si(3), and Si(2)—Si(3) bond distances and shorter Si(4)—Si(1), Si(4)—Si(2), and Si(4)—Si(3) bond distances, as is indeed found by calculation (Table 2). Isomer **11** is minimum for Ge, Sn, and Pb. It is less stable than **7** and more stable than the classical T_d structure **1** (Table 1). The A—A bond in **11-Ge** is slightly longer than that in **1**, whereas in **11-Sn**, it is equivalent to that in **1** and in **11-Pb** it is less than that in **1** (Table 2). The bonding in **11** is traced to be a classical 2c—2e bond between A—A. There are three lone pairs, one each on the divalent atom A.

Isomer **10**, which is the lowest energy structure for Si_4H_4, so far, is also computed in the present study.[30] It is a minimum for C, Ge, Sn, and Pb as well. Structure **10** is 9.5, 49.4, 68.3, 66.0, and 93.4 kcal/mol more stable than **1** for C, Si, Ge, Sn, and Pb, respectively. The nonplanarity of the A_4 ring decreases from **10-C** to **10-Pb** (Table 2). The A(1)—A(2) and A(2)—A(3) distances are shorter in **10-C** and **10-Si** and longer in **10-Sn** and **10-Pb** compared to cyclic A_4H_8 (C—C 1.545 Å; Si—Si 2.355 Å; Sn—Sn 2.862 Å; Pb—Pb 2.914 Å).[14] However, in **10-Ge** these distances are very close to that in cyclic A_4H_8 (2.510 Å). The NBO analysis shows a classical 2c—2e bond between A(1)—A(2), A(2)—A(3), A(3)—A(4), and A(1)—A(4) forming a four-membered ring. The bonding of hydrogens with the heavy atoms is also found to be the classical 2c—2e type. A(3) is a divalent atom with a lone pair. The extra two electrons, one each from A(2) and A(4), make use of the empty p orbital on A(3), forming a 3c—2e delocalized π-bond.

Calculations with the quasirelativistic pseudopotential basis set (TZ2P+) for Ge, Sn, and Pb have shown the following results. For Ge the D_{2d} structure **7** has become more stable than the four-membered-ring structure **10**. Interestingly the T_d structure **6** is 24.6 kcal/mol more stable than the classical structure **1** for Ge, whereas it is 2.2 kcal/mol higher in energy than **1** with the LANL1DZ basis. Similarly, **9-Ge** exists at this level and it is 38.4 kcal/mol more stable than the classical structure **1-Ge**. Sn has not shown any difference in results with the LANL1DZ basis, except all the structures became more stable than the classical structure **1**. In the case of Pb there is a difference in the stability order of **7** and **8**. At the LANL1DZ basis, **7** and **8** are nearly isoenergetic, whereas at the TZ2P+ basis the D_{2d} structure **7** is more stabilized and 5.1 kcal/mol lower in energy than **8**. Thus with relativistic pseudopotentials the D_{2d} structure **7** is the most stable among the structures considered in the present study for Ge, Sn, and Pb.

The remarkable differences in stability of the isomers from C to Pb are due to strong reluctance of the heavier atoms to form s—p hybrid orbitals. It is mainly due to the difference in the size of the valence ns and np atomic orbitals (the difference increases from Si to Pb) and in their energies.[45] This is also evident from the NBO analysis. The lone pair orbitals in isomers **6**, **7**, **8**, **9**, and **11** have predominant s character ($\sim$75

(45) (a)Nagase, S. *Acc. Chem. Res.* **1995**, *28*, 469. (b) Nagase, S.; Kobayashi, K.; Kudo, T. *Main. Group Met. Chem.* **1994**, *17*, 171. (c) Kudo, T.; Nagase, S. *Rev. Heteroat. Chem.* **1993**, *8*, 122. (d) Nagase, S. *Polyhedron* **1991**, *10*, 1299. (e) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (f) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

to 90% for Si to Pb). This leaves maximum p character for the other bonds in these isomers. The gradual decrease in the s−p mixing for these elements is clearly reflected in the relative stabilities of the tetrahedrane isomers studied here. The classical T_d structure **1** is more stable for C and the triply H-bridged C_{3v} structure **2** (contains one classical and three divalent Si atoms) is more stable for Si. However, for Ge to Pb the quadruply H-bridged D_{2d} structure **7** is found to be most the stable structure. If one considers all four H-bridged systems **6**, **7**, and **8** alone, the relative stabilities are as explained below. Leaving the four lone pairs in these systems (**6**, **7**, and **8**), isomers **7** and **8** have two 2c−2e A−A bonds and four 3c−2e H−bridged bonds with twelve valence electrons (established by NBO analysis). On the other hand, **6** has 4c−3e type bonding (as established by FMO method) with the four capping H atoms. This makes **6** less stable compared to **7** and **8**.

Therefore the results in the present study provide the qualitative and quantitative differences of C with the heavier analogs, Si to Pb, for the tetrahedranes. The structures derived from the organometallic chemistry are competitive for heavier elements (Si to Pb) compared to the classical structure adopted by the C. The present study suggests that the periodic variations start with the second period only. The elements Li to Ne are the exceptions.[27,45] Though structure **2-Si** is 20.7 kcal/mol more stable than **1-Si**, the tetrahedral structure observed for Si₄R₄ experimentally points to the effect of substituents in controlling the structures; the propensity for bridging does not seem to go beyond hydrogens.[10]

We feel that the best way to obtain various tetrahedral structures discussed here is by adding protons to the A_4^{4-} (T_d) system. The attack of H⁺ ions on atom A in A_4^{4-} leads to structure **1** (path I). If the H⁺ attacks A−A bonds, isomers **7** and **8** can be obtained (path II). On the other hand, if H⁺ attacks on the A₃ faces, the T_d structure **6** is the result (path III). Structures **2** and **9** (for Si) can be achieved by the mixed paths of I and II.
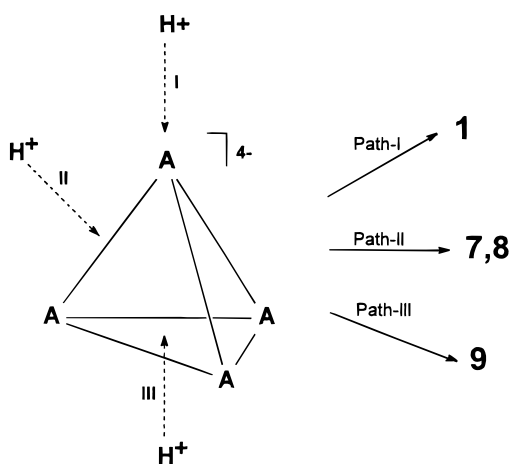
One interesting observation in this direction is the crystal structure of NaPb.[31] The Pb atoms in the unit cell of NaPb are arranged in regular tetrahedral units (Pb₄). Each Pb₄ group is surrounded by sodium atoms. Thus one might see NaPb in the solid state as Pb_4^{4-} (T_d) ions surrounded by Na⁺ ions. The greater reactivity of NaPb toward the alkyl halides is explained in terms of gradual removal of sodium atoms by halides, with consequent exposure of lead atoms to allyl radicals.[31] Quite possibly a similar mechanism, where NaPb is treated with protic acids, might lead to various tetrahedral structures discussed for Pb in this study via paths I, II, or III. Equation 1 is highly exothermic due to the charges that are involved. Similar experiments can also be tried with the structures that contain Si_4^{4-} and Ge_4^{4-}.[31,32] We expect that these experimental studies are in the realm of possiblility.

$$Pb_4^{4-} + 4H^+ \rightarrow Pb_4H_4 \qquad (1)$$

Summary and Conclusions

Only C has shown the classical T_d structure to be more favorable, among the tetrahedrane structures considered here. Si and Ge prefer the triply H-bridged structure, **2**, over the other bridged structures at the MP2/6-31G* level. But isomer **10** is 28.7 and 12.7 kcal/mol more stable than **2** for Si and Ge, respectively. However, for Sn, **2** is the lowest energy isomer, even lower than **10** by 3.3 kcal/mol. Interestingly, **7-Sn**, **8-Sn**, and **10-Sn** are very close in energy. The situation in Pb is entirely different. The most stable isomer for Pb obtained in the present study is the four H-bridged C_s structure, **8**. The D_{2d} structure, **7**, and the C_{3v} structure, **2**, are 1.9 and 10.3 kcal/mol higher in energy than **8**. Compared to **10-Pb**, **8-Pb** is more stable by 28.3 kcal/mol. But the calculations with quasirelativistic pseudopotentials show structure **7** to be the most stable structure for Ge, Sn, and Pb. This study further supports the relation between the organometallic and main group chemistry by various analogies. Although the parent tetrahedranes **1-C** and **1-Si** are not known experimentally, the structural and the energetic differences of Si to Pb and C make them excellent experimental targets. These H-bridged structures may be generated experimentally from the tetraanions, A_4^{4-}, known already.[31,32]

Supporting Information Available: Table S1 summarizing the total energies and zero-point energies of all the isomers studied (1 page). See any current masthead page for ordering and Internet access instructions.

JA972070K