Ions Related to Silynes and Disilynes: Computational Studies

Robert Damrauer* and Anna Louise Noble

Chemistry Department, Downtown Campus, University of Colorado, Denver Campus, Box 194, P.O. Box 173364, Denver, Colorado 80217-3364

Received December 5, 2007

Ab initio computational studies of two series of silicon-containing compounds related to disilyne and silyne, HSiSiH and HSiCH, have been carried out. Studies of these [2H,2Si] and [2H,C,Si] series probe the relationships between the structural characteristics of the parent compounds and various associated radical cation, radical anion, singlet dianion, and triplet dianion species. Various new species are reported: trans HSiSiH radical anion, triplet H_2SiSi dianion, three [2H,C,Si] radical anions, four [2H,C,Si] singlet dianions, and three [2H,C,Si] triplet dianions. Additional computations of species previously reported have been carried out to provide a large data set computed under identical conditions. Optimizations at the MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p) level as well as coupled cluster [CCSD(T)] single-point energy computations on all the unique optimized species are reported. It was necessary to include f functions to locate certain geometries in computations without symmetry constraints. Energy and geometry relationships are discussed. The computations allow the determination of various thermodynamic relationships: ionization energies, electron affinities, and singlet–triplet splittings.

Introduction

Multiply bonded silicon species, silicon−carbon, silicon−silicon, and silicon−heteroatom, have been studied over a long period, yet continue to be of substantial interest.[1–23] Such studies have led to important questions: (1) what are the similarities and differences with analogous stable carbon−carbon and carbon−heteroatom multiply bonded species and (2) what unusual structural features do silicon-containing multiply bonded analogues exhibit that corresponding carbon species do not? That doubly bonded silicon molecules can be synthesized, but must be sterically hindered for isolation, makes clear that the silicon−carbon double bond is quite reactive.[24–28] Concomitant with this synthetic work are many computational studies examining the stability of isomeric [4H,C,Si] species. Even the seemingly simple question of the most stable [4H,C,Si] isomer was finally placed in perspective by Schaefer[22] and updated by Apeloig.[2,29] Their reviews summarize the computational studies on silaethylene and methylsilylene (H_3CSiH), indicating their near energy equality on the [4H,C,Si] potential energy surface. Some of the lessons learned in comparing doubly bonded carbon species with silicon analogues are that (1) computational studies are excellent guides that inform sometimes difficult experimentation,[2,29] (2) silicon provides some interesting structural and bonding alternatives to those seen in carbon molecules, and (3) silicon does not readily form isolable double bonds.

---

* Corresponding author. E-mail: robert.damrauer@cudenver.edu.

(1) *The Chemistry of Organic Silicon Compounds*; John Wiley and Sons: Chichester, 1989; Vol. 1.

(2) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds in The Chemistry of Functional Groups Series*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; Vol. 1, pp 57–225.

(3) *The Chemistry of Organic Silicon Compounds*; John Wiley and Sons: Chichester, 1998; Vol. 2.

(4) *The Chemistry of Organic Silicon Compounds*; John Wiley and Sons: Chichester, 2001; Vol. 3.

(5) Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: Chichester, 1998; Vol. 2, pp 857–1062.

(6) Karni, M.; Kapp, J.; Schleyer, P. v. R.; Apeloig Y. In *The Chemistry of Organic Silicon Compounds in The Chemistry of Functional Groups*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: Chichester, 2001; Vol. 3, pp 1–163.

(7) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds in The Chemistry of Functional Groups*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: Chichester, 2001; Vol. 3, pp 391–428.

(8) Danovich, D.; Ogliaro, F.; Karni, M.; Apeloig, Y.; Cooper, D. L.; Shaik, S. *Angew. Chem. Int. Ed.* **2001**, *40*, 4023–4026.

(9) Apeloig, Y.; Karni, M. *Organometallics* **1997**, *16*, 310–312.

(10) Weidenbruch, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 514–516.

(11) Lischka, H.; Köhler, H.-J. *J. Am. Chem. Soc.* **1983**, *105*, 6646–6649.

(12) Sekiguchi, A.; R., K.; Ichinohe, M. *Science* **2004**, *305*, 1755–1757.

(13) Grunenberg, J. *Angew. Chem. Int. Ed.* **2001**, *40*, 4027–4029.

(14) Karni, M.; Apeloig, Y.; Schröder, D.; Zummack, W.; Rabezzana, R.; Schwarz, H. *Angew. Chem. Int. Ed.* **1999**, *38*, 332–335.

(15) Damrauer, R.; DePuy, C. H.; Barlow, S. E.; Gronert, S. *J. Am. Chem. Soc.* **1988**, *110*, 2005–6.

(16) Kosa, M.; Karni, M.; Apeloig, Y. *J. Chem. Theory Comput.* **2006**, *2*, 956–964.

(17) Apeloig, Y.; Albrecht, K. *J. Am. Chem. Soc.* **1995**, *117*, 7263–7264.

(18) Wiberg, N.; Niedermayer, W.; Fischer, G.; Nöth, H.; Suter, M. *Eur. J. Inorg. Chem.* **2002**, *2002*, 1066–1070.

(19) Wiberg, N.; Vasisht, S. K.; Fischer, G.; Mayer, P. Z. *Anorg. Allg. Chem.* **2004**, *630*, 1823–1828.

(20) Sekiguchi, A.; Ichinohe, M.; Kinjo, R. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 825–832.

(21) Kravchenko, V.; R., K.; Sekiguchi, A.; Ichinohe, M.; West, R.; Balazs, Y. S.; Schmidt, A.; Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **2006**, *126*, 825–832.

(22) Power, P. P. *Organometallics* **2007**, *26*, 4362–4372.

(23) Takahashi, M.; Kawazoe, Y. *Organometallics* **2005**, *24*, 2433–2440.

(24) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds in The Chemistry of Functional Groups Series*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; pp 1015–1142.

(25) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *Chem. Commun.* **1981**, *1981*, 191–2.

(26) Wiberg, N.; Wagner, G.; Mueller, G. *Angew. Chem. Int. Ed.* **1985**, *24*, 229–31.

(27) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343–1344.

(28) Morkin, T. L.; Owens, T. R.; Leigh, W. J. In *The Chemistry of Organic Silicon Compounds in The Chemistry of Functional Groups*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: Chichester, 2001; Vol. 3, pp 949–1026.

(29) Schaefer, H. F. *Acc. Chem. Res.* **1982**, *15*, 283–190.

10.1021/om701220s CCC: $40.75

Computational studies of ethyne-related silicon species, [2H,2Si] and [2H,C,Si], and their charged species are the subject of this report. Significant computational work on such species has been carried out already by many workers and will be summarized briefly along with selected related experimental findings. In these reports and here, questions similar to those just considered for silicon−carbon double-bond species are considered.

Neutral Carbon Species. Ethyne and its singlet isomer vinylidene, $H_2C{=}C$, have been studied in great detail experimentally and computationally.[30–36] Singlet vinylidene is less stable than ethyne by about 45 kcal/mol and has not been isolated because its interconversion barrier to ethyne is low. Nevertheless, it "resides" in a shallow potential energy well of ~2 kcal/mol that allows its detection.[30,36] The experimental studies of Ervin, Ho, and Lineberger as well as a recent computational study by Liévin and co-workers have characterized this system in detail.[30,36]

Cationic Carbon Species. The recent computational study by Liévin and co-workers of the radical cations $[2H,2C]^{\bullet+}$ (both acetylene and vinylidene in various electronic states) not only indicates certain similarities between the potential energy surfaces of the neutral and cationic acetylene−vinylidene couple but provides an excellent up-to-date review of the neutral and cationic studies carried out through 2006.[36] Thus, the vinylidene radical cation is higher in energy than the corresponding acetylene radical cation by about 43 kcal/mol. It resides in a very shallow potential energy well with no barriers of sufficient height to allow its detection or isolation, consistent with the experimental facts.[36] An intrinsic reaction coordinate (IRC) of the vinylidene radical cation ($^2A_1$) to acetylene radical cation ($^2\Pi_u$) shows a remarkable similarity to the corresponding neutral IRC.

Anionic Carbon Species. $[HCCH]^{\bullet-}$, the radical anion of ethyne, is unstable with respect to electron loss in the gas phase despite the presumed importance of similar radical anions as intermediates in dissolving metal reductions of dialkylalkynes.[37–43] Vinylidene radical anion, $[H_2CC]^{\bullet-}$, in contrast, has been studied both experimentally and computationally, particularly in efforts to understand the vinylidene−acetylene "couple" (resulting from electron detachment of vinylidene radical anion).[30,31] Various electronic states of vinylidene as well as its vibrational structure have been reported, all accessed by photoelectron–electron detachment studies of the anion.[30,31] The lifetime of vinylidene has been estimated to be ~0.04–2 ps.[27] Such gas-phase studies emphasize the stability of vinylidene radical anion with respect to acetylene radical anion.

Isolation of the corresponding dianions of acetylene and vinylidene has not been reported, although computational studies have.[43] Dianions in the gas phase are known to be unstable unless some unusual structural features provide stability, which is normally not the case with small dianions.[44–47]

Neutral Ethyne-Related Silicon Species ([2H,2Si] and [2H,C,Si]). A recent review by Power has summarized the bonding and reactivity of group 14 "alkyne-related" analogues.[22] Particular attention is paid to experiments that have produced stable compounds with the equivalent of the silicon−silicon triple bond. These have been prepared by Wiberg and Sekiguchi and their respective co-workers.[12,18–21] The first X-ray structure of the silicon−silicon triply bonded compound $[[(Me_3Si)_2CH]_2(i\text{-}Pr)Si]_2$ was reported by Sekiguchi and co-workers in 2004.[12] Although there is some controversy about the triply bonded nature of these bonds, Power argues persuasively for a triple-bond formulation.[22]

Several spectroscopic studies have carefully characterized $H_2C{=}Si$. Initial work by Leclercq and Dubois reported the preparation and detailed rotational spectra of this species and labeled analogues.[48] A more recent report has examined forbidden transitions in $H_2C{=}Si$ and $D_2C{=}Si$.[49]

As important are computational studies of both silicon−silicon and carbon−silicon species to assess the importance of various structures that are not perturbed by bulky substituents. These have been reviewed thoroughly, leading to the following general conclusions (at least):[2,6,7,10,24,28,50–52] (1) a doubly hydrogen bridged (butterfly) structure, $[Si(H_2)Si]$, is the most stable of several [2H,2Si] isomers, (2) the only [2H,2Si] species having HSiSiH connectivity has a trans structure and a higher energy than the doubly bridged structure, (3) H_2CSi is the most stable of several possible [2H,C,Si] species, and (4) the only [2H,C,Si] species having HCSiH connectivity has a trans structure and an energy higher than H_2CSi.

Cationic Ethyne-Related Silicon Species ($[2H,2Si]^{\bullet+}$ and $[2H,C,Si]^{\bullet+}$). Analogous cationic species of both the 2Si and C,Si variety have been studied in some detail, both experimentally[53,54] and computationally.[55–58] The gas-phase experimental studies have been directed at beginning to understand the details of plasma interactions among ions and neutral molecules with the eventual goal of controlling silicon film formation. Such studies, where only mass spectroscopic data (*m*/*z*) result, require either additional experimentation or computational guidance to garner structural information.[53,54] Thus, structural and mechanistic information obtained computationally has been critical.[55–58]

---

(30) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 5974–5992.

(31) Stanton, J. F.; Gauss, J. *J. Chem. Phys.* **1999**, *110*, 6079–6080.

(32) Jensen, M. J.; Pederson, U. V.; Anderson, L. H. *Phys. Rev. Lett.* **2000**, *84*, 1128–1131.

(33) Zou, S.; Bowman, J. M. *J. Chem. Phys.* **2002**, *117*, 5507–5510.

(34) Zou, S.; Bowman, J. M. *J. Chem. Phys.* **2003**, *118*, 10012–10023.

(35) Osamura, Y.; Schaefer, H. F.; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904–1907.

(36) Boÿe-Péronne, S.; Gauyacq, D.; Liévin, J. *J. Chem. Phys.* **2006**, *124*, 214305–1214305–14.

(37) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F.; Nandi, S.; Ellison, G. B. *Chem. Rev.* **2002**, *102*, 231–282.

(38) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341–348.

(39) Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557–588.

(40) Huang, M.-B.; Liu, Y. *J. Phys. Chem. A* **2001**, *105*, 923–929.

(41) Wang, X.-B.; Wang, L.-S. *Nature* **1999**, *400*, 245–248.

(42) Jordon, K. D.; Wang, F. *Annu. Rev. Phys. Chem.* **2003**, *54*, 367–396.

(43) Damrauer, R. *J. Org. Chem.* **2006**, *71*, 9165–9171.

(44) Dreuw, A.; Cederbaum, L. S. *Chem. Rev.* **2002**, *102*, 181–200.

(45) Sommerfeld, T. *J. Phys. Chem.* **2000**, *104*, 8806–8813.

(46) Wang, X.-B.; Yang, X.; Nicholas, J. B.; Wang, L.-S. *Science* **2001**, *294*, 1322–1325.

(47) Roos, G.; DeProft, F.; Geerlings, P. *J. Phys. Chem.* **2005**, *109*, 652–658.

(48) Leclercq, H.; Dubois, I. *J. Mol. Spectrosc.* **1979**, *76*, 39–54.

(49) Smith, T. C.; Evans, C. J.; Clouthier, D. J. *J. Chem. Phys.* **2003**, *118*, 1642–1648.

(50) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419–509.

(51) Jutzi, P. *Angew. Chem. Int. Ed.* **2000**, *39*, 3797–3800.

(52) Pak, C.; Rienstra-Kiracofe, C.; Schaefer, H. F. *J. Phys. Chem.* **2000**, *104*, 11232–11242.

(53) Antioniotti; P.; Operti, L.; Rabezzana, R.; Vaglio, G. A.; Volpe, P. *Int. J. Mass Spectrom.* **1999**, *190/191*, 243–251.

(54) Reents, W. D., Jr.; Mandich, M. L.; Wang, C. R. C. *J. Chem. Phys.* **1992**, *97*, 7226–7233.

(55) Balamurugan, D.; Prasad, R. *Phys. Rev. B* **2006**, *73*, 235415–1235415–11.

(56) Raghavachari, K. *J. Chem. Phys.* **1988**, *88*, 1688–1702.

(57) Al-Laham, M. A.; Raghavachari, K. *J. Chem. Phys.* **1991**, *95*, 2560–2567.

(58) Curtiss, L. A.; Raghavachari, K.; Deutsch, P. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 2433–2444.

The doubly bridged radical cation, $[\mathrm{Si(H_2)Si}]^{\bullet+}$, has been shown to be the lowest energy isomer on the radical cation potential energy surface, with $[\mathrm{H_2SiSi}]^{\bullet+}$ having an energy about 5 kcal/mol higher.[56,58] Other species examined include both a trans $[\mathrm{HSiSiH}]^{\bullet+}$ (higher by ~14 kcal/mol) and a singly hydrogen bridged radical cation (~8 kcal/mol) (both energies relative to the doubly bridged butterfly cation).

The carbon–silicon radical cation, $[\mathrm{2H,C,Si}]^{\bullet+}$, has been studied in only modest detail experimentally and computationally. Its heat of formation has been reported by Armentrout and co-workers in ion beam studies of the reaction of $^2\mathrm{P}\ \mathrm{Si}^+$ with methane and ethane.[59,60] Mass spectroscopic studies of the reactions of allene and $\mathrm{SiH_2}^+$ in which $[\mathrm{2H,C,Si}]^{\bullet+}$ has been studied also have been reported.[61] In none of these studies has structural information on $[\mathrm{2H,C,Si}]^{\bullet+}$ been reported. Limited structural information has been published in computational studies by several workers.[62–64] The lowest energy $[\mathrm{2H,C,Si}]^{\bullet+}$ isomer has $\mathrm{H_2CSi}$ connectivity with a C_{2v} structure, while both $[\mathrm{HCSiH}]^{\bullet+}$ and $[\mathrm{H_2SiC}]^{\bullet+}$ are higher in energy by 55 and 106 kcal/mol.[62]

Anionic Ethyne-Related Silicon Species ($[\mathrm{2H,2Si}]^{\bullet-}$ and $[\mathrm{2H,C,Si}]^{\bullet-}$) and Their Corresponding Dianions. Fewer studies have been reported on these anionic species. The only experimental study (by Sekiguchi and co-workers) reports the preparation of the radical anion of $[[(\mathrm{Me_3Si})_2\mathrm{CH}]_2(i\text{-Pr})\mathrm{Si}]_2$, prepared by reaction with $\mathrm{KC_8}$.[65] This crystalline anion, isolated as its $\mathrm{K(DME)_4}$ salt (DME = dimethoxyethane), was shown to have a trans structure by X-ray analysis. The silicon–silicon bond length reported indicates double-bond character.

In a recent computational study, the lowest energy $[\mathrm{2H,2Si}]^{\bullet-}$ isomer is reported to have a doubly hydrogen bridged structure. The discussion of these computations is very brief, and it is not clear the extent to which other isomers were investigated.[55] Pak, Rienstra-Kiracofe, and Schaefer have computed the electron affinities of [2Si,2H] isomers.[52] Various [2H,2Si] radical anions are considered, as are the neutral compounds in this study.

The dianion isomers of $[\mathrm{2H,2Si}]^{-2}$ have been studied as well; comparison of the [2H,2Si] dianion isomers indicates that the lowest energy species is trans with HSiSiH connectivity.[23] The cis isomer is only a little less stable, but the doubly bridged butterfly structure is ~47 kcal/mol less stable than the trans.

Whereas many experimental and computational studies of simple, silicon-containing compounds and ions related to the carbon–carbon triple bond have been reported, some species, particularly simple silicon- and carbon-containing anions and various dianions, have not been studied in detail. In this report various of these are considered to fill these gaps and to provide a systematic and consistent computational approach. Details of structure as well as estimates of thermodynamic quantities like ionization energies, electron affinities, and singlet–triplet splittings are reported.

Computational Methods

Different computational methods were explored before arriving at the ones used here. Geometry optimizations without symmetry constraints at the Möller–Plesset second-order perturbation theory (MP2)[66] level with a 6-311++G(d,p) basis set,[67] and single-point computations on the optimized structures using density functional theory (DFT) with the B3LYP exchange–correlation functional[68–70] and the Dunning aug-cc-pVTZ basis [B3LYP/aug-cc-pVTZ//MP2/6-311++G(d,p)] were carried out.[71,72] The radical calculations (radical anions, radical cations, and triplet dianions) were performed using restricted open-shell Hartree–Fock (ROHF) methods, since unrestricted Hartree–Fock (UHF) methodology indicated large spin contaminations.

Because (1) some of the aforementioned single-point computations did not converge and (2) optimizations using the MP2/6-311++G(d,p) basis sometimes gave uncertain geometries (see text), computations using another basis set were explored. Noting particularly the work of Takahashi and Kawazoe[23] on various [2H,2Si] neutrals and radical anions, where the importance of including 3d and f basis functions on heavy atoms was evident, we explored a series of geometry optimizations [MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p)] starting from structures without symmetry constraint (C_1). These proved to be well behaved for the species reported here. Although the work of Takahashi and Kawazoe[23] focused on silicon-containing species, earlier work on heavy atom systems (sulfur dioxide) indicated the necessity of including inner polarization functions in the sulfur basis to obtain accurate energies.[74,75] The results given in the body of this paper exclusively use the 6-311++G(3df,3p) basis. Frequency calculations and zero-point energy corrections (ZPC) were carried out by standard techniques on these optimized structures and were used to determine that the stationary points found all were local minima. The single-point energies of each of the unique optimized species were computed using coupled cluster theory at CCSD(T) [CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p)].[73]

All optimizations were carried out using the GAMESS suite of programs,[76] with MacMolPlot[77] being used to visualize the molecular structures. For each species investigated, geometry optimizations began from a series of "standard" geometry inputs to be discussed shortly. The single-point energies were computed using ACES2 (Advanced Concepts in Electronic Structure II).[78] Explicit energy data from the MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p) and CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p) studies can be found for the [2H,2Si] and [2H,C,Si] series in the Supporting Information. The Supporting Information also includes explicit data supporting the results given in the paper including electron affinities, EAs, ionization energies, and singlet–triplet splittings for [2H,2Si] and [2H,C,Si] species,

---

(59) Boo, B. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 6401–6408.

(60) Boo, B. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1990**, *112*, 2083–2088.

(61) Benzi, P.; Operti, L.; Rabezzana, R. *Eur. J. Inorg. Chem.* **2000**, *2000*, 505–512.

(62) Luna, A.; Yáñez, M. *J. Phys. Chem.* **1993**, *97*, 10659–10669.

(63) Ketvirtis, A. E.; Bohme, D. K.; Hopkinson, A. C. *J. Phys. Chem.* **1995**, *99*, 16121–16127.

(64) Flores, J. R.; Barrientos, C.; Largo, A. *J. Phys. Chem.* **1994**, *98*, 1090–1099.

(65) Kinjo, R.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2006**, *129*, 26–27.

(66) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–622.

(67) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.

(68) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–52.

(69) Stephens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

(70) Hertwig, R. H.; Koch, W. *Chem. Phys. Lett.* **1997**, *268*, 345–351.

(71) Dunning, T. H., Jr *J. Chem. Phys.* **1989**, *90*, 1007.

(72) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(73) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479–483, Thanks to Prof. John F. Stanton for carrying out the coupled cluster single point calculations.

(74) Bauschlicher, C. W., Jr.; Partridge, H. *Chem. Phys. Lett.* **1995**, *240*, 533–540.

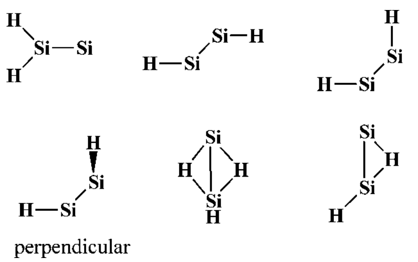
(75) Martin, J. M. L. *J. Chem. Phys.* **1998**, *108*, 2791–2800.

(76) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A. *J. Comput. Chem.* **1993**, *14*, 1347–63.

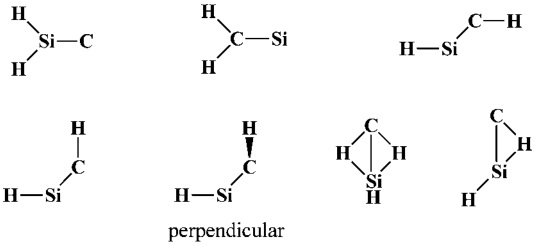
(77) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics Mod.* **1998**, *16*, 133–138.

(78) Stanton, J. F.; Gauss, J.; Lauderdale, W. J.; Watts, J. D.; Bartlett, R. J. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 879.

Scheme 1. Input Geometries for [2H,2Si] Computations



Scheme 2. Input Geometries for [2H,C,Si]Computations



Mulliken and Löwdin charges for assorted [2H,2Si] and [2H,C,Si] species, and Cartesian coordinates for [2H,2Si] and [2H,C,Si] series, all at MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p).

Results and Discussion

The neutral, radical anion, radical cation, singlet dianion, and triplet dianion species have been studied in both the [2H,2Si] and [2H,C,Si] series, each beginning with an unrestrained (C_1) geometry optimization from one of the standard geometry sets shown in Scheme 1 and Scheme 2. These initial geometries were chosen as representative of the common structural features reported for such species, both experimentally and computationally. Other initial geometries also were explored, but none yielded an optimized structure that differed from those obtained from the standard sets. The computational protocol adopted was geometry optimization at the MP2/6-311++G(3df,3p) level starting from the standard geometry sets (Schemes 1 and 2) followed by frequency determination for each species (neutral, radical cation, etc.) for both the [2H,2Si] and [2H,C,Si] series. Single-point energies using the CCSD(T) coupled cluster methodology were determined for all the unique species found.[73]

Careful studies by others have unambiguously established the relative energies of the optimized species for various [2H,2Si] and [2H,C,Si] species. The studies reported here were undertaken to establish the applicability of the computational approach, to examine new species that had not been reported previously, and to provide a consistent computational data set for new species and others reported previously. Several species that have been studied in less detail or are new are reported: (1) the [2H,2Si] triplet dianion, which has been studied briefly,[23] (2) the [2H,C,Si] anion radical, (3) the [2H,C,Si] anion dianion, and (4) the [2H,C,Si] triplet dianion. The results obtained allow the estimation of a variety of thermodynamic quantities that may guide experimental studies.

The relative computational energies for all species studied are summarized in Tables 1 and 2 with results from previous studies presented in curved () parentheses. The CCSD(T) single-point results are presented in square [] brackets. In relative energy comparisons that follow in the text itself, curved parentheses are used to compare various energies obtained at the MP2/6-311++G(3df,3p)//MP2/6-311G++(3df,3p) level, while single-point CCSD(T)/6-311G++(3df,3p) energy comparisons are indicated between square brackets. References given in the tables are judged to be the best for a particular species and do not survey the literature. The references given in the text are more general, giving a better survey of the literature. Some of the reported structures could not be located unless f functions were added to the basis, even using otherwise similar computational methods. The use of these functions has been reported by various workers in their studies of third-row elements,[23,74,75] although only for finding more accurate energies, not in the context of locating new structures.

Neutral Species. The results reported in Tables 1 and 2 for the neutral [2H,2Si] and [2H,C,Si] series using the protocols previously described agree with the best previous studies in terms of the relative energies of the isomeric species.[23,79] The lowest energy [2H,2Si] neutral is the doubly hydrogen bridged isomer, [Si(H_2)Si], followed by the singly hydrogen bridged (∼9 kcal/mol) [∼10 kcal/mol], H_2SiSi (∼15 kcal/mol) [∼12 kcal/mol], and trans HSiSiH (∼19 kcal/mol) [∼18 kcal/mol] isomers. The lowest energy [2H,C,Si] species is H_2CSi with the trans HCSiH isomer (∼36 kcal/mol) [∼38 kcal/mol] and H_2SiC (∼92 kcal/mol) [∼87 kcal/mol] following. The [2H,2Si] (Table 1) and [2H,C,Si] (Table 2) neutral results reported here conform well to previous reports and verify the applicability of the protocols used herein.

Radical Cation Species. The lowest energy radical cation obtained from the six standard [2H,2Si] isomers is the doubly hydrogen bridged isomer with only H_2SiSi (∼7 kcal/mol) [∼6 kcal/mol] and trans HSiSiH (∼17 kcal/mol) [∼16 kcal/mol] also found. These results agree well with studies by Curtiss, Raghavachari, Deutsch, and Pople[58] with one exception: the singly hydrogen bridged structure found by Curtiss et al. using G2 methodology in which geometry optimization is carried out using a MP2(full)/6-31G(d)[80] basis has not been located using the methodology employed here where f functions are employed on the heavy atoms [MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p)].

Optimization studies of the seven standard geometries in the [2H,C,Si] series give three minima, the lowest of which is H_2CSi, also in accordance with previous studies.[62] The next higher energy species are trans HCSiH (∼47 kcal/mol) [∼60 kcal/mol] and H_2SiC (∼99 kcal/mol) [∼96 kcal/mol]. The structure of the HCSiH isomer that has been reported was not explicitly described,[62] although the similarity in energy with the trans structure reported here using MP2 suggests similar structural features (*vide infra*).

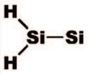
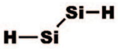
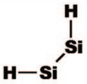
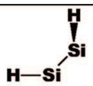
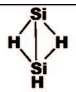
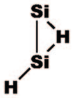
Radical Anion Species. H_2SiSi is the lowest energy [2H,2Si] isomer found here, which is consistent with studies by Pak, Rienstra-Kiracofe, and Schaefer.[52] Certain differences have been found using the 6-311++G(3df,3p) basis. For example, a trans HSiSiH (∼9 kcal/mol) [∼5 kcal/mol] was found, although Pak et al. reported no trans structure.[52] At MP2/6-311++G(d,p), the trans isomer could not be located. Higher energy isomers, a singly bridged (∼13 kcal/mol) [∼13 kcal/mol] and an HSiSiH twisted isomer (with a ∼40° dihedral angle and H−Si−Si angles of ∼97.7°) (∼15 kcal/mol) [∼14 kcal/mol], were obtained using the MP2/6-311++G(3df,3p) basis (both found by Pak et al.).[52] The two twisted structures are quite similar; the one reported here was found without symmetry constraints; that located by Pak et al. was constrained to C_2. A doubly bridged isomer was found in both studies, but that located using the MP2/6-311++G(3df,3p) basis had an imaginary frequency (more correctly, a negative force constant).

---

(79) Stegmann, R.; Frenking, G. *J. Comput. Chem.* **1996**, *17*, 781–789.

(80) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods, 2nd Edition; Gaussian*, Inc.: Pittsburgh, 1996.

Table 1. [2H,2Si] Structures RHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), ROHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), RHF CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), and ROHF CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p)[a]

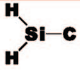
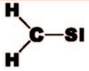
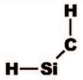
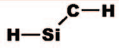
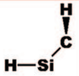
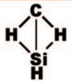
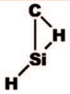
Job Type						
Neutral [2H,2Si]	14.6 [12.2] (14.9)[23]	18.7 [17.5] (19.0)	goes to singly bridged	goes to doubly bridged	0.0 [0.0] (0.0)	8.8 [9.9] (8.8)
Radical Cation $[2H,2Si]^{\bullet+}$	6.8 [5.9] (5.4)[58]	17.3 [15.5] (14.3)	goes to trans	goes to doubly bridged	0.0 [0.0] (0.0)	goes to doubly bridged (7.4)
Radical anion $[2H,2Si]^{\bullet-}$	0.0 [0.0] (0.0)[52]	8.9 [4.5]	goes to singly bridged with imaginary frequency	15.2 [14.0] to structure with ~40 ° dihedral angle (11.9)	goes to doubly bridged with imaginary frequency (24.3)	12.8 [12.7] (12.6)
Dianion, singlet $[2H,2Si]^{2-}$	14.7 [13.4] (12.9)[23] [b]	0.0 [0.0] (0.0)	5.3 [3.2] (3.5)	goes to cis	45.0 [48.4] (50.8)	goes to cis
Dianion, triplet $[2H,2Si]^{2-}$	4.7 [3.2]	goes to twisted	goes to cis with imaginary frequency	0.0 [0.0] Also found.[23]	goes to twisted	goes to twisted

[a] Values reported without parentheses are relative energies optimized at MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p). Those reported in square brackets [] are relative single-point energies computed at CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p). The relative energies given in curved parentheses () are appropriately referenced literature values. [b]These data are $\Delta G_{298.15}$.[23]

No similar study of the radical anions of [2H,C,Si] has been reported. Three isomers are found in this study. The H_2CSi isomer is more stable than a planar, trans-like HCSiH radical anion by ~31 kcal/mol [~27 kcal/mol], with a third radical anion, H_2SiC, considerably higher in energy (~58 kcal/mol) [~56 kcal/mol]. The lowest energy isomer, H_2CSi, continues a trend in which the H_2CSi connectivity has the lowest energy (neutral, radical cation, and now radical anion).

Singlet Dianion Species. The singlet [2H,2Si] dianions reported in Table 1 have similarities with an earlier report by Takahashi and Kawazoe in which the lowest energy isomer using B3LYP/6-311++G(3df,3pd) methodology is the trans

Table 2. [2H,C,Si] Structures RHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), ROHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), RHF CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), and ROHF CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p)[a]

Job Type							
Neutral [2H,C,Si]	92.4 [87.4] (88.0)[79]	0.0 [0.0] (0.0)	goes to trans	35.9 [38.5] (35.8)	goes to trans	goes to H_2CSi	goes to H_2CSi
Radical Cation $[2H,C,Si]^{\bullet+}$	99.2 [95.9] (~106)[62]	0.0 [0.0] (0.0)	goes to trans	46.6 [60.1] (~55—connectivity is HCSiH, but structure is not given	goes to trans	goes to H_2CSi	goes to trans
Radical anion $[2H,C,Si]^{\bullet—}$	58.3 [56.3]	0.0 [0.0]	goes to trans-like	30.9 [27.0] to trans-like	goes to trans-like	goes to H_2CSi	goes to trans-like
Dianion, singlet $[2H,C,Si]^{2—}$	51.1 [55.5]	0.0 [0.0]	17.2 [16.0]	12.0 [21.2]	goes to cis	goes to H_2CSi	goes to cis
Dianion, triplet $[2H,C,Si]^{2—}$	66.2 [64.7]	0.0 [0.0]	fails under many circumstances	31.2 [29.1] to trans-like	goes to trans-like	goes to H_2CSi	goes to trans-like

[a] Values reported without parentheses are relative energies optimized at MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p). Those reported in square brackets [] are relative single-point energies computed at CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p). The relative energies given in curved parentheses () are appropriately referenced literature values.

HSiSiH species and in which cis (~4 kcal/mol), H_2SiSi (~13 kcal/mol), and doubly bridged (~51 kcal/mol) isomers also are found.[23] The results reported here are quite similar: the lowest energy trans is followed by cis (~5 kcal/mol) [~3 kcal/mol], H_2SiSi (~15 kcal/mol) [~13 kcal/mol], and a doubly bridged (~45 kcal/mol) [~48 kcal/mol] isomer.

No singlet dianion studies in the [2H,C,Si] series have been reported. Perusal of Table 2 demonstrates again that the H_2CSi structure is the lowest energy isomer. The trans, cis, and H_2SiC isomers have relative energies of ~12 kcal/mol [~21 kcal/mol], ~17 kcal/mol [~16 kcal/mol], and ~51 kcal/mol [~56 kcal/mol]. Comments on their structural characteristics are presented in a later section.

Triplet Dianion Species. With the exception of a twisted HSiSiH structure found by Takahashi and Kawazoe,[23] triplet dianions have not been reported in either the [2H,2Si] or [2H,C,Si] series. The results in Table 1 reveal that only two triplet dianions were found with the twisted HSiSiH isomer lower in energy than H_2SiSi by ~5 kcal/mol [~3 kcal/mol]. The twisted structure was found only when using the 6-311++G-(3df,3p) basis; using other computational techniques with smaller basis sets, the twisted isomer could not be located.

In the [2H,C,Si] triplet dianion series, H_2CSi is the most stable isomer by a wide margin over a trans-like structure (~31 kcal/mol) [~29 kcal/mol] and by a wider margin over H_2SiC (~66 kcal/mol) [~65 kcal/mol]. The trans-like structure reveals vastly different bonding characteristics for silicon and carbon (see next section).

Charge Comparisons. Although Mulliken and Löwdin population analyses are subject to criticism (Löwdin charges are considered more reliable),[81,82] their charges can reveal "intuitively acceptable" results. For example, for H_2SiSi and H_2CSi, the H-bound atom, silicon in the first case, carbon in the second, is more negative than the terminal silicon using either population analysis method. This suggests for H_2SiSi (where the differences are small) that the electron lone pair in a nearly pure 3s orbital on the terminal silicon atom[83,84] donates some electron density toward SiH_2 despite hybridization differences between the two silicon atoms (nearly pure s and sp^2)[83,84] that would suggest electron movement in the opposite direction. The case of H_2CSi is more straightforward, since the carbon atom is considerably more negative as a consequence of its being more electronegative. This analysis is consistent with a thorough study of the neutral [2H,C,Si] isomers using natural bond order (NBO) population analysis, where considerable negative charge localizes on carbon in all isomers.[79] The NBO method interestingly gives bond orders for the σ and π C−Si bonds of 0.48 and 0.64. The weaker σ bond is attributed to its greater polarization.[79] The other [2H,C,Si] isomers, H_2SiC, trans, and a linear species, all have more negative carbon atoms. Various other comments concerning Mulliken and Löwdin charges are given in the following section.

Structural Comparisons: Geometries. Two aspects of the structure of those species that have not been reported previously will be addressed in this and the following section: the geometric features of particular optimized structures that point to bonding characteristics and the stability of various structures (geometries) across various species (neutral, radical cation, radical anion, etc.). Only major geometric differences will be discussed; Table 3 contains more complete geometry information.

The trans HSiSiH radical anion in the [2H,2Si] series has not been reported by others (*vide supra*). Its geometry (Table 3) varies considerably from neutral trans HSiSiH, having longer Si−Si and Si−H bonds (by ~0.1 and ~0.03 Å) and a much smaller H−Si−Si angle (by ~18°). The longer bond distances can be explained by electron–electron repulsion, since the Löwdin charges on silicon and hydrogen are increased in the radical anion by ~0.4 and ~0.1. The smaller bond angle (~107°) suggests a considerable hybridization change at silicon in the radical anion compared with neutral trans HSiSiH (~126°).

In the triplet dianion [2H,2Si] series, only H_2SiSi (slightly higher in energy than the twisted isomer) is new. Its structure compared with neutral H_2SiSi indicates quite different H−Si−H and H−Si−Si bond angles. Its nearly identical bond distances imply similar bonding characteristics, while the larger bond angles for the dianion hint at some accommodation of the extra electrons. The Si−Si bond length reported here is in line with many calculations of 2Si species that suggest the presence of a silicon−silicon double bond.[2,6] The H−Si−H and H−Si−Si angles for neutral H_2SiSi also correspond closely with other computations.[84] Mulliken and Löwdin population analyses comparing the neutral, radical anion, and triplet dianion H_2SiSi species indicate that extra electron density is largely located on the terminal silicon as a single electron and then two are added.

The lowest energy twisted HSiSiH triplet dianion has no neutral counterpart, but has significantly longer Si−Si and Si−H bonds than neutral trans HSiSiH or H_2SiSi. Its ~100° H−Si−Si bond angle suggests considerably more p character at silicon than either neutral trans HSiSiH or H_2SiSi. Its 93.4° twist (dihedral) angle is essentially identical with that reported.[23]

Table 3. [2H,2Si] and [2H,C,Si] Series: Geometric Parameters for Newly Reported Species at RHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p) or ROHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p)

structure	description	geometric parameter	value (in deg or Å)[a]
trans HSiSiH	radical anion	Si−Si bond	2.19(2.10)
		Si−H bond	1.52(1.49)
		H−Si−Si angle	107.4(125.5)
H_2SiSi	dianion triplet	Si−Si bond	2.22(2.21)
		Si−H bond	1.50(1.48)
		H−Si−H angle	106.8(113.3)
		H−Si−Si angle	126.6(123.4)
HSiSiH	twisted dianion triplet	Si−Si bond	2.43(2.10)
		Si−H bond	1.55(1.49)
		H−Si−Si angle	100.9(125.5)
		dihedral angle	93.4
H_2CSi	radical anion	C−Si bond	1.77(1.71)
		C−H bond	1.09(1.09)
		H−C−H angle	112.9(114.0)
		H−C−Si angle	123.5(123.0)
H_2SiC	radical anion	Si−C bond	1.75(1.78)
		Si−H bond	1.51(1.47)
		H−Si−H angle	105.1(118.8)
		H−Si−C angle	127.4(120.6)
HCSiH	radical anion trans	Si−C bond	1.73(1.62)
		C−H bond	1.09(1.08)
		Si−H bond	1.54(1.46)
		H−C−Si angle	142.7(149.2)
		C−Si−H angle	101.7(147.9)
H_2CSi	dianion singlet	C−Si bond	1.80(1.71)
		C−H bond	1.09(1.09)
		H−C−H angle	115.6(114.0)
		H−C−Si angle	122.2(123.0)
H_2SiC	dianion singlet	Si−C bond	1.72(1.78)
		Si−H bond	1.57(1.47)
		H−Si−H angle	94.7(118.8)
		H−Si−C Angle	132.6(120.6)
HCSiH	dianion singlet cis	Si−C bond	1.77
		C−H bond	1.11
		Si−H bond	1.64
		H−C−Si angle	111.6
		C−Si−H angle	109.5
HCSiH	dianion singlet trans	Si−C bond	1.74(1.62)
		C−H bond	1.10(1.08)
		Si−H bond	1.55(1.46)
		H−C−Si angle	111.9(149.2)
		C−Si−H angle	109.1(147.9)
H_2CSi	dianion triplet	C−Si bond	1.77(1.71)
		C−H bond	1.09(1.09)
		H−C−H angle	110.5(114.0)
		H−C−Si angle	124.7(123.0)
H_2SiC	dianion triplet	Si−C bond	1.75(1.78)
		Si−H bond	1.50(1.47)
		H−Si−H angle	104.4(118.8)
		H−Si−C angle	127.8(120.6)
HCSiH	dianion triplet trans	Si−C bond	1.72(1.62)
		C−H bond	1.08(1.08)
		Si−H bond	1.56(1.46)
		H−C−Si angle	162.9(149.2)
		C−Si−H angle	101.4(147.9)

[a] The values given in parentheses are for the neutral compounds of the same connectivity.

Comparisons of three new radical anion structures, H_2CSi, H_2SiC, and trans HCSiH, with their neutral analogues reveal that the lowest energy isomer H_2CSi has a slightly longer C−Si bond than the neutral, but equal C−H bonds. The H−C−H and H−C−Si bond angles in the radical anion and the neutral are nearly identical, suggesting only minor perturbation in bonding characteristics with the added electron, which is consistent with its charge distribution. Both Mulliken and Löwdin population

---

(81) Leach, A. R. *Molecular Modeling: Principles and Applications*, 2nd ed.; Prentice Hall: Harlow, England, 2001.

(82) Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*; John Wiley and Sons: Chichester, 2002.

(83) Koseki, S.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 118–125.

(84) Colegrove, B. T.; Schaefer, H. F., III *J. Phys. Chem.* **1990**, *94*, 5593–5602.

Table 4. [2H,2Si] Series: Ionization Energies, Electron Affinities (EA), and Singlet–Triplet Splittings at RHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), ROHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), RHF CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), and ROHF CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p)[a]

isomer	ionization energy (in kcal/mol)	EA[b] (in kcal/mol)	singlet “second” EA[c] (in kcal/mol)	triplet “second” EA[d] (in kcal/mol)	singlet−triplet energy difference[e] (in kcal/mol)
H_2SiSi	180.4 [181.4]	40.4 [40.4]	−85.2 [87.2]	−102.5 [−100.3]	17.3[f] [14.0]
trans	186.9 [185.7]	35.6 [41.2]	−61.7 [−69.5]	−89.0[g] [−93.6] (triplet to 93.4° twist)	27.3[g][24.1] (triplet to 93.4° twist)
cis			−60.7 [−63.1] (to 40° dihedral angle)		22.0[g][21.0] (triplet to 93.4° twist)
singly bridged		21.7 [25.5]			
doubly bridged	188.3 [187.7]		−61.3		—17.7[g][−24.3] (triplet to 93.4° twist)

[a] The CCSD(T) results are given in square brackets []. [b] The EA is the zero-point-corrected energy difference between the optimized anion radical and the corresponding optimized neutral species. [c] The singlet “second” EA is the zero-point-corrected energy difference between the optimized anion radical and the corresponding optimized singlet dianion. [d] The triplet “second” EA is the zero-point-corrected energy difference between the optimized anion radical and the corresponding optimized triplet dianion. [e] The singlet–triplet zero-point-corrected energy differences were computed using the optimized geometry of the singlet dianion as well as the optimized geometry of the triplet dianion. A positive value indicates a more stable singlet. [f] Both singlet and triplet have H_2SiSi structure. [g] The singlet structures are as indicated; the triplets have a 93.4° twisted structure.

Table 5. [2H,C,Si] Series: Ionization Energies, Electron Affinities (EA), and Singlet–Triplet Splittings at RHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), ROHF MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), RHF CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p), and ROHF CCSD(T)/6-311++G(3df,3p)//MP2/6-311++G(3df,3p)[a]

isomer	ionization energy (in kcal/mol)	EA[b] (in kcal/mol)	singlet “second” EA[c] (in kcal/mol)	triplet “second” EA[d] (in kcal/mol)	singlet−triple energy difference[e] (in kcal/mol)
H_2SiC	209.2 [209.9]	50.0 [47.3]	−98.9 [−103.4]	−107.1 [−106.7]	8.2 [3.3]
H_2CSi	202.5 [201.4]	16.1 [16.2]	−106.3 [−104.1]	−99.4 [−98.3]	−6.9 [−5.9]
trans	213.2 [223.0]	21.1 [27.6]	−87.4 [−93.2]	−99.8 [−100.3]	12.3 [7.2]

[a] The CCSD(T) results are given in square brackets []. [b] The EA is the zero-point-corrected energy difference between the optimized anion radical and the corresponding optimized neutral species. [c] The singlet “second” EA is the zero-point-corrected energy difference between the optimized anion radical and the corresponding optimized singlet dianion. [d] The triplet “second” EA is the zero-point-corrected energy difference between the optimized anion radical and the corresponding optimized triplet dianion. [e] The singlet–triplet zero-point-corrected energy differences were computed using the optimized geometry of the singlet dianion as well as the optimized geometry of the triplet dianion. A positive value indicates a more stable singlet.

analyses indicate only slightly greater electron density on carbon compared with neutral H_2CSi, with most of the additional charge on silicon. For example, in neutral H_2CSi, carbon and silicon have ∼−0.55 and ∼0.35 Löwdin charges. In the radical anion, the corresponding charges are ∼−0.71 and ∼−0.37, a net change for carbon of ∼−0.2 and for silicon of ∼−0.7.

The radical anion and neutral isomer of H_2SiC not only are both much higher energy species (Table 2) but differ significantly in geometry. Such differences suggest that the higher energy H_2SiC radical anion and neutral are very different in bonding terms. The trans HCSiH radical anion and the trans neutral also differ dramatically. Mulliken and Löwdin population analyses indicate greater electron density on both carbon and silicon compared with neutral H_2SiC.

Of the four new singlet dianion structures (H_2CSi, H_2SiC, and cis and trans HCSiH), the lowest energy singlet dianion (H_2CSi) is quite similar to its neutral counterpart, with the Si−C distance being close to a double bond.[2] The singlet dianion H_2SiC species, on the other hand, has a dramatically different structures: its H−Si−H and H−Si−C bond angles are ∼25° narrower and ∼12° wider than the neutral. The trans HCSiH singlet dianion also differs significantly from its neutral, notably in the Si−C bond length (1.73 versus 1.62 Å). This suggests that the Si−C bond is closer to a double than a triple bond. The trans singlet dianion and the corresponding neutral also show large angle differences. None of the dianion singlets studied have Si−C bond lengths nearing that of a triple bond.[2]

The three new triplet dianion structures found (H_2CSi, H_2SiC, and trans HCSiH) also reveal some striking geometric differences from neutral species. Comparisons of H_2CSi and its neutral reveal large angle differences in H_2SiC (∼7–14°). Its Si−C bond length is ∼0.06 Å longer than the corresponding neutral, indicating less double-bond character. The trans triplet dianion HCSiH varies significantly from its neutral, again suggesting major bonding differences between the triplet dianions and their corresponding neutrals. This is readily seen in the lengthened Si−C bond (by ∼0.1 Å), which is more characteristic of a Si−C double than a triple bond.[2]

Structural Comparisons: Across Species. Analysis of the newly reported species, the triplet dianion H_2SiSi in the [2H,2Si] series and radical anions, singlet dianions, and triplet dianions in the [2H,C,Si] series, provides the opportunity to compare such species with other members of the same series. For example, H_2SiSi in the [2H,2Si] series shows no obvious pattern: it is the second most stable species of the triplet dianions and radical cations, but it is the most stable radical anion. Examination of the geometries of these species does not obviously link structure with stability.

Patterns in the [2H,C,Si] series are more regular, with H_2CSi being the lowest energy among the neutral, radical, cation, radical anion, singlet dianion, and triplet dianion species despite significant structural differences. A fairly regular energy pattern results beyond the H_2CSi species, with trans HCSiH always being the next higher energy isomer among the neutral, radical cation, radical anion, singlet dianion, and triplet dianions. The next higher energy species is H_2SiC for the neutral, radical cation, radical anion, and triplet dianions, but not the singlet dianion series, where cis HCSiH invervenes.

Thermodynamic Considerations. Tables 4 and 5 capture some thermodynamic parameters that can be obtained from the computations presented here. These include estimates of the ionization energies, electron affinities, “second” electron affinities, and singlet–triplet energy differences for many of the species studied. Data are reported for the appropriate [2H,2Si]

(Table 4) and [2H,C,Si] (Table 5) series that have been found as stable species on the potential energy surface. Thus, ionization energy (IE) (strictly speaking, the adiabatic ionization energy)[85] estimates require the pairing of an optimized neutral with its corresponding radical cation, which specifically can be determined for H_2SiSi, trans HSiSiH, and the doubly bridged isomers in the [2H,2Si] series and H_2SiC, H_2CSi, and trans HCSiH in the [2H,C,Si] series. In the [2H,2Si] series, the ionization energies range between ~180 and 188 kcal/mol [~181 and 187 kcal/mol from CCSD(T)] with the [2H,C,Si] series species having ionization energies about 20 kcal/mol higher (~202–213 kcal/mol) [~201–223 kcal/mol]. Comparisons of analogous carbon and silicon species are difficult since no evident trends exist. Thus, the IE of methane and silane are ~291 and ~258 kcal/mol, but the IE of toluene and phenylsilane are ~203 and ~212 kcal/mol and that of propene and vinylsilane are ~224 and ~240 kcal/mol. Limited experimental and computational studies of [2H,2Si] ionization energies have been reported without specific mention of what isomers are being reported.[58,86] The experimental ionization energy reported was ~189 kcal/mol; the computational one, ~191 kcal/mol. Both values correspond well with the ionization energies reported in Table 4 for the lowest energy doubly bridged isomer (~188 kcal/mol) [188 kcal/mol]. A report of the computationally determined ionization energy of H_2CSi of ~205 kcal/mol compares favorably with the values reported in Table 5 (~202 kcal/mol) [201 kcal/mol].[63]

Examination of the electron affinity (EA)[37,85] results meets the expectation that the addition of an electron to a silicon-containing system should be more favorable than such an addition to an all-carbon one simply because of the greater electropositive character of silicon. While the EAs of simple hydrocarbons often are close to zero or slightly negative (meaning unstable with respect to electron loss), analogous silicon-containing compounds have positive EA values.[87–90] The comparisons reported here are made between geometry-optimized species in line with the definition of a computational EA.[37] Such EA values in the [2H,2Si] and [2H,C,Si] series reveal no obvious trends; nevertheless several large EAs indicate high stability for the radical anions involved (examples, the H_2SiSi, trans HSiSiH, and H_2CSi). Interestingly, these radical anions are the more stable ones of each species. Several EAs of [2H,2Si] species have been reported and are consistent with our results with one exception. Although Pak, Rienstra-Kiracofe, and Schaefer have reported an EA for the doubly bridged, $Si(H_2)Si$, isomer,[52,91,92] the radical anion of this structure reported here has an imaginary frequency at MP2/6-311++G(3df,3p). Using various density functional theory functionals, Pak, Rienstra-Kiracofe, and Schaefer also reported imaginary frequency values for this doubly bridged radical anion.[52] Computationally determined EA values by Kalcher and Sax for both the trans HSiSiH and H_2SiSi isomers (~41 and ~40 kcal/mol) have similar values to the results in Table 4 (~36 and 40 kcal/mol) [~41 and 40 kcal/mol].[91,92]

Use of the term "second" EA requires some explanation. It is meant to convey the process of adding a second electron to a radical anion. The "second" EA estimate has been made by comparing the energy difference between optimized radical anions and their corresponding optimized dianions, either singlet or triplet.[37] Given that small dianions in the gas phase are generally unstable because their charge cannot be dispersed in a small volume,[44–47] it is not surprising that the values reported in Tables 4 and 5 are all negative in both the singlet and triplet manifolds. Only one "second" EA seems to have been reported, that for trans HSiSiH. It is not directly reported, but is given as the difference in energy between neutral HSiSiH and the corresponding singlet dianion (~−28 kcal/mol).[23] A value of ~−26 kcal/mol [~−28 kcal/mol] is obtained for comparison by summing the EA and "second" EA of trans HSiSiH in Table 4.

Singlet–triplet splitting is positive for five species in the [2H,2Si] and [2H,C,Si] series and negative for two (one in each series), where a positive singlet–triplet splitting indicates that the singlet is more stable than the triplet. In the [2H,2Si] series (Table 4), the first entry has H_2SiSi connectivity for both the singlet and triplet. The trans HSiSiH, cis-HSiSiH, and the doubly bridged entries, on the other hand, have the structures just indicated for the singlet, but the twisted one for the triplet. In the case of H_2SiSi, the singlet–triplet splitting is ~17 kcal/mol [~14 kcal/mol], while the singlet–triplet splittings for the cis-to-twisted and doubly bridged-to-twisted are ~22 and ~−18 kcal/mol [~21 and ~−24 kcal/mol]. Only in the doubly bridged case is the triplet more stable than the singlet. Takahashi and Kawazoe have also indicated that the trans dianion singlet is more stable than the twisted triplet dianion (~20 kcal/mol).[23] It is important to realize that the singlet–triplet gap reported by Takahashi and Kawazoe for the trans isomer to the twisted triplet dianion does not correspond to the lowest energy species for the trans structure. The results obtained here give a somewhat larger singlet–triplet gap (~27 kcal/mol) [~24 kcal/mol].

In the [2H,C,Si] series, where neither the singlet nor the triplet dianions have previously been reported, the optimized structures for the singlet and triplet H_2SiC, H_2CSi, and trans HCSiH are similar. The corresponding singlet–triplet splittings are ~8, −7, and 12 kcal/mol [~3, −6, and 7 kcal/mol], thus indicating that the most stable H_2CSi species has a more stable triplet.

Acknowledgment. R.D. thanks Professor John F. Stanton for performing the CCSD(T) single-point computations and for advice relating to these calculations. R.D. thanks Professor G. Barney Ellison for many helpful discussions over many years; while we disagree about the importance of computational work without experimentation, we do so with great cheer. R.D. also thanks the University of Colorado Denver for providing sabbatical support for this work.

Supporting Information Available: Tables containing the absolute and relative energies for the species reported as well as Cartesian coordinates for these structures are available free of charge via the Internet at http://pubs.acs.org.

OM701220S

---

(85) http://webbook.nist.gov/chemistry/ion/#A.

(86) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1991**, *95*, 2416–2433.

(87) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051–3.

(88) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968–73.

(89) Damrauer, R.; Hankin, J. A. *Chem. Rev.* **1995**, *95*, 1137–1160.

(90) Damrauer, R. *Adv. Silicon Chem.* **1993**, *2*, 91–135.

(91) Kalcher, J.; Sax, A. F. *Chem. Phys. Lett.* **1992**, *192*, 451–454.

(92) Kalcher, J.; Sax, A. F. *Chem. Phys. Lett.* **1987**, *133*, 135–138.