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Theoretical Study on Planar Anionic Polysilicon Chains and Cyclic Si_6 Anions with D_{6h} Symmetry

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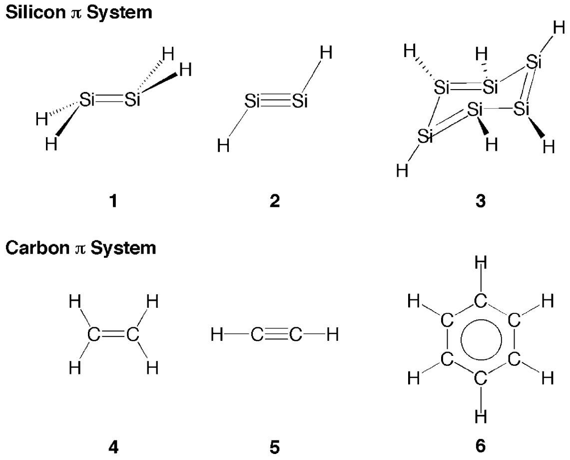
The structures of neutral and anionic hydrogen-terminated oligomers (H−Si_n−H: n = 2, 4, 6, 8) and silicon six-membered rings (c-Si_6) have been investigated using quantum-chemical methods to find stable planar polysilicon chains and aromatic silicon six-membered rings. Among 18 calculated molecules, planar equilibrium structures have been obtained for seven anionic chains ($Si_2H_2^{2-}$, $Si_4H_2^{2-}$, $Si_4H_2^{4-}$, $Si_6H_2^{4-}$, $Si_6H_2^{6-}$, $Si_8H_2^{4-}$, $Si_8H_2^{6-}$) and three anionic six-membered rings (c-Si_6^{2-}, c-Si_6^{4-}, c-Si_6^{6-}). The number of π electrons formally accommodated in the out-of-plane π orbitals is the same as the number of silicon atoms and is independent of the number of doped electrons. An anionic six-membered ring, c-Si_6^{2-}, shows a large negative value of nucleus-independent chemical shift (NICS), which indicates that c-Si_6^{2-} is an aromatic molecule.

Introduction

Silicon π-electron systems (**1**−**3**) differ remarkably in structure and stability from carbon π-electron systems (**4**−**6**), although formally the same hybridization occurs (Chart 1).[1] The carbon π system is usually stable, while enormous efforts have been required for the isolation of stable unsaturated silicon compounds. The isolation of a stable disilene (**7**) (Chart 2) in 1981 by West et al. was a breakthrough in unsaturated silicon chemistry.[2] Recently, the synthesis and X-ray crystal analysis of the formally sp-hybridized trisilaallene **8** have been reported by Kira et al.[3] and the Si=Si=Si skeleton of **8** has been revealed to be significantly bent with a bond angle of 136.5°. It differs from the linear C=C=C skeleton of allene ($H_2C{=}C{=}CH_2$). The bonding at the central silicon atom of **8** cannot be described as a simple sp hybridization. Very recently, linear trisilaallenes have been designed theoretically by Apeloig et al.,[4] where σ-donor, π-acceptor R_2B substituents are used. Another heavy-group analogue of sp-hybridized carbon, RPbPbR (**9**, R = C_6H_3-2,6-$Trip_2$; Trip = C_6H_2-2,4,6-^{i}Pr_3), reported by Power et al. also has shown a bent structure with a C−Pb−Pb angle of approximately 90°.[5] The structure of RPbPbR is distinct from that of linear acetylene (**5**) and from that of trans bending disilyne (**2**) because of the sharp bond angle and the very long Pb−Pb distance. The unusual bonding nature has been investigated intensively and has been elucidated theoretically.[6] A recent highlight in unsaturated silicon chemistry was the synthesis of a silicon−silicon triple-bonded compound (**10**) reported by Sekiguchi et al.,[7] which has been desired ever since the first synthesis of the double-bonded compound by West et al. The revelations of the trans bending of disilene (**1**)[8,9] and disilyne (**2**)[10] and of the chair form of a silicon analogue of benzene (**3**)[11] all go back over 20 years. A donor−acceptor bonding model[9] has well explained the trans bending of disilene and disilyne. The planar tendency in ethylene (**4**) and benzene (**6**) is essential for the π conjugation and sp^2 hybridization. However, planar polysilicon chains and planar silicon six-membered rings have not been obtained for neutral molecules, neither theoretically nor experimentally.

Chart 1. Carbon and Silicon π-Electron Systems



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(1) For recent reviews, see: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (c) Kira, M.; Iwamoto, T. *J. Organomet. Chem.* **2000**, *611*, 236. (d) Jutzi, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3797. (e) West, R. *Polyhedron* **2002**, *21*, 467. (f) Weidenbruch, M. *J. Organomet. Chem.* **2002**, *646*, 39. (g) Weidenbruch, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2222. (h) Sekiguchi, A.; Lee, V. Y. *Chem. Rev.* **2003**, *103*, 1429. (i) Tokitoh, N. *Acc. Chem. Res.* **2004**, *37*, 86.

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

(3) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Nature* **2003**, *421*, 725.

(4) Kosa, M.; Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **2004**, *126*, 10544.

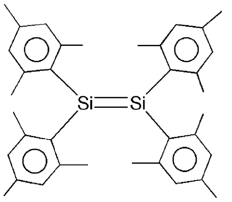
(5) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524.

(6) (a) Chen, Y.; Hartmann, M.; Diedenhofen, M.; Frenking, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2052. (b) Danovich, D.; Ogliaro, F.; Karni, M.; Apeloig, Y.; Cooper, D. L.; Shaik, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4023. (c) Grunenberg, J. *Angew. Chem., Int. Ed.* **2001**, *40,* 4027.

(7) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755.

10.1021/om050025c CCC: $30.25

Chart 2. Experimentally Obtained Heavy-Group Analogues of Carbon π-Electron Systems



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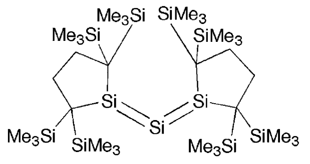

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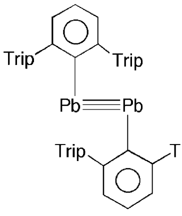

Trip = C_6H_2-2,4,6-^{i}Pr_3

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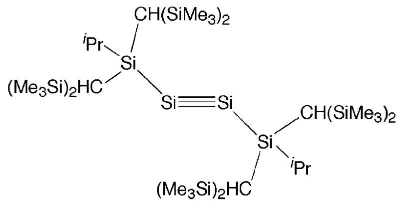

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We have been investigating theoretically the stability[12-14] and reactivity[15,16] of unsaturated silicon compounds. Recently we found that charged systems are helpful for understanding systematically the stability of silicon π systems.[13] In this paper we consider chains and rings consisting of bent disilyne units. We have found that disilyne derivatives, even with π-accepting substituents, take a bent structure.[14] The substituent effect is distinct from disilene derivatives, where π-accepting substituents lead to planar structures.[8e] In the present system, no linear structure is expected, and each silicon atom has a lone-electron-pair orbital and a vacant π orbital as in the observed unusual structure of RPbPbR.[5,6a] In addition, to stabilize the planar chain and ring of silicon, electrons are doped in the vacant π orbitals, forming anions. Since radicals are usually unstable, even numbers of electrons are doped. In contrast to cations, anions can stabilize themselves by spontaneous emission of an electron, the so-called autodetachment. Thus, it is not a priori clear whether anions exist in the gas phase as stable entities. Today it is well established that most of the elements form atomic negative ions.[17] Multiply charged anions are commonly observed in crystals and in solution, and no stable isolated multiply charged anions are known in the gas phase. To date, theoretical investigations for the anions of unsaturated silicon systems are limited to monoanion radicals and electron affinities.[18] On the other hand, several multiply charged anions of unsaturated silicon systems have been found in the crystal state, and their structures have been elucidated.[19]

Calculations

Ab initio molecular orbital and density functional theory (DFT) calculations were performed using the Gaussian 03 software package.[20] In the DFT calculations, the functional of Becke3−Lee−Yang−Parr (B3LYP)[21] was employed, which is proven by some systematic comparisons[22] to have the best overall performance among other functionals due to its higher

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(8) Theoretical studies: (a) Krogh-Jespersen, K. *J. Phys. Chem.* **1982**, *86*, 1492. (b) Nagase, S.; Kudo, T. *J. Mol. Struct. (THEOCHEM)* **1983**, *103*, 35. (c) Olbrich, G. *Chem. Phys. Lett.* **1986**. *130*, 115. (d) Teramae, H. *J. Am. Chem. Soc.* **1987**, *109*, 4140. (e) Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8589. (f) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667. (g) Chen, W.-C.; Su, M.-D.; Chu, S.-Y. *Organometallics* **2001**, *20*, 564. Experimental studies: (h) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1010. (i) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793. (j) Shepherd, B. D.; Campana, C. F.; West, R. *Heteroat. Chem.* **1990**, *1*, 1. (k) Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428. (l) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* **1995**, *14*, 1016. (m) Kira, M. *Pure Appl. Chem.* **2000**, *72*, 2333. (n) Sari, L.; McCarthy, M. C.; Schaefer, H. F., III; Thaddeus, P. *J. Am. Chem. Soc.* **2003**, *125*, 11409.

(9) (a) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (b) Malrieu, J.-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916. (c) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130. (d) Trinquier, G.; Malrieu, J.-P. *J. Phys. Chem.* **1990**, *94*, 6184.

(10) (a) Lischka, H.; Köhler, H.-J. *J. Am. Chem. Soc.* **1983**, *105*, 6646. (b) Binkley, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 603. (c) Kalcher, J.; Sax, A.; Olbrich, G. *Int. J. Quantum Chem.* **1984**, *25*, 543. (d) Köhler, H.-J.; Lischka, H. *Chem. Phys. Lett.* **1984**, *112*, 33. (e) Koseki, S.; Gordon, M. S. *J. Phys. Chem.* **1988**, *92*, 364. (f) Koseki, S.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 118. (g) Colegrove, B. T.; Schaefer, H. F., III. *J. Phys. Chem.* **1990**, *94*, 5593. (h) Grev, R. S.; Deleeuw, B. J.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1990**, *165*, 257. (i) Colegrove, B. T.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1991**, *113*, 1557. (j) Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J. L. *Phys. Rev. Lett.* **1991**, *66*, 413. (k) Cordonnier, M.; Bogey, M.; Demuynck, C.; Destombes, J.-L. *J. Chem. Phys.* **1992**, *97*, 7984. (l) Nguyen, M. T.; Sengupta, D.; Vanquickenborne, L. G. *Chem. Phys. Lett.* **1995**, *244*, 83. (m) Stegmann, R.; Frenking, G. *J. Comput. Chem.* **1996**, *17*, 781. (n) Grev, R. S.; Schaefer, H. F., III. *J. Chem. Phys.* **1992**, *97*, 7990. (o) Apeloig, Y.; Karni, M. *Organometallics* **1997**, *16*, 310. (p) Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489. (q) Karni, M.; Apeloig, Y.; Schröder, D.; Zummack, W.; Rabezzana, R.; Schwarz, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 331. (r) Grützmacher, H.; Fässler, T. F. *Chem. Eur. J.* **2000**, *6*, 2317. (s) Nagase, S.; Kobayashi, K.; Takagi, N. *J. Organomet. Chem.* **2000**, *611*, 264. (t) Kobayashi, K.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 234. (u) Takagi, N.; Nagase, S. *Chem. Lett.* **2001**, 966. (v) Takagi, N.; Nagase, S. *Eur. J. Inorg. Chem.* **2002**, 2775.

(11) (a) Nagase, S.; Kudo, T.; Aoki, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1121. (b) Clabo, D. A., Jr.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *84*, 1664. (c) Nagase, S.; Teramae, H.; Kudo, T. *J. Chem. Phys.* **1987**, *86*, 4513. (d) Janoschek, R. *J. Inorg. Organomet. Polymers* **1995**, *5*, 155.

(12) (a) Veszprémi, T.; Takahashi, M.; Hajgató, B.; Ogasawara, J.; Sakamoto, K.; Kira, M. *J. Phys. Chem. A* **1998**, *102*, 10530. (b) Takahashi, M.; Tsutsui, S.; Sakamoto, K.; Kira, M.; Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **2001**, *123*, 347. (c) Takahashi, M.; Kira, M.; Sakamoto, K.; Müller, T.; Apeloig, Y. *J. Comput. Chem.* **2001**, *22*, 1536.

(13) (a) Takahashi, M.; Sakamoto, K. *Organometallics* **2002**, *21*, 4212. (b) Takahashi, M.; Sakamoto, K. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2002**, *177*, 1721.

(14) Takahashi, M.; Sakamoto, K. *J. Phys. Chem. A* **2004**, *108*, 5710.

(15) Thermal reactions: (a) Veszprémi, T.; Takahashi, M.; Ogasawara, J.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 2408. (b) Takahashi, M.; Veszprémi, T.; Hajgató, B.; Kira, M. *Organometallics* **2000**, *19*, 4660. (c) Veszprémi, T.; Takahashi, M.; Hajgató, B.; Kira, M. *J. Am. Chem. Soc.* **2001**, *123*, 6629. (d) Takahashi, M.; Veszprémi, T.; Sakamoto, K.; Kira, M. *Mol. Phys.* **2002**, *100*, 1703. (e) Hajgató, B.; Takahashi, M.; Kira, M.; Veszprémi, T. *Chem. Eur. J.* **2002**, *8*, 2126. (f) Takahashi, M.; Veszprémi, T.; Kira, M. *Organometallics* **2004**, *23*, 5768.

(16) Photochemical reactions: Takahashi, M.; Sakamoto, K. *J. Phys. Chem. A* **2004**, *108*, 7301.

(17) For recent reviews, see: (a) Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data Ser.* **1985**, *14*, 731. (b) Andersen, T.; Haugen, H. K.; Hotop, H. *J. Phys. Chem. Ref. Data Ser.* **1999**, *28*, 1511. (c) Dreuw, A.; Cederbaum, L. S. *Chem. Rev.* **2002**, *102*, 181. (d) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F., III. *Chem. Rev.* **2002**, *102*, 231.

(18) (a) Korkin, A. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 8720. (b) Kalcher, J.; Sax, A. F. *Chem. Phys. Lett.* **1992**, *192*, 451. (c) Kalcher, J.; Sax, A. F. *J. Mol. Struct. (THEOCHEM)* **1994**, *119*, 41. (d) Pak, C.; Rienstra-Kiracofe, J. C.; Schaefer, H. F., III. *J. Phys. Chem. A* **2000**, *104*, 11232. (e) Li, G. L.; Li, Q. S.; Xu, W. G.; Xie, Y. M.; Schaefer, H. F., III. *Mol. Phys.* **2001**, *99*, 1053. (f) Pak, C.; Sari, L.; Rienstra-Kiracofe, J. C.; Wesolowski, S. S.; Horný, L.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Chem. Phys.* **2003**, *118*, 7256.

(19) (a) Sekiguchi, A.; Ichinohe, M.; Kabuto, C.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2981. (b) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457. (c) Wiberg, N. *Coord. Chem. Rev.* **1997**, *163*, 217. (d) Nesper, R.; Currao, A.; Wengert, S. *Chem. Eur. J.* **1998**, *4*, 2251. (e) Xu, C.; Taylor, T. R.; Burton, G. R.; Neumark, D. M. *J. Chem. Phys.* **1998**, *108*, 7645. (f) Sekiguchi, A.; Inoue, S.; Ichinohe, M.; Arai, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9626. (g) Gehrhus, B.; Hitchcock, P. B.; Zhang, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1124.

correlation level, lower spin contamination, and less dependence on the basis set. Geometry optimization was performed with both the MP2 and B3LYP methods using 6-311++G(3df,3pd) basis sets. In our preceding study on Si−Si double-bonded systems, excellent results were obtained using the 6-311++G(d,p) basis.[15c] However, since high-exponent d and f functions are required for the calculations of second-row species to obtain reliable results,[23] we used 6-311++G(3df,3pd) basis sets. All optimized structures were confirmed to be thermodynamically stable by verifying the absence of imaginary vibrational frequencies in the harmonic approximation, unless otherwise noted. For larger molecules, Si_nH_2 (n = 6, 8), c-Si_6, and P_6, the characterization of the minimum by frequency analysis was performed for the 6-311++G(d,p) geometry with MP2 and B3LYP methods.

The calculated energy data were corrected by the zero-point energy (ZPE). For bond dissociation energy, a BSSE correction was carried out according to the counterpoise procedure.[24] To obtain accurate thermodynamic data, the G2[25] and CBS-Q[26] methods were used. Natural bond orbital analysis was performed using the NBO version 3.1 of the Gaussian 03 software package.[27] The aromaticity of ring systems was estimated by nucleus-independent chemical shift (NICS) criteria, developed by Schleyer et al.[28]

Results and Discussion

First, we report hydrogen-terminated oligomers (H−Si_n−H: $n = 2, 4, 6, 8$) consisting of disilyne units. The smallest oligomer is a dimer (H−Si_2−H). A neutral molecule with the formula of Si_2H_2 has four isomers (**11a**−**d**) with an energetic array as shown in Figure 1, and a hydrogen-terminated dimer with a triple bond in a trans configuration, **11a**, is the least stable, as reported in a previous theoretical study.[1d] Optimized geometries obtained with the B3LYP and MP2 methods are similar, with differences of 0.02 Å and 1° (Table 1). Triplet **11a** has a trans-bent structure, as reported in a previous theoretical study,[10f] and the Gibbs free energy at 298.15 K is higher by 1.1 kcal mol^{-1} than singlet **11a** at the B3LYP/6-311++G(3df,3pd) level.[29] For $Si_2H_2^{2-}$, four isomers were obtained (**12a**−**d**), and two of them are hydrogen-terminated dimers in trans and cis configurations (Figure 1), where the monobridged **11c** changes to the cis **12c′** when two extra electrons are doped. In contrast to neutral Si_2H_2, **12a** and **12c′** are the most stable isomers. At 298.15 K the Gibbs free energies of the least stable **12d** are 46.2 and 51.0 kcal mol^{-1} higher than that of **12a** at the B3LYP/6-311++G(3df,3pd) and MP2/6-311++G(3df,3pd) levels, respectively. **12d** is a minimum at the B3LYP/6-311++G(3df,3pd) level, but it is a transition state for a dyotropic rearrangement of two hydrogen atoms at the MP2/6-311++G(3df,3pd) level. The formation of **12a** and **12c′** is qualitatively explained by the construction from SiH units (Figure 2).[1d] When two electrons are doped in two vacant p orbitals of **11a** (or **11c**), one by one, the donor−acceptor bond[9] is broken and then a new σ bond and two lone pair orbitals form. The existence of cis and trans isomers is the same as in ethylene: ethylene derivatives RHC=CHR have cis and trans isomers. The trans isomer **12a** is more stable by 2.8 and 3.4 kcal mol^{-1} in Gibbs free energy than the cis isomer **12c′** at the B3LYP/6-311++G(3df,3pd) and MP2/6-311++G(3df,3pd) levels, respectively. Triplet **12a** has an approximately 90° H−Si−Si−H dihedral angle. The twisted structure is also the same as in triplet ethylene. The singlet is much more stable, by about 19.6 kcal mol^{-1} in Gibbs free energy at 298.15 K, than the triplet. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **12a** and

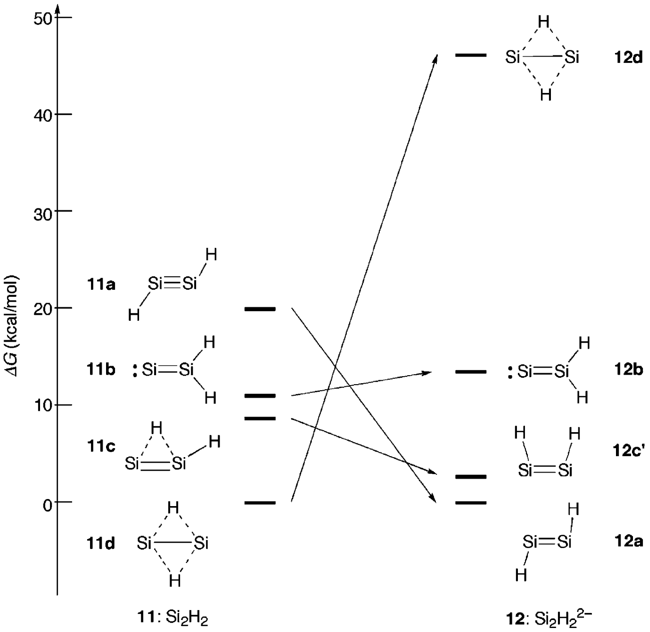

Figure 1. Relative Gibbs free energies at the B3LYP/6-311++G(3df,3pd) level of the four singlet isomers of neutral Si_2H_2 (**11**) and the dianion (**12**).

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(20) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(21) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(22) Soliva, R.; Orozco, M.; Luque, F. J. *J. Comput. Chem.* **1997**, *18*, 980.

(23) (a) Bauschlicher, C. W., Jr.; Partridge, H. *Chem. Phys. Lett.* **1995**, *240*, 533. (b) Martin, J. M. L. *J. Chem. Phys.* **1998**, *108*, 2791.

(24) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(25) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(26) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

(27) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (e) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (f) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41.

(28) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669. (c) West, R.; Buffy, J. J.; Haaf, M.; Müller, T.; Gehrhus, B.; Lappert, M. F.; Apeloig, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1639.

(29) The degree of spin contamination is small for the triplet states: $\langle S^2 \rangle = 2.01$ for both Si_2H_2 and $Si_2H_2^{2-}$.

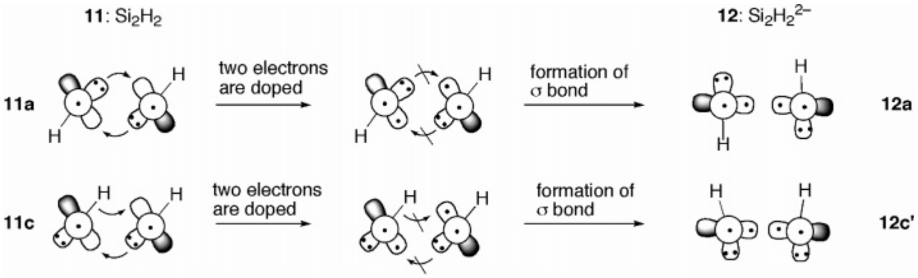

Figure 2. Construction of **12a** and **12c′** from **11a** and **11c**, respectively.

Table 1. Optimized Geometric Parameters and the Energies of 11a–d and 12a–d[a]

			B3LYP	MP2				B3LYP	MP2
11a	S	r(SiSi)/Å	2.100	2.098	**12a**	S	r(SiSi)/Å	2.288	2.279
		r(SiH)/Å	1.491	1.481			r(SiH)/Å	1.556	1.544
		a(HSiSi)/deg	124.9	125.7			a(HSiSi)/deg	98.1	97.5
		δ(HSiSiH)/deg	180	180			δ(HSiSiH)/deg	180	180
		E/au	−580.124 62	−579.139 41			E/au	−580.089 40	−579.094 12
		ΔE_{zero}/kcal mol^{-1}	19.0	18.9			ΔE_{zero}/kcal mol^{-1}	0.0	0.0
		ΔG/kcal mol^{-1}	18.1	18.4			ΔG/kcal mol^{-1}	0.0	0.0
11a	T	r(SiSi)/Å	2.291		**12a**	T	r(SiSi)/Å	2.444	
		r(SiH)/Å	1.511				r(SiH)/Å	1.556	
		a(HSiSi)/deg	104.7				a(HSiSi)/deg	101.4	
		δ(HSiSiH)/deg	180				δ(HSiSiH)/deg	94.0	
		E/au	−580.122 46				E/au	−580.055 11	
		ΔE_{zero}/kcal mol^{-1}	20.6				ΔE_{zero}/kcal mol^{-1}	20.5	
		ΔG/kcal mol^{-1}	19.2				ΔG/kcal mol^{-1}	19.6	
11b	S	r(SiSi)/Å	2.201	2.204	**12b**	S	r(SiSi)/Å	2.220	2.205
		r(SiH)/Å	1.483	1.476			r(SiH)/Å	1.537	1.529
		a(HSiSi)/deg	123.9	123.5			a(HSiSi)/deg	131.0	131.3
		δ(HSiSiH)/deg	180.0	180.0			δ(HSiSiH)/deg	180	180
		E/au	−580.138 12	−579.144 75			E/au	−580.068 04	−579.073 83
		ΔE_{zero}/kcal mol^{-1}	11.2	14.9			ΔE_{zero}/kcal mol^{-1}	13.4	12.9
		ΔG/kcal mol^{-1}	10.9	14.5			ΔG/kcal mol^{-1}	13.5	13.0
11c	S	r(SiSi)/Å	2.112	2.123	**12c′**	S	r(SiSi)/Å	2.307	2.298
		r(SiH)/Å	1.489,[b] 1.718[c]	1.482,[b] 1.695[c]			r(SiH)/Å	1.562	1.549
		a(HSiSi)/deg	160.2,[b] 49.2[c]	159.1,[b] 48.9[c]			a(HSiSi)/deg	103.2	102.0
		δ(HSiSiH)/deg	0	0			δ(HSiSiH)/deg	0	0
		E/au	−580.140 37	−579.154 22			E/au	−580.084 34	−579.088 03
		ΔE_{zero}/kcal mol^{-1}	9.4	8.8			ΔE_{zero}/kcal mol^{-1}	2.8	3.5
		ΔG/kcal mol^{-1}	8.7	8.3			ΔG/kcal mol^{-1}	2.8	3.4
11d	S	r(SiSi)/Å	2.213	2.214	**12d**[d]	S	r(SiSi)/Å	2.502	2.387
		r(SiH)/Å	1.673	1.657			r(SiH)/Å	1.679	1.708
		a(HSiSi)/deg	48.6	48.1			a(HSiSi)/deg	41.8	45.7
		δ(HSiSiH)/deg	104	105			δ(HSiSiH)/deg	136	100
		E/au	−580.157 13	−579.169 96			E/au	−580.013 81	−579.004 06
		ΔE_{zero}/kcal mol^{-1}	0.0	0.0			ΔE_{zero}/kcal mol^{-1}	46.3	50.8
		ΔG/kcal mol^{-1}	0.0	0.0			ΔG/kcal mol^{-1}	46.2	51.0

[a] Optimized structures and the energies at the B3LYP and MP2 levels using the 6-311++G(3df,3pd) basis set. Legend: E, total energy; ΔE_{zero}, total energy + ZPE relative to that of the most stable isomer; ΔG, Gibbs free energy at 298.15 K relative to that of the most stable isomer; S, singlet; T, triplet. [b] $r(^1\mathrm{SiH})$, $a(\mathrm{H}^1\mathrm{Si}^2\mathrm{Si})$. [c] $r(^2\mathrm{SiH})$, $a(\mathrm{H}^2\mathrm{Si}^1\mathrm{Si})$. [d] Transition state at the MP2 level.

12c′ are π and π*, respectively. It is concluded that the hydrogen-terminated dimer with two electrons doped (dianion) shows the same feature as ethylene in the existence of the cis and trans isomers and in the character of the HOMO and LUMO levels.

It is important to verify whether the required level of electron doping is attainable in a material. At the MP2/6-311++G(3df,3pd) + ZPE level **12a** is unstable, by 27.0 kcal mol^{-1}, relative to **11a**. At the B3LYP/6-311++G(3df,3pd) + ZPE level, the energy difference between **11a** and **12a** is 22.0 kcal mol^{-1}. We estimate the energy difference between **11a** and **12a** more accurately using the G2 and CBS-Q methods. The G2 and CBS-Q methods reportedly give highly accurate thermodynamic data with standard deviations of 0.9 and 0.8 kcal mol^{-1}, respectively.[30] The results using the G2 and CBS-Q methods are listed in Table 2. Geometric parameters optimized using the G2 and CBS-Q methods are similar to those at the B3LYP/6-311++G(3df,3pd)

Table 2. Thermodynamic Data and the Optimized Geometric Parameters of 11a and 12a[a]

		G2	CBS-Q
11a	G/au	−579.2124 68	−579.220 68
	r(SiSi)/Å	2.103	2.106
	r(SiH)/ Å	1.491	1.491
	a(HSiSi)/deg	124.6	124.7
	δ(HSiSiH)/deg	180.0	180.0
12a	G/au	−579.180 33	−579.175 68
	FE / kcal mol^{-1}	27.8	28.2
	r(SiSi)/Å	2.287	2.292
	r(SiH)/Å	1.571	1.571
	a(HSiSi)/deg	97.5	97.5
	δ(HSiSiH)/deg	180.0	180.0

[a] Results are calculated using the method indicated. Legend: G, free energy. FE = $G(\mathrm{Si_2H_2}^{2-}) - G(\mathrm{Si_2H_2})$.

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(30) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*; Gaussian Inc.: Pittsburgh, PA, 1993; pp 141–161.

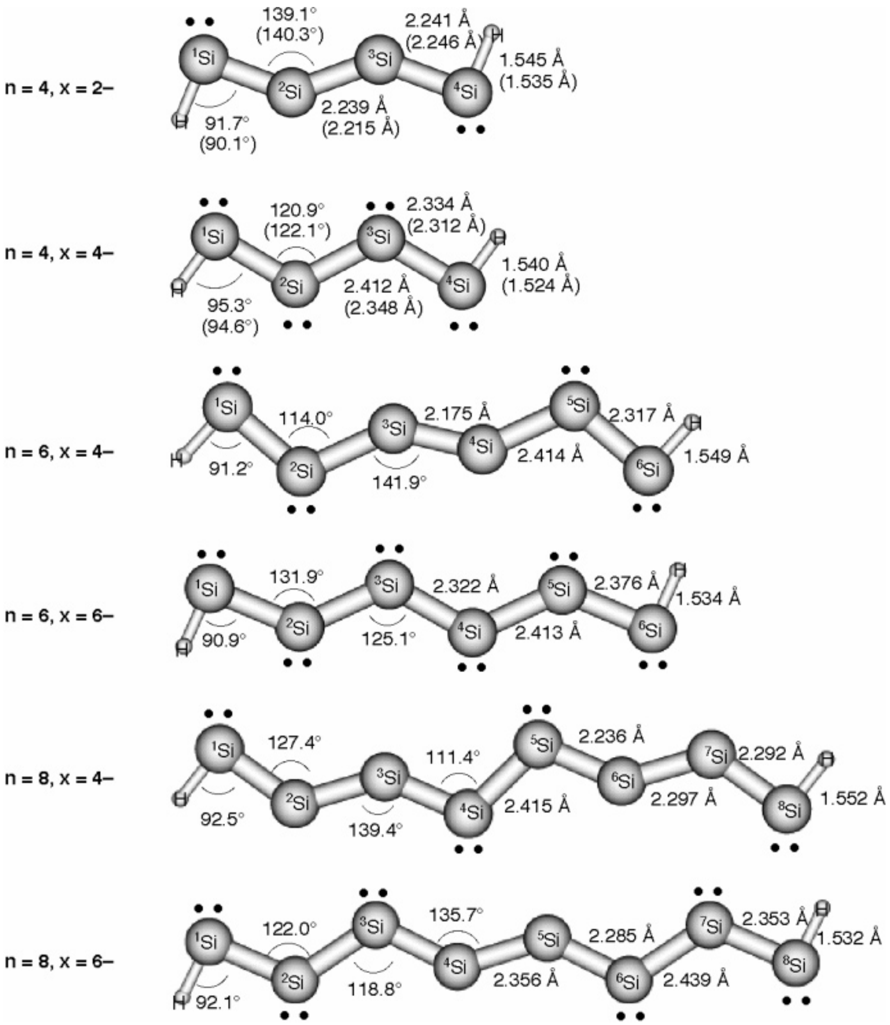

Figure 3. Optimized structures of $Si_nH_2^x$ (n = 4, 6, 8; x = 2−, 4−, 6−) at the B3LYP/6-311++G(3df,3pd) level. Bond lengths are given in Å and bond and dihedral angles in deg. The results at the MP2/6-311++G(3df,3dp) level are shown in parentheses. The position of lone pair orbitals is indicated by double dots.

level with differences of 0.02 Å and 1° (Table 2). The free energy differences between the G2 and CBS-Q methods are small: 2.5 and 2.9 kcal mol^{-1} for **11a** and **12a**, respectively. The energy difference between **11a** and **12a**, that is, the energy for the formation of the dianion, is estimated to be 28 kcal mol^{-1} with both the G2 and the CBS-Q methods. The value is closer to that at the MP2/6-311++G(3df,3pd) + ZPE level than that at the B3LYP/6-311++G(3df,3pd) + ZPE level. Since the energy for the formation of the dianion is large enough, it seems that **12a** is very difficult to attain. Comprehensive studies on the electron affinities of silicon hydrides have been reported by Schaefer et al.,[18d] and the zero-point corrected electron affinity of SiH has been estimated to be 1.30 eV (29.9 kcal mol^{-1}) with the B3LYP method, in good accord with the experimental laser photoelectron value of 1.277 eV.[31] The zero-point corrected electron affinity EA_{zero} is defined as EA_{zero}= E(zero-point corrected neutral) − E(zero-point corrected anion). The positive value means SiH^- is more stable than SiH. Here we calculate the Si−Si bond dissociation energy (BDE) of $[H-Si_2-H]^{2-}$ as BDE = $2E(SiH^-) - E(Si_2H_2^{2-})$ using B3LYP/6-311++G(3df,3pd). The zero-point corrected BDE with BSSE correction[24] is 12.3 kcal mol^{-1}. The calculated BDE is positive, and thus the Si−Si bond in $[H-Si_2-H]^{2-}$ can be formed from SiH^-.

We extend our study to hydrogen-terminated $H-Si_n-H$ (n = 4, 6, 8) oligomers. Neutral (Si_nH_2; n = 4, 6, 8) and multiply charged ($Si_4H_2^{2-}$, $Si_4H_2^{4-}$, $Si_6H_2^{2-}$, $Si_6H_2^{4-}$, $Si_6H_2^{6-}$, $Si_8H_2^{2-}$, $Si_8H_2^{4-}$, $Si_8H_2^{6-}$, $Si_8H_2^{8-}$) oligomers are optimized. As the number of silicon atoms increases, the number of isomers of the silicon hydrides Si_nH_2 increases tremendously. Even for the reaction of the four-membered ring of Si_4 with H_2, 14 minima and 4 transition states have been reported.[32] As a model of a one-dimensional conjugating polymer with high conductivity, we are interested in planar chain compounds. The initial structures for the geometry optimization are selected to be trans-zigzag chains. The optimization was performed under the constraint of planarity, but no other symmetry was imposed during the optimization. Six planar chains are obtained as minima (Figure 3), and the resultant optimized structures of the six planar chains have C_{2h} symmetry. The other planar structures are transition states or ring-containing structures. In several cases, no stationary point with a planar struc-

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[31] Kasdan, A.; Herbst, E.; Lineberger, W. C. *J. Chem. Phys.* **1975**, *62*, 541.

[32] Wang, W.-N.; Tang, H.-R.; Fan, K.-N.; Iwata, S. *J. Chem. Phys.* **2001**, *114*, 1278.

Table 3. Stationary Points of the Planar Hydrogen-Terminated Si_nH_2 (n = 4, 6, 8), the Planar Silicon Six-Membered Ring c-Si_6, and the Multiply Charged Anions[a]

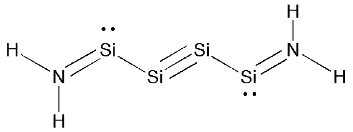
oligomer	stationary point
Si_4H_2	first TS
$Si_4H_2^{2-}$	MIN
$Si_4H_2^{4-}$	MIN
Si_6H_2	first TS
$Si_6H_2^{2-}$	TS (first (DFT), second (MP))
$Si_6H_2^{4-}$	MIN (DFT), second TS (MP)
$Si_6H_2^{6-}$	MIN (DFT), ND (MP)
Si_8H_2	ND (DFT), second TS (MP)
$Si_8H_2^{2-}$	second TS (DFT), CYC (MP)
$Si_8H_2^{4-}$	MIN (DFT), third TS (MP)
$Si_8H_2^{6-}$	MIN (DFT), sixth TS (MP)
$Si_8H_2^{8-}$	ND
c-Si_6	ND
c-Si_6^{2-}	MIN (MP), second TS (DFT)
c-Si_6^{4-}	MIN (MP), third TS (DFT)
c-Si_6^{6-}	MIN[b]

[a] The 6-311++G(d,p) basis set is used. The results are obtained by both B3LYP and MP2 methods otherwise noted, while imposing a planar structure. Legend: DFT, the results of B3LYP; MP, the results of MP2; TS, transition state; MIN, minimum; CYC, ring-containing structure; ND, no planar stationary point was determined. [b] Using the 6-311++G(d,p) basis set, the minimum by the MP2 method is slightly chair form: δ(SiSiSiSi) = ±14.6°. However, with optimization at the MP2/6-311++G(3df,3pd) level, the structure changes to completely planar.

ture is found in searches with the 6-311++G(d,p) basis set (Table 3). The six planar chains are all anionic, and no neutral planar chain is obtained as a minimum.

Optimized $Si_4H_2^{4-}$ has an approximately 120° Si−Si−Si bond angle and two short and one long Si−Si bond. This suggests that $Si_4H_2^{4-}$ consists of two double and one single bond, and an sp^2 hybridization at silicon is expected. The Si−Si bond distances are long compared to the corresponding single and double bonds of neutral silicon compounds (Si_2H_6, 2.350 and 2.339 Å at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)levels, respectively; Si_2H_4, 2.173 and 2.163 Å at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)levels, respectively). This may be due to strong electron repulsion in the present multiply anionic system. From a natural bond orbital (NBO) analysis, it is proved that 20 doubly occupied (more than 1.999 occupation) core, seven bonding, and four lone pair orbitals exist in $[H-{}^1Si-{}^2Si-{}^3Si-{}^4Si-H]^{4-}$, where the occupancy threshold is taken as 1.80. The seven bonding orbitals are two ${}^1Si-{}^2Si$, two ${}^3Si-{}^4Si$, one ${}^2Si-{}^3Si$, and two Si−H bonds. The hybridization at ${}^1Si$ and ${}^4Si$ are p_π and $sp^{2.05}$. Each silicon atom has a lone-pair orbital. The lone pair orbital in $[H-{}^1Si-{}^2Si-{}^3Si-{}^4Si-H]^{4-}$ looks like a C−H bonding orbital at each carbon atom in butadiene ($H_2C{=}CHCH{=}CH_2$). From the structure and the hybridization, $Si_4H_2^{4-}$ is a planar molecule with a π system on an sp^2 silicon backbone.

The Si−Si−Si bond angles of optimized dianion $Si_4H_2^{2-}$ are large (140°) and Si−Si bond lengths are short compared with those of $Si_4H_2^{4-}$. From an NBO analysis under the occupancy threshold of 1.90, eight bonding orbitals and two lone pair orbitals are found. The eight bonding orbitals are six Si−Si bonds and two Si−H bonds. Out-of-plane π orbitals are located at ${}^1Si-{}^2Si$ and ${}^3Si-{}^4Si$, and the in-plane π orbital is located at a ${}^2Si-{}^3Si$ bond. Four π electrons are accommodated in the out-of-plane π orbitals. Two lone pair orbitals are located at ${}^1Si$ and ${}^4Si$, and the absence of lone pair orbitals at ${}^2Si$ and ${}^3Si$ seems to enlarge the two Si−Si−Si bond angles. The Lewis structure is a chain of three double bonds with lone pair electrons at two terminal silicon atoms.



r(Si–Si) = 2.390 (2.379)
r(Si≡Si) = 2.120 (2.128)
r(Si=N) = 1.718 (1.713)
a(Si–Si≡Si) = 122.7 (122.7)
a(Si–Si=N) = 100.8 (99.8)

Figure 4. Lewis structure of $Si_4(NH_2)_2$ and the optimized geometric parameters at the B3LYP/6-311++G(3df,3pd) level. Bond lengths are given in Å and bond and dihedral angles in deg. The results at the MP2/6-311++G(3df,3dp) level are shown in parentheses.

Next, we consider a neutral acyclic silicon oligomer where substituents at the terminals act as electron dopant. This molecule is neutral, but the silicon chain is electron-rich because the terminal substituents push electrons in the silicon chain. This can be a model of the anionic silicon oligomer when looking at the silicon chain. The amino group is known as a π-electron-donating substituent. We consider a diamino-substituted silicon tetramer, $H_2N-{}^1Si-{}^2Si-{}^3Si-{}^4Si-NH_2$. The planar chain structure is optimized as a minimum (Figure 4) only with the MP2 method. The B3LYP/6-311++G(3df,3pd) structure is a transition state. It can be supposed that the planar chain structure is constructed in a very sophisticated balance of weak interactions on the potential energy surface. One short and two long Si−Si bonds and Si−Si−Si bond angles of approximately 120° are obtained. From an NBO analysis, three out-of-plane π orbitals are located at $N-{}^1Si$, ${}^2Si-{}^3Si$, and ${}^4Si-N$, and the sum of occupation of the out-of-plane π orbitals is 5.89. Lone pair orbitals are located at ${}^1Si$ and ${}^4Si$, and one in-plane π orbital is at ${}^2Si-{}^3Si$. The Lewis structure is depicted in Figure 4. The structure of ${}^1Si-{}^2Si-{}^3Si-{}^4Si$ is similar to the central four silicon atoms of $Si_6H_2^{4-}$ in Si−Si bond length and the position of the lone pair, but there are differences in the Si−Si−Si bond angles (Figure 3).

For longer chain oligomers, MP2 and B3LYP methods give different characteristics of stationary points (Table 3). Minima are obtained only with the B3LYP method for $Si_6H_2^{4-}$, $Si_6H_2^{6-}$ $Si_8H_2^{4-}$, and $Si_8H_2^{6-}$. This may be due to the advantage of density functional theory for spatially extended delocalization such as in bulk crystals. An NBO analysis reveals that the number of π electrons formally accommodated in the out-of-plane π orbitals is the same as the number of silicon atoms and is independent of the number of doped electrons for the six planar polysilicon chains in Figure 3: the summed out-of-plane π orbital occupations are 3.88 ($Si_4H_2^{2-}$), 3.88 ($Si_4H_2^{4-}$), 5.67 ($Si_6H_2^{4-}$), 5.60 ($Si_6H_2^{6-}$), 7.39 ($Si_8H_2^{4-}$), and 7.42 ($Si_8H_2^{6-}$). The difference in the number of doped electrons is found in the number of lone pair electrons. The positions of lone pair electrons are depicted by double dots in Figure 3. The existence of lone pair electrons is important to keep the planar polysilicon chain structures. Fewer numbers of lone pair electrons lead to a ring-containing structure in one case

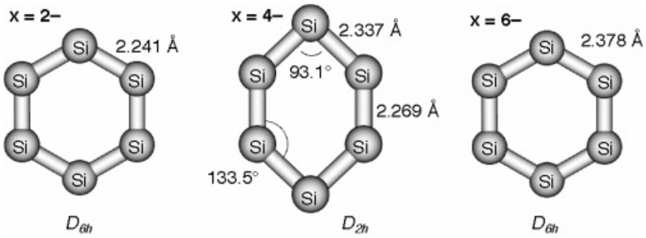


Figure 5. Optimized structures of c-Si_6^x ($x = 2-, 4-, 6-$) at the MP2/6-311++G(3df,3dp) level.

(see CYC in Table 3) and to a nonplanar structure deduced from the imaginary mode of a planar transition state in another case (see TS in Table 3). When too many electrons are doped in the system, it is impossible to keep the bonding between silicon atoms because of the electron repulsion, and thus, we could not obtain stationary points (see ND in Table 3).

The present anionic polysilicon chains may seem to be hypothetical and unlikely ever to be synthesized for organosilicon chemists. However, multiply charged silicon systems are well-established in silicides[33] and anionic silicon chains have been observed already experimentally.[34] Therefore, we believe that our calculated system might be realizable.

Next, we construct silicon six-membered rings (c-Si_6) consisting of three disilyne units with a cis configuration. We focus on a planar six-membered ring, since the target is an aromatic ring. We could not locate the minimum of a planar neutral c-Si_6, but we could obtain minima of a planar six-membered ring in a charged system. By doping two and six electrons, we obtain planar c-Si_6 with D_{6h} symmetry as minima. We obtain planar four-electron doped c-Si_6 as a minimum, but the symmetry is lowered to D_{2h}. Optimized structures of the D_{6h} c-Si_6^{2-}, D_{6h} c-Si_6^{6-}, and D_{2h} c-Si_6^{4-} are shown in Figure 5. The minima are located only with the MP2 method for c-Si_6^{2-} and c-Si_6^{4-} because of the sophisticated potential energy surface, which is a sharp contrast to the longer chain anions such as $Si_6H_2^{4-}$, $Si_6H_2^{6-}$, $Si_8H_2^{4-}$, and $Si_8H_2^{6-}$, where planar minimum structures are found only at the B3LYP level. When both the MP2 and B3LYP methods give minima as in case of shorter chain anions, the existence of the molecules is certain. However, the fact that one of those methods fails to locate a minimum does not always deny the possibility of the existence of the molecule, because both methods have their shortcomings.

An NBO analysis of D_{6h} c-Si_6^{6-} shows 30 doubly occupied (more than 1.999 occupation) core orbitals as well as nine bonding and six lone pair orbitals when the occupancy threshold is taken to be 1.60. The nine bonding orbitals are six Si−Si bonds with an $sp^{2.1}$ hybridization and three Si−Si bonds with a p_π hybridization. Six lone pair orbitals exist at silicon instead of six C−H bonding orbitals in benzene (**6**). From the D_{6h} symmetry and the hybridization, c-Si_6^{6-} is a system of six π electrons on an sp^2 silicon backbone like benzene, but Si−Si bond distances of D_{6h} c-Si_6^{6-} (2.378 Å) are longer than that of the Si−Si single bond of neutral silicon compound (in Si_2H_6, 2.339 Å at the MP2/6-311++G(d,p) level).

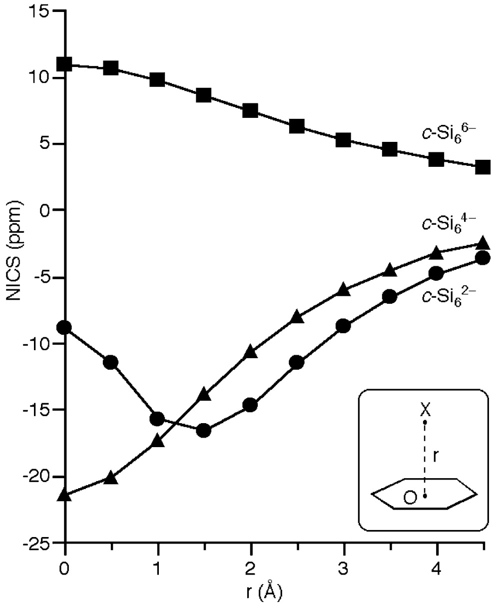


Figure 6. Nucleus-independent chemical shifts (NICS) of c-Si_6^{2-} (circle), c-Si_6^{4-} (triangle), and c-Si_6^{6-} (square) at X versus distance, r, from the center O.

In D_{6h} c-Si_6^{2-}, the Si−Si bond lengths are 2.24 Å. The lengths are the same as those of a tetramer, $Si_4H_2^{2-}$, and are between the distances of Si−Si single and double bonds (2.339 Å for Si_2H_6 and 2.163 Å for Si_2H_4 at the MP2/6-311++G(d,p) level). This feature is the same as in **6**, where the C−C bond length is between the distances of C−C single and double bonds. An NBO analysis with an occupancy threshold of 1.60 shows three out-of-plane π, three in-plane π, three σ with $sp^{1.6}$ hybridization, and three σ with $sp^{0.8}$ hybridization. Here, the occupancy of the corresponding antibonding orbitals is not negligible: 0.330 for the out-of-plane π^*, 0.421 for the in-plane π^*, 0.257 for the σ^* with $sp^{1.6}$ hybridization, and 0.927 for the σ^* with $sp^{0.8}$ hybridization. Since the occupancy of the out-of-plane π orbital is 1.661, the sum of occupation of each set of out-of-plane π and π^* orbitals is nearly two (1.99). Therefore, it can be concluded that D_{6h} c-Si_6^{2-} is a π-conjugating system where six π electrons delocalize. The other in-plane orbitals accommodate a total of 20 electrons in a complicated manner using antibonding orbitals.

From the symmetry, c-Si_6^{2-} and c-Si_6^{6-} are candidates for aromatic six-membered rings of silicon. To estimate the aromaticity of c-Si_6^{2-}, c-Si_6^{4-}, and c-Si_6^{6-}, a nucleus-independent chemical shift (NICS)[28] at the center of the ring (O) and above the ring (X) was calculated and the estimated NICS values at X are plotted versus distance r between O and X (Figure 6). The NICS values for D_{6h} c-Si_6^{2-} and D_{2h} c-Si_6^{4-} are negative, and those of D_{6h} c-Si_6^{6-} are positive. This indicates that D_{6h} c-Si_6^{6-} is

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(33) (a) Nikitin, E. N.; Tkalenko, E. N.; Zaitsev, V. K.; Zaslavskii, A. I.; Kuznetsov, A. K. *Inorg. Mater.* **1968**, *4*, 1656. (b) Witte, H. *Naturwissenschaften* **1937**, *25*, 795. (c) Turban, K.; Schäfer, H. *Z. Naturforsch., B* **1973**, *28*, 220. (d) Eisenman, B.; Schäfer, H. *Z. Naturforsch., B* **1974**, *29*, 13. (e) Currao, A.; Wengert, S.; Nesper, R.; Curda, J.; Hillebrecht, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 501. (f) Wynnycky, J. R.; Pidgeon, L. M. *High Temp. Sci.* **1972**, *4*, 192. (g) Axel, H.; Eisenman, B.; Schäfer, H.; Weiss, A. *Z. Naturforsch., B* **1969**, *24*, 815. (h) Eisenman, B.; Weiss, A.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1972**, *391*, 241.

(34) (a) Hellner, E. *Z. Anorg. Allg. Chem.* **1950**, *261,* 226. (b) Hellner, E. *Angew. Chem.* **1950**, *62*, 125. (c) Rocktäschel, G.; Weiss, A. *Z. Anorg. Allg. Chem.* **1962**, *316*, 231. (d) Rieger, W.; Parthé, E. *Acta Crystallogr.* **1967**, *22*, 919. (e) Böhm, J.; Hassel, O. *Z. Anorg. Allg. Chem.* **1927**, 160, 152. (f) Janzon, K. H.; Schäfer, H.; Weiss, A. *Z. Naturforsch., B* **1968**, *23*, 1544. (h) Evers, J. *J. Solid State Chem.* **1979**, *28*, 369.

antiaromatic, although the NBO analysis gives the same Lewis structure for c-Si_6^{6-} and benzene, possibly because the Si−Si bond length of c-Si_6^{6-} is longer than the Si−Si single bond and the interaction of π orbitals is very weak in c-Si_6^{6-}. Since the NICS value of D_{2h} c-Si_6^{4-} has a minimum at the ring center ($r = 0$), the chemical shift is not mainly due to the π ring current. The NICS value of D_{6h} c-Si_6^{2-} has a minimum around 1.5 Å above the ring, which means the π ring current causes the chemical shift.[28c] As mentioned above, c-Si_6^{2-} is a six-π-electron system from the NBO analysis. It is concluded that D_{6h} c-Si_6^{2-} is an aromatic six-membered ring with diamagnetic π ring current effects. D_{6h} c-Si_6^{2-} shows the same feature in the structure and the aromaticity as benzene.

Related to our present calculations on anionic silicon six-membered ring compounds, the crystal structure of nonaromatic planar silicon ring reported by Nesper et al. in 1998[19d] is impressive. The crystal structure contains planar hexasilylhexasilacyclohexane anions with a formal charge of $-(21 \pm 2\delta)$. The system is not completely the same as our calculated ring compounds, but we would anticipate that multiply charged anions are experimentally attainable and the structure of the anionic silicon six-membered ring can be planar.

Finally, we show here two realistic models of c-Si_6^{2-}. The two models shown here are obtained as minima only at the MP2 levels. One is a neutral molecule where a countercation balances the negative charges of the anionic silicon ring. To realize c-Si_6^{2-}, we select Be as countercation. The optimized equilibrium structure is a D_{6h} silicon six-membered ring with Be at the center slightly above the ring by 0.149 Å at the MP2/6-311+G(d) level. With Be, the molecule is neutral and the symmetry of the optimized structure is C_{6v}. A natural population analysis charge of Be gives a strongly positive value (1.029). The Si−Si bond length is almost the same as in c-Si_6^{2-} (2.250 Å). From Bader's topological analysis,[35] the electron density Laplacian is negative (−0.058) in Si−Si bonds and positive (0.040) in Si−Be bonds, and then the Si−Si and Si−Be bondings are characterized as covalent and as ionic, respectively. The other model is the isoelectronic replacement by phosphorus. P_6^{4+} is isoelectronic with *c*-Si_6^{2-}. It is well-known that neutral P_6 has eight structures: planar D_{6h} hexagon, benzvalene, Dewar benzene, triangular prismane, bicyclopropenyl, Claus benzene, chair form, and twisted-boat form.[36,37] Theoretical calculations have revealed that the planar hexagon is energy-rich and is located at a shallow energy potential.[37] In sharp contrast to the neutral P_6 system, our present calculations of the charged system P_6^{4+} indicate only one structure, a planar D_{6h} hexagon, as a minimum (r(PP) = 2.111 Å) at the MP2/6-311+G(3df) level.

Summary

The structures of neutral and anionic hydrogen-terminated oligomers (H−Si_n−H: n = 2, 4, 6, 8) and silicon six-membered rings (c-Si_6) have been investigated using quantum-chemical methods to realize planar polysilicon chains and aromatic silicon six-membered rings. The results are summarized as follows. (1) Among 18 calculated molecules, the equilibrium structures of seven anionic chains ($Si_2H_2^{2-}$, $Si_4H_2^{2-}$, $Si_4H_2^{4-}$, $Si_6H_2^{4-}$, $Si_6H_2^{6-}$, $Si_8H_2^{4-}$, $Si_8H_2^{6-}$) and three anionic six-membered rings (c-Si_6^{2-}, c-Si_6^{4-}, c-Si_6^{6-}) are planar, in which π electrons delocalize. (2) The number of π electrons formally accommodated in the out-of-plane π orbitals is the same as the number of silicon atoms and is independent of the number of doped electrons. (3) An anionic six-membered ring, c-Si_6^{2-} shows a large negative value of nucleus-independent chemical shift (NICS), which indicates that c-Si_6^{2-} is an aromatic molecule.

The present anionic system may seem to be hypothetical and unlikely ever to be synthesized; however, multiply charged silicon systems are well established in silicides.[33] Anionic silicon chains[34] and an anionic six-membered ring with D_{6h} symmetry[19d] have been already observed experimentally. Therefore, we believe that our calculated system might be realized and provide a new silicon π system.

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Supporting Information Available: Tables giving Cartesian coordinates and absolute energies of all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) (a) Bader, R. F. W. *Atoms in Molecules*; Oxford University Press: Oxford, U.K., 1990; Part A (Quantum Theory). (b) Kraka, E.; Cremer, D. Chemical Implication of Local Features of the Electron Density Distribution. In *Theoretical Models of Chemical Bonding*; Maksic, Z. B., Ed., Springer: Berlin, 1990; Part 2. (c) Bader, R. F. W.; Popelier, P. L. A.; Keith, T. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 620.

(36) (a) Nagase, S.; Ito, K. *Chem. Phys. Lett.* **1986**, *126*, 43. (b) Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Chem. Commun.* **1986**, 383. (c) Janoschek, R. *Chem. Ber.* **1989**, *122*, 2121. (d) Warren, D. S.; Gimarc, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 5378.

(37) Jones, R. O.; Hohl, D. *J. Chem. Phys.* **1990**, *92*, 6710.