

Structure and Stability of Y-Conjugated Silylium Cations [Si(XH)₃]⁺ (X = O, S, Se, and Te)

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Received July 7, 1997[⊗]

Abstract: Quantum mechanical ab initio calculations at the HF and MP2 levels of theory with valence basis sets up to TZ+2P quality are reported for the Y-conjugated silylium cations [Si(XH)₃]⁺ and the di- and monosubstituted analogues [HSi(XH)₂]⁺ and [H₂Si(XH)]⁺ (X = O–Te). The X→Si p(π) donation and the thermodynamic stabilization increase in the order O < S < Se < Te. This trend is given by the calculated complexation energies of the water complexes and the reaction energies of isodesmic reactions. A comparison with the respective carbenium ions shows that the chalcogen substituents stabilize the carbenium ions more than the silylium ions. While the stabilization of the carbenium ions by chalcogens from O to Te remains nearly the same, it strongly varies within the series of silylium ions in the order Te > Se > S > O. The silylium ions and the carbenium ions are more strongly stabilized by the chalcogens than by the respective halogen atom. The analysis of the Si–X bonds in [Si(XH)₃]⁺ shows that the covalent character increases from Si–O to Si–Te, which has a nearly unpolar bond.

Introduction

The longtime elusive goal of a silylium cation SiR₃⁺ that is stable in solution was finally achieved by Lambert,¹ who recently succeeded in the synthesis of the trimesitylsilylium ion. The success of Lambert's work came after a long period of frustrating failures to isolate stable SiR₃⁺ species and after premature success reports, which later turned out to be wrong.^{2–6} Silylium ions have also been a topic of theoretical work. Pioneering contributions in this field have been made by Schleyer⁷ and Apeloig.⁸ A recent theoretical study predicted that a combination of electronic and steric effects should lead

to a stable silylium cation.⁹ The choice of R = trimesityl was made for the same reason.¹ This shows that a knowledge of the electronic structure of SiR₃⁺ is helpful in the design and understanding of stable silylium cations.

The electronic structure of Y-conjugated species YX₃ and the electronic influence of the substituent X on the stability of the neutral or charged molecule is still not completely understood. It has recently been shown¹⁰ that Y-conjugated ions such as the trimethylenemethane dianion [C(CH₂)₃]²⁻ and the guanidinium cation [C(NH₂)₃]⁺ have nonplanar equilibrium geometries, and that they are not aromatic as had been suggested earlier.¹¹ Although the resonance stabilization of the Y-conjugated species was found to be lower than generally assumed, it is an important factor for the stabilization of the molecules.^{10b} A surprising result was found more recently for the trend of the halogens X = F–I in CX₃⁺.¹² Unlike previously suggested,¹³ the π-donation and the stabilizing effect of the π-donor substituent increases with F < Cl < Br < I. This

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

(1) Lambert, J. B.; Zhao, Y. *Angew. Chem.* **1997**, *109*, 389; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 400.

(2) Reviews: (a) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191. (b) Chojnowski, J.; Stanczyk, W. *Main Group Chem. News* **1993**, *93*, 1371. (c) Lickiss, P. D. *J. Chem. Soc., Dalton Trans.* **1992**, 1333. (d) Eaborn, C. *J. Organomet. Chem.* **1991**, *405*, 173. (e) Lambert, J. B.; Schulz, W. J., Jr. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Part 2, pp 1007.

(3) (a) Lambert, J. B.; Sun, H. *J. Am. Chem. Soc.* **1976**, *98*, 5611. (b) Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671. (c) Lambert, J. B.; McConnell, J. A.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 2482. (d) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201. (e) Lambert, J. B.; McConnell, J. A.; Schilf, W.; Schulz, W. J., Jr. *J. Chem. Soc., Chem. Commun.* **1988**, 455. (f) Lambert, J. B.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 6364. (g) Lambert, J. B.; Kania, L.; Schilf, W.; McConnell, J. A. *Organometallics* **1991**, *10*, 2578. (h) Lambert, J. B.; Kuhlmann, B. *J. Chem. Soc., Chem. Commun.* **1992**, 931. (i) Lambert, J. B.; McConnell, J. A.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 2482. (j) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. (k) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430.

(4) (a) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485. (b) Olah, G. A.; Laali, K.; Farooq, O. *Organometallics* **1984**, *3*, 1337. (c) Prakash, G. K. S.; Keyaniyan, S.; Aniszfeld, R.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H.-K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123. (d) Olah, G. A.; Heiliger, L.; Li, X.-Y.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1990**, *112*, 5991. (e) Olah, G. A.; Rasul, G.; Heiliger, L.; Bausch, J.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 7737. (f) Olah, G. A.; Rasul, G.; Li, X.-Y.; Buchholz, H. A.; Sandford, G.; Prakash, G. K. S. *Science* **1994**, *263*, 983. (g) Olah, G. A.; Rasul, G.; Buchholz, H. A.; Li, X.-Y.; Prakash, G. K. S. *Bull. Soc. Chim. Fr.* **1995**, *132*, 569. (h) Olah, G. A.; Rasul, G.; Prakash, G. K. S. *J. Organomet. Chem.* In press.

(5) (a) Strauss, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801. (b) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884. (c) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 358. (d) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495.

(6) (a) Xie, Z.; Lison, D. J.; Jelinek, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384. (b) Xie, Z.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2519. (c) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402. (d) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697. (e) Bahr, S. R.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 4514.

(7) Review: Maerker, C.; Kapp, J.; Schleyer, P. v. R. *Organosilicon Chemistry*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1996; Vol. II, and references cited therein.

(8) Reviews: (a) Apeloig, Y. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; pp 57. (b) Apeloig, Y. *Heteroatom Chemistry*, Block, E., Ed.; VCH: Weinheim, 1990, and further references therein.

(9) Pidun, U.; Stahl, M.; Frenking, G. *Chem. Eur. J.* **1996**, *2*, 869.

(10) (a) Gobbi, A.; MacDougall, P. J.; Frenking, G. *Angew. Chem.* **1991**, *103*, 1023; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1001. (b) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1993**, *115*, 2362.

(11) Gund, P. *J. Chem. Educ.* **1972**, *49*, 100.

(12) Frenking, G.; Fau, S.; Marchand, C. M.; Grützmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 6648.

means that Cl_3^+ is the most stable trishalocarbenium cation and CF_3^+ is least stable. The same trend with increasing stability of the heavier trishalogen cation was calculated for the heavy-atom analogues of the carbenium ion YX_3^+ ($Y = Si, Ge, Sn, and Pb$).¹² However, in a combined theoretical and experimental study of $[C(XH)_3]^+$ ($X = O, S, Se, and Te$) it has been reported that oxygen stabilizes the carbenium ion more than the heavier analogues $S-Te$.^{14,15} The stabilization of the singly substituted cations $[H_2C(XH)]^+$ ($X = O, S, Se, and Te$) by the chalcogens was calculated to increase slightly from oxygen to tellurium. An increase of the π -donor ability for the heavier atoms within a group has been calculated for $[H_2C(XH_n)]^+$ ($X = N-Sb, O-Te, F-I$).¹⁶

The conflicting results about the π -donor ability and the stabilization of cations by the chalcogens prompted us to investigate the silylium cations $[Si(XH)_3]^+$ ($X = O, S, Se, and Te$) and to compare them with the previously reported¹⁴ set of carbenium cations $[C(XH)_3]^+$. Besides the Y-conjugated cations $[Si(XH)_3]^+$ we also studied the di- and monosubstituted silylium cations $[HSi(XH)_2]^+$ and $[H_2Si(XH)]^+$ ($X = O, S, Se, and Te$). The results of this work are not only interesting for an understanding of the chemical bonding in the molecules. They may also help as a guideline for future experimental work in the field of silylium cations.

Methods

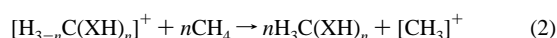
The geometries of the molecules have been fully optimized at the HF and MP2 levels of theory. The nature of the stationary points was investigated at the HF and MP2 levels by calculation of the second derivatives of the energies with respect to the nuclear coordinates. The calculated zero-point vibrational energies have not been scaled.

The following basis sets have been employed. HF calculations were carried out with 6-31G(d) basis sets¹⁷ for H, C, O, Si, and S and quasirelativistic effective core potentials (ECP) for Se and Te with (31/31/1) valence basis sets.¹⁸ This level of theory is denoted HF/DZP. The exponents for the d-type polarization functions of Se ($\zeta = 0.338$) and Te ($\zeta = 0.237$) have been taken from Huzinaga.¹⁹ Basis sets of TZ2P quality have been used for the MP2 calculations. 6-311G(2p,-2d) basis sets²⁰ were employed for H, C, O, Si, and S, while the same ECPs as above with (211/211/11) valence basis sets were used for Se and Te. Accordingly, this level of theory is denoted MP2/TZ2P. The

(13) Olah, G. A.; Rasul, G.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1996**, *118*, 3580.

(14) (a) Ohlmann, D.; Marchand, C. M.; Grützmacher, H.; Chen, G. S.; Farmer, D.; Glaser, R.; Currau, A.; Nesper, R.; Pritzkow, H. *Angew. Chem.* **1996**, *108*, 317; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 300. (b) Chen, G. S.; Marchand, C. M.; Glaser, R.; Grützmacher, H. *J. Am. Chem. Soc.* Submitted for publication. (c) Chen, G. S.; Marchand, C. M.; Farmer, D.; Glaser, R.; Grützmacher, H. *J. Am. Chem. Soc.* Submitted for publication.

(15) Note that in ref 14a the stabilization energy SE of the carbenium ions was calculated by using anisodesmic reaction, which is different than in our work:



Reaction 2 gives for doubly and triply substituted ions ($n = 2, 3$) different SE values than reaction 1, because the right-hand side of reaction 2 always has singly substituted neutral compounds as a reference. Because reaction 1 always has the same number of substituents XH in the neutral compound and the cation, the calculated SE values should be a better expression for the stabilizing effect of XH.

(16) Kapp, J.; Schade, C.; El-Nahas, A. M.; Schleyer, P. v. R. *Angew. Chem.* **1996**, *108*, 2373; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2236.

(17) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(18) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(19) Andzelm, J.; Huzinaga, S.; Klobukowski, M.; Radzio, E.; Sakai, Y.; Tatekawi, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

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

exponents for the two d-type polarization functions are $\zeta(Se) = 0.144$, 0.489 and $\zeta(Te) = 0.096$, 0.305.¹⁹ Unless otherwise noted, we discuss only the results obtained at MP2/TZ2P.

The topological analysis of the electron density distribution²¹ has been carried out at the MP2 level of theory with all-electron basis sets for Se and Te at MP2/TZ2P optimized geometries, because the ECP approach sometimes gives an incorrect density distribution that has no (3,-1) critical points between chemically linked atoms.²² For Se and Te we used the basis sets which have been suggested by Huzinaga,¹⁹ i.e. (43321/4321/311) for Se and (433321/43321/4211) for Te in conjunction with 6-31G(d) for the other elements. This level of theory is denoted MP2/DZP(AE).

The geometry optimizations and energy calculations have been carried out with the program package Gaussian94.²³ Atomic partial charges were calculated by using the natural bond orbital (NBO) partitioning scheme.²⁴ The topological analysis of the electron density distribution was done with the program Morphy.²⁵

Geometries and Energies

Tables 1 and 2 show the calculated energies of all structures which have been investigated in our study. The energetically lowest lying equilibrium geometries of the molecules predicted at the MP2/TZ2P level of theory are displayed in Figure 1. A complete list of all optimized geometries calculated at MP2/TZ2P is given as Supporting Information.

All cations listed in Table 1 have a planar equilibrium structure. The calculations predict that the $[Si(XH)_3]^+$ cations exhibit propeller-like geometries with C_{3h} symmetry (compounds **1a-4a**, Figure 1). The isomeric forms with C_s symmetry **1b-4b**, where one XH group of the C_{3h} form is rotated 180° about the Si-XH bond, are at HF/DZP slightly higher lying minima (Table 1). At MP2/TZ2P, only the C_s form of $[Si(OH)_3]^+$ **1b** is still an energy minimum, while **2b-4b** are transition states (Table 1). It follows that only **1a-4a** need to be considered for the discussion.

The neutral silicon compounds $HSi(XH)_3$ (**5-8**) have also been calculated with two different conformations. The C_1 symmetric forms **5b-7b** are slightly (0.2-0.6 kcal/mol) lower in energy at the HF/DZP and MP2/TZ2P level than the C_3 -symmetric forms **5a-7a** (Table 1). Only for $HSi(TeH)_3$ is the C_3 isomer **8a** 0.2 kcal/mol lower in energy than **8b**. The small energy and geometry differences between the different conformations of **5-8** are not important for the present study.

The most important difference between the geometries of the cations **1-4** and the neutral compounds **5-8** is found for the Si-X bond lengths. The Si-X bonds of the cations **1a-4a** are significantly shorter than in the respective neutral compounds. The shortening is between 0.069 Å for the Si-O bond (**5b** \rightarrow **1a**) and 0.079 Å for the Si-S bond (**6b** \rightarrow **2a**). The Si-X bonds of the silylium cations are shortened less than the C-X bonds of the corresponding carbenium cations. Here, the C-O bond of $[C(OH)_3]^+$ is 0.128 Å shorter than that in $HC(OH)_3$, and the C-S bond of $[C(SH)_3]^+$ is 0.114 Å shorter than

(21) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press, Oxford, 1990.

(22) (a) Vyboishchikov, S. F.; Sierraalta, A.; Frenking, G. *J. Comput. Chem.* **1996**, *18*, 416. (b) Sierraalta, A.; Ruete, F. *J. Comput. Chem.* **1994**, *15*, 313.

(23) Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomberts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, I.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 1995.

(24) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(25) Popelier, P. L. A. *Comput. Phys. Commun.* **1996**, *93*, 212.

Table 1. Calculated Total Energies, E_{tot} [hartree], Relative Energies, E_{rel} [kcal/mol], Number of Imaginary Frequencies, i , and Zero-Point Vibrational Energies, ZPE [kcal/mol]

	sym	X	HF/DZP			MP2/TZ2P			
			E_{tot}	i		E_{tot}	E_{rel}	ZPE	i
[Si(XH) ₃] ⁺									
1a	<i>C</i> _{3h}	O	-515.10845	0		-516.18224	0.0	27.0	0
2a	<i>C</i> _{3h}	S	-1483.00254	0		-1484.20212	0.0	19.0	0
3a	<i>C</i> _{3h}	Se	-317.90297	0		-318.54823	0.0	16.5	0
4a	<i>C</i> _{3h}	Te	-314.05951	0		-314.66343	0.0	14.6	0
1b	<i>C</i> _{3s}	O	-515.10376	0		-516.17850	2.3	27.5	0
2b	<i>C</i> _{3s}	S	-1483.00094	0		-1484.20111	0.6	19.0	1
3b	<i>C</i> _{3s}	Se	-317.90222	0		-318.54776	0.3	16.4	1
4b	<i>C</i> _{3s}	Te	-314.05908	0		-314.66314	0.2	14.5	1
HSi(XH) ₃									
5a	<i>C</i> ₃	O	-515.96836	2		-517.07219	0.6	32.4	2
6a	<i>C</i> ₃	S	-1483.86235	0		-1485.08326	0.5	24.3	0
7a	<i>C</i> ₃	Se	-318.75097	0		-319.41943	0.2	21.6	0
8a	<i>C</i> ₃	Te	-314.89481	0		-315.51900	0.0	19.5	0
5b	<i>C</i> ₁	O	-515.96897	0		-517.07313	0.0	33.0	0
6b	<i>C</i> ₁	S	-1483.86349	0		-1485.08410	0.0	24.4	0
7b	<i>C</i> ₁	Se	-318.75119	0		-319.41973	0.0	21.7	0
8b	<i>C</i> ₁	Te	-314.89448	0		-315.51869	0.2	19.6	0
[HSi(XH) ₂] ⁺									
9a	<i>C</i> _{2v} ^a	O	-440.18230	0		-440.98673	2.0	23.3	0
10a	<i>C</i> _{2v} ^a	S	-1085.45016	0		-1086.33690	0.0	18.0	0
11a	<i>C</i> _{2v} ^a	Se	-308.71868	0		-309.23464	0.1	16.3	0
12a	<i>C</i> _{2v} ^a	Te	-306.15629	0		-306.64530	0.8	14.9	0
9b	<i>C</i> _{2v} ^b	O	-440.18578	0		-440.98988	0.1	23.5	0
10b	<i>C</i> _{2v} ^b	S	-1085.44964	0		-1086.33585	0.7	18.1	0
11b	<i>C</i> _{2v} ^b	Se	-308.71875	0		-309.23460	0.1	16.4	0
12b	<i>C</i> _{2v} ^b	Te	-306.15761	0		-306.64662	0.0	15.0	0
9c	<i>C</i> _s	O	-440.18615	0		-440.98997	0.0	23.5	0
10c	<i>C</i> _s	S	-1085.45064	0		-1086.33682	0.1	18.1	0
11c	<i>C</i> _s	Se	-308.71902	0		-309.23479	0.0	16.3	0
12c	<i>C</i> _s	Te	-306.15707	0		-306.64603	0.4	15.0	0
H ₂ Si(XH) ₂									
13a	<i>C</i> ₂	O	-441.04791	0		-441.88322	0.0	29.3	0
14a	<i>C</i> ₂	S	-1086.31856	0		-1087.22850	0.0	23.3	0
15a	<i>C</i> ₂	Se	-309.57698	0		-310.11820	0.0	21.6	0
16a	<i>C</i> ₂	Te	-307.00525	0		-307.51655	0.0	20.1	0
13b	<i>C</i> ₁	O	-441.04566	0		-441.88121	1.3	28.9	0
14b	<i>C</i> ₁	S	-1086.31661	0		-1087.22698	0.9	23.3	0
15b	<i>C</i> ₁	Se	-309.57584	0		-310.11727	0.6	21.6	0
16b	<i>C</i> ₁	Te	-307.00487	0		-307.51643	0.1	20.1	0
[H ₂ Si(XH)] ⁺									
17	<i>C</i> _s	O	-365.25793	0		-365.78891		19.3	0
18	<i>C</i> _s	S	-687.89420	0		-688.46628		16.6	0
19	<i>C</i> _s	Se	-299.52922	0		-299.91609		15.7	0
20	<i>C</i> _s	Te	-298.24844	0		-298.62313		15.0	0
H ₃ Si(XH)									
21	<i>C</i> _s	O	-366.13040	0		-366.69532		24.8	0
22	<i>C</i> _s	S	-688.77072	0		-689.37234		22.0	0
23	<i>C</i> _s	Se	-300.40057	0		-300.81744		21.1	0
24	<i>C</i> _s	Te	-299.11515	0		-299.51688		20.3	0

^a Hydrogen "up". ^b Hydrogen "down".**Table 2.** Calculated Total Energies, E_{tot} [hartree], and Complexation Energies, E_{compl} [kcal/mol], of the H₂O Complexes

	sym	X	HF/DZP			MP2/TZ2P		
			E_{tot}	E_{compl}	i	E_{tot}	E_{compl}^a	i
[Si(XH) ₃] ⁺ •H ₂ O								
25	<i>C</i> ₁	O	-591.19919	-50.2	0	-592.57197	-49.4 (-52.1)	0
26	<i>C</i> ₁	S	-1559.06971	-35.4	0	-1560.56813	-34.5 (-37.2)	0
27	<i>C</i> ₁	Se	-393.96044	-29.3	0	-394.90815	-30.7 (-33.3)	0
28	<i>C</i> ₁	Te	-390.10729	-23.2	0	-391.01350	-24.5 (-26.8)	0
[C(XH) ₃] ⁺ •H ₂ O ^b								
29	<i>C</i> ₁	O	-339.99021	-15.1	0	-341.25357	-15.7 (-17.4) ^c	
30	<i>C</i> ₁	S	-1307.88007	-9.5	0	-1309.31323	-18.4 (-20.1) ^d	
31	<i>C</i> ₁	Se	-142.76599	-12.9	0	-143.65332	-16.8 (-18.6) ^e	
32	<i>C</i> ₁	Te	-138.91986	-11.6	0	-139.77372	-15.6 (-17.6) ^e	

^a Values in parentheses include ZPE contributions. ^b Taken from ref 14. ^c Pyramidal complex. ^d Pyramidal complex, the stabilization energy of a planar complex is slightly higher. ^e Planar complex.

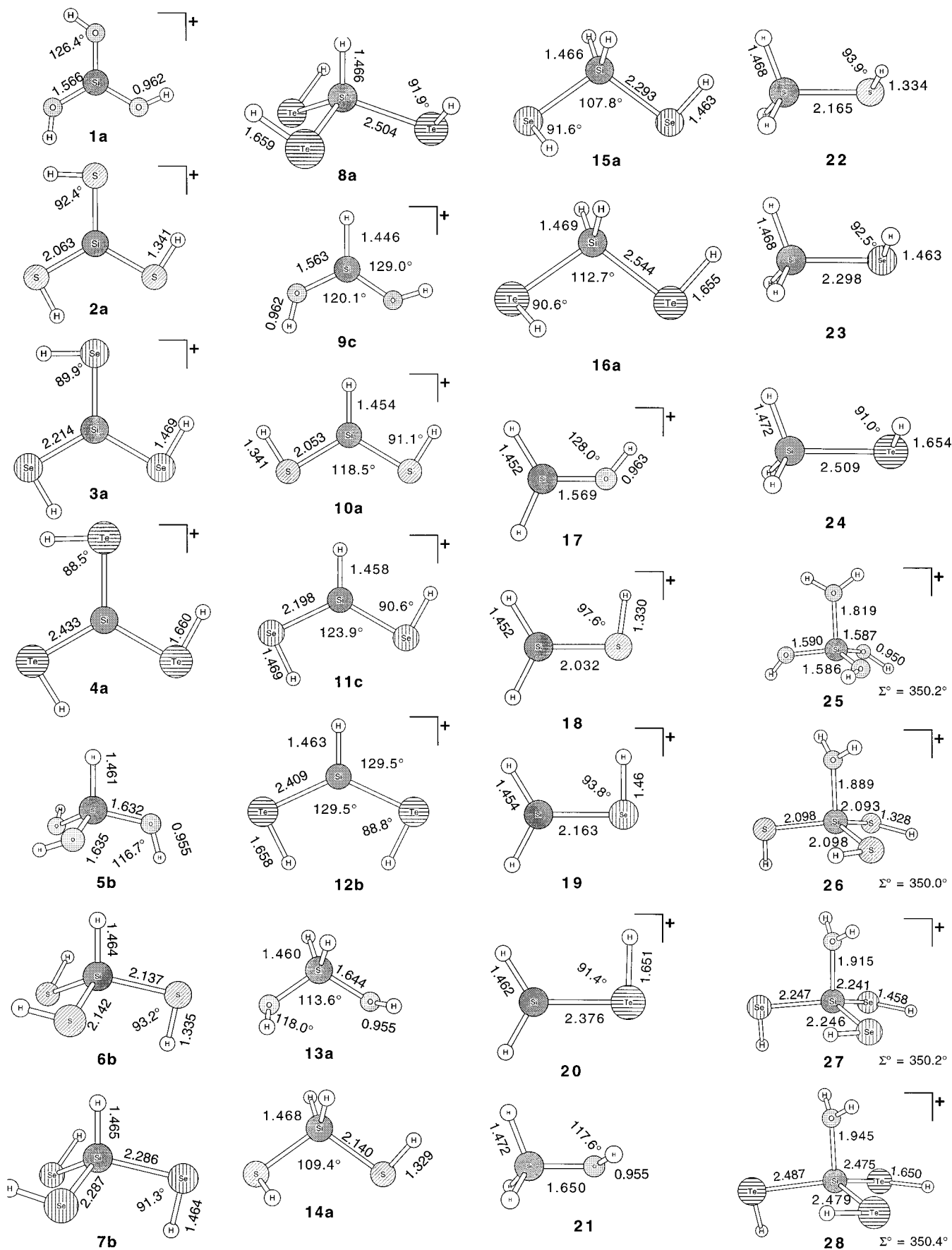


Figure 1. Optimized geometries at MP2/TZ2P of the most stable forms of the silylium cations and neutral compounds 1–28. Bond distances are in angstroms and bond angles are in degrees.

that in $\text{HC}(\text{SH})_3$.¹⁴ It is interesting to note that the Si–O–H bond angle of the cation 1a is larger than that in neutral 5b,

while the cations 2a–4a have slightly smaller Si–X–H bond angles than the respective neutral compounds 6b–8a.

Three energetically nearly degenerate conformations have been calculated for the disubstituted silylium cations $[\text{HSi}(\text{XH})_2]^+$ (**9–12**; see Table 1). The lowest lying forms of $[\text{HSi}(\text{OH})_2]^+$ (**9c**) and $[\text{HSi}(\text{SeH})_2]^+$ (**11c**) have C_s symmetry, while the most stable conformations of $[\text{HSi}(\text{SH})_2]^+$ (**10a**, hydrogens cis) and $[\text{HSi}(\text{TeH})_2]^+$ (**12b**, hydrogens trans) have C_{2v} symmetry (Figure 1). The Si–X bonds of the disubstituted cations $[\text{HSi}(\text{XH})_2]^+$ (**9c–12b**) are shorter than those in the respective trisubstituted cations $\text{Si}(\text{XH})_3^+$ (**1a–4a**, Figure 1). This is an interesting result, because the neutral compounds $\text{H}_2\text{Si}(\text{XH})_2$ (**13a–16a**) have slightly longer Si–X bonds than $\text{HSi}(\text{XH})_3$ (**5b–8a**). The most stable conformations of the neutral molecules $\text{H}_2\text{Si}(\text{XH})_2$ have C_2 symmetry (**13a–16a**; Figure 1). The C_1 -symmetric forms **13b–16b** are slightly higher in energy (Table 1).

Only one conformation has been found as an energy minimum for the monosubstituted cations $[\text{H}_2\text{SiXH}]^+$ (**17–20**) and the respective neutral molecules H_3SiXH (**21–24**). The calculated geometries (Figure 1) show that $[\text{H}_2\text{SiOH}]^+$ (**17**) has a slightly longer Si–O bond than $[\text{HSi}(\text{OH})_2]^+$ (**9c**) and $[\text{Si}(\text{OH})_3]^+$ (**1a**), but the other $[\text{H}_2\text{SiXH}]^+$ cations **18–20** have shorter Si–X bonds than the respective di- and trisubstituted species **10a–12b** and **1a–4a** (Figure 1). Bond shortening due to electrostatic attractive interactions is expected to be more pronounced for the more polar Si–O bonds. The polarity of the Si–O bonds increases with the number of OH substituents, and hence increasing bond shortening on electrostatic grounds is expected in the order $[\text{H}_2\text{Si}(\text{OH})]^+ > [\text{HSi}(\text{OH})_2]^+ > [\text{Si}(\text{OH})_3]^+$. On the other hand, the total π -charge transfer to the formally vacant $p(\pi)$ orbital at the Si^+ center increases with the number of XH substituents as well. As will be shown below, π -donation is more effective for the heavier chalcogens. However, while the total $\text{X} \rightarrow \text{Si}^+$ π -donation increases with the number of XH substituents, the π -donation per XH group becomes smaller and, hence, leads to a lengthening of the individual Si–X bonds in the order $[\text{Si}(\text{XH})_3]^+ > [\text{HSi}(\text{XH})_2]^+ > [\text{H}_2\text{Si}(\text{XH})]^+$. The observed irregularities of the Si–O bonds lengths, which follow the order $[\text{HSi}(\text{OH})_2]^+ < [\text{Si}(\text{OH})_3]^+ < [\text{H}_2\text{Si}(\text{OH})]^+$, are caused by a counter balance of $\text{Si}^+ \text{--} \text{O}$ charge attraction and $\text{O} \rightarrow \text{Si}^+$ π -donation. In the silylium ions which are substituted by the heavier chalcogens, the bond length variation is predominantly governed by π charge transfer and therefore shows the expected trend $[\text{H}_2\text{Si}(\text{XH})]^+ < [\text{HSi}(\text{XH})_2]^+ > [\text{Si}(\text{XH})_3]^+$.

Figure 1 also shows the optimized geometries of the energetically lowest lying $[\text{Si}(\text{XH})_3(\text{H}_2\text{O})]^+$ complexes **25–28**. Rotation about the Si–OH bond gave slightly higher lying forms of the complexes which are not important for this work. The $\text{Si}(\text{XH})_3$ moiety of the water complexes is only slightly distorted from planarity, and the Si–X bond lengths are a little longer by 0.02–0.06 Å than in free $[\text{Si}(\text{XH})_3]^+$. The most important result of the geometry optimization is the Si–OH₂ bond length. Figure 1 shows that the bond becomes significantly longer from $[\text{Si}(\text{OH})_3(\text{H}_2\text{O})]^+$ (**25**) (Si–OH₂ = 1.819 Å) to $[\text{Si}(\text{TeH})_3(\text{H}_2\text{O})]^+$ (Si–OH₂ = 1.945 Å). The trend of the Si–OH₂ bond length is in agreement with the calculated complexation energies. Table 2 shows that the water complexation energy of **25–28** decreases strongly from $[\text{Si}(\text{OH})_3(\text{H}_2\text{O})]^+$ (**25**) (D_e = 49.4 kcal/mol) to $[\text{Si}(\text{TeH})_3(\text{H}_2\text{O})]^+$ (**28**) (D_e = 24.5 kcal/mol).

Discussion

The topics of the discussion are the trends which are predicted for the stabilization of the silylium cations by the π -donor substituents XH (X = O–Te) and the differences between the silylium and the respective carbenium cations. The calculated

Table 3. Calculated Stabilization Energies, SE [kcal/mol], of Reaction 1 for Chalcogen Substituted $[\text{H}_{3-n}\text{A}(\text{XH})_n]^+$ Ions and Halogen Substituted $[\text{H}_{3-n}\text{AY}_n]^+$ Ions^a

X/Y	A = Si			A = C		
	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3
O	18.9	27.1	28.6	63.6	88.9	100.6
S	19.1	28.2	34.2	63.5	85.5	97.0
Se	22.0	33.3	40.8	61.9	83.9	94.5
Te	26.8	41.8	50.8	64.6	87.5	97.1
F	–1.2	n.c. ^b	–34.9	25.1	n.c. ^b	18.8
Cl	1.1	n.c. ^b	–3.6	24.8	n.c. ^b	42.9
Br	5.7	n.c. ^b	11.5	29.8	n.c. ^b	54.7
I	10.3	n.c. ^b	25.5	33.5	n.c. ^b	63.1

^a In kcal/mol. The values for the halogen-substituted cations were taken from ref 12. ^b Not calculated.

Si–OH₂ bond lengths and complexation energies of **25–28** shown in Figure 1 and Table 2 indicate that the $[\text{Si}(\text{XH})_3]^+$ cations become more stable in the order OH < SH < SeH < TeH. The complexation energy of $[\text{Si}(\text{TeH})_3]^+$ (24.5 kcal/mol) is only half of what is calculated for $[\text{Si}(\text{OH})_3]^+$ (49.4 kcal/mol). Table 2 shows that the complexation energies of the respective carbenium ions $[\text{C}(\text{XH})_3]^+$ are significantly lower (10.9–16.8 kcal/mol) and that the trend is less uniform than for the silylium ions. However, the complexation energies of the carbenium ions cannot directly be taken as a probe of the substituent effects, although the low bond energies indicate that the carbenium ions are more stable than the silylium ions. Only $[\text{C}(\text{OH})_3(\text{H}_2\text{O})]^+$ and $[\text{C}(\text{SH})_3(\text{H}_2\text{O})]^+$ have pyramidal equilibrium structures with very long C–OH₂ distances (2.56 Å for $[\text{C}(\text{OH})_3(\text{H}_2\text{O})]^+$ and 2.92 Å for $[\text{C}(\text{SH})_3(\text{H}_2\text{O})]^+$).¹⁴ The calculated complexation energies of $[\text{C}(\text{SeH})_3(\text{H}_2\text{O})]^+$ and $[\text{C}(\text{TeH})_3(\text{H}_2\text{O})]^+$ are taken from planar hydrogen-bonded equilibrium geometries, which were found as the only energy minimum forms.¹⁴

Another way to compare the influence of the substituents XH on the stability of the silylium ions with the carbenium ions is given by the isodesmic reaction 1:

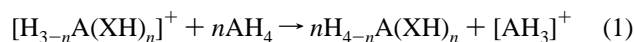
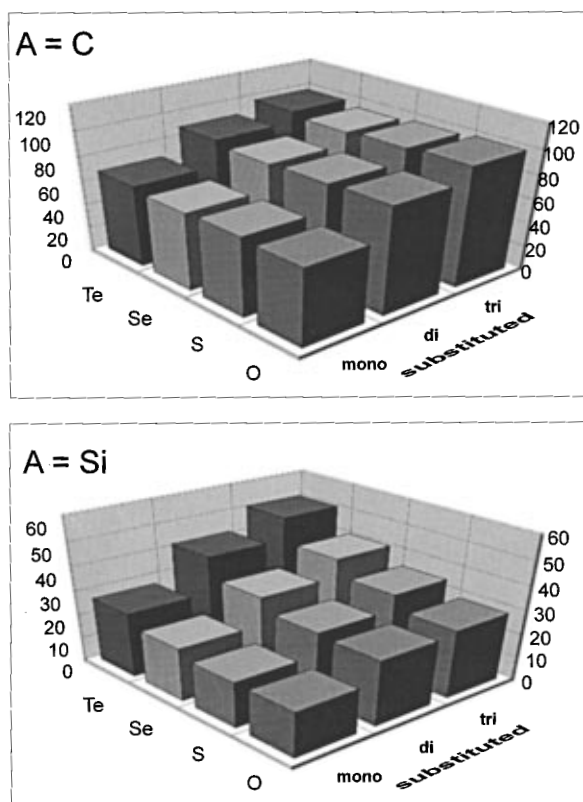
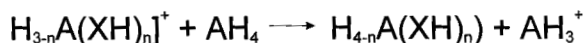


Table 3 shows the theoretically predicted stabilization energies (SE) of reaction 1 for the silylium ions (A = Si) and the carbenium ions (A = C). Positive SE values mean that the substituent XH stabilizes the cation relative to AH_3^+ . All substituents XH stabilize the silylium and the carbenium ions. The calculated trends show interesting differences, however. This becomes obvious from Figure 2, which displays graphically the SE values of reaction 1 for the silylium ions and the carbenium ions.

The substituent effect upon the stability of the silylium ions shows the order OH < SH < SeH < TeH, which is in agreement with the calculated complexation energies of the water complexes. The increase is larger for the triply substituted silylium ions $[\text{Si}(\text{XH})_3]^+$ than for the doubly substituted ions $[\text{HSi}(\text{XH})_2]^+$, which become in turn more stabilized than the singly substituted cations $[\text{H}_2\text{Si}(\text{XH})]^+$. The largest increase in the stabilization is found from Se to Te. It is interesting to note that the stabilization energies of $[\text{Si}(\text{OH})_3]^+$, $[\text{HSi}(\text{OH})_2]^+$, and $[\text{HSi}(\text{SH})_2]^+$ are very similar to each other, as are the SE values of $[\text{H}_2\text{Si}(\text{OH})]^+$ and $[\text{H}_2\text{Si}(\text{SH})]^+$ (Table 3). The absolute values and the trend of the stabilization energies of the carbenium ions are quite different. The SE values are much higher compared to the silylium ions, which is in agreement with the experimentally observed higher stability of the carbenium ions. The calculated trend shows that there is little variation of the

Table 4. Calculated NBO Charges and Wiberg Bond Indices

	$[Si(XH)_3]^+$	$[HSi(XH)_2]^+$	$[H_2Si(XH)]^+$	$HSi(XH)_3$	$H_2Si(XH)_2$	$H_3Si(XH)$
NBO Charges						
Si	2.453	2.116	1.768	2.036	1.686	1.280
H (Si)		-0.159	-0.150	-0.302	-0.272	-0.230
O	-1.043	-1.040	-1.018	-1.069	-1.058	-1.046
H (O)	0.559	0.561	0.560	0.491	0.487	0.485
Si	0.980	1.048	1.168	0.850	0.835	0.805
H (Si)		-0.117	-0.118	-0.196	-0.187	-0.185
S	-0.185	-0.160	-0.127	-0.363	-0.377	-0.384
H (S)	0.191	0.194	0.195	0.149	0.146	0.140
Si	0.666	0.823	1.037	0.630	0.683	0.726
H (Si)		-0.112	-0.116	-0.180	-0.177	-0.177
Se	-0.007	0.020	0.065	-0.232	-0.249	-0.265
H (Se)	0.118	0.120	0.130	0.084	0.083	0.076
Si	0.161	0.470	0.841	0.268	0.434	0.599
H (Si)		-0.124	-0.118	-0.174	-0.167	-0.170
Te	0.284	0.331	0.380	0.001	-0.024	-0.055
H (Te)	-0.005	-0.004	0.017	-0.032	-0.026	-0.032
Bond Indices						
Si-O	0.764	0.790	0.829	0.626	0.625	0.634
Si-S	1.141	1.225	1.355	0.900	0.907	0.912
Si-Se	1.170	1.270	1.441	0.925	0.932	0.936
Si-Te	1.201	1.322	1.547	0.950	0.962	0.968

**Figure 2.** Plot of the calculated stabilization energies (kcal/mol) at MP2/TZ2P of reaction 1 for the carbenium ions $[H_{3-n}C(XH)_n]^+$ (top) and silylium ions $[H_{3-n}Si(XH)_n]^+$ (bottom).

substituents XH concerning the stabilization of the carbenium ions. TeH is slightly less stabilizing than OH in $[C(XH)_3]^+$ and $[HC(XH)_2]^+$, while TeH stabilizes $[H_2C(XH)]^+$ a little more than OH (Table 3). However, the differences among the substituents XH are much less in the carbenium ions than in the silylium ions.

Table 3 also shows the calculated stabilization energies of reaction 1 for the singly and triply substituted halosilylium and halocarbenium ions $[SiY_3]^+$, $[CY_3]^+$, $[H_2SiY]^+$, and $[H_2CY]^+$,

which have been discussed in detail in a previous study.¹² It becomes obvious that the absolute values and the trend when one goes from the lighter to the heavier chalcogens may be very different from that of the halogens. The chalcogen substituents stabilize the silylium and carbenium ions more than the respective halogen atom of the same row of the periodic system. This is not surprising, because the chalcogens are less electronegative than the respective halogens. The trend of the stabilization of the silylium ions is the same for the chalcogen substituents as for the halogen substituents, i.e. $F < Cl < Br < I$. However, fluorine and chlorine in $[SiF_3]^+$ and $[SiCl_3]^+$ destabilize the cation relative to $[SiH_3]^+$, while oxygen and sulfur stabilize the silylium ions. It is interesting to note that the stabilizing effect of the halogens on the carbenium ions $[CY_3]^+$ increases strongly with $F < Cl < Br < I$, while the chalcogens in $[C(XH)_3]^+$ show little differences among O–Te (Table 3). There is even a small decrease in the stabilization from $[C(OH)_3]^+$ to $[C(TeH)_3]^+$.

To understand the effect of the chalcogen substituents on the structure and stability we analyzed the electronic structure of the silylium cations. Table 4 shows the calculated atomic partial charges and Si–XH bond orders of the cations and neutral compounds. The silicon atom always carries a positive charge in the silylium cations and in the neutral compounds. This is reasonable, because Si is less electronegative than the chalcogens.²⁶ Oxygen carries a strongly negative charge in the silylium cations, while the heavier chalcogens have low negative or even positive charges and the hydrogens are always negatively charged. The calculated charges demonstrate that the higher stability of the heavier chalcogen substituted silylium cations is not due to Coulomb interactions. The Si–Te bonds are destabilized by Coulomb interactions, while the Si–O bonds are strongly stabilized by charge attraction. Yet, the tellurium-substituted silylium cations are clearly more stable than the oxygen-substituted ions.

It is noteworthy that the partial charge at Si in the silylium cations is not much higher than that in the respective neutral compound. The positive charge at Si in $[Si(TeH)_3]^+$ (+0.161) is even *less* than in $HSi(TeH)_3$ (+0.268). This indicates that

(26) The electronegativities of the chalcogens given by the Allred-Rochow scale are 3.5 for oxygen, 2.4 for sulfur, 2.5 for selenium, 2.0 for tellurium, and 1.7 for silicon.

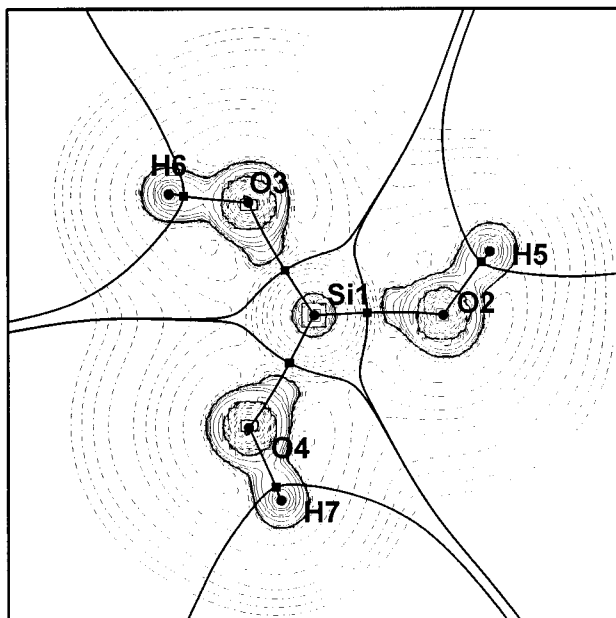
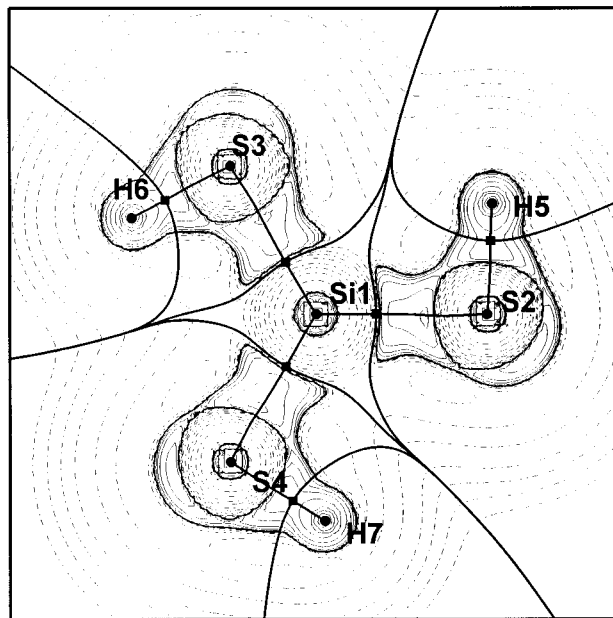
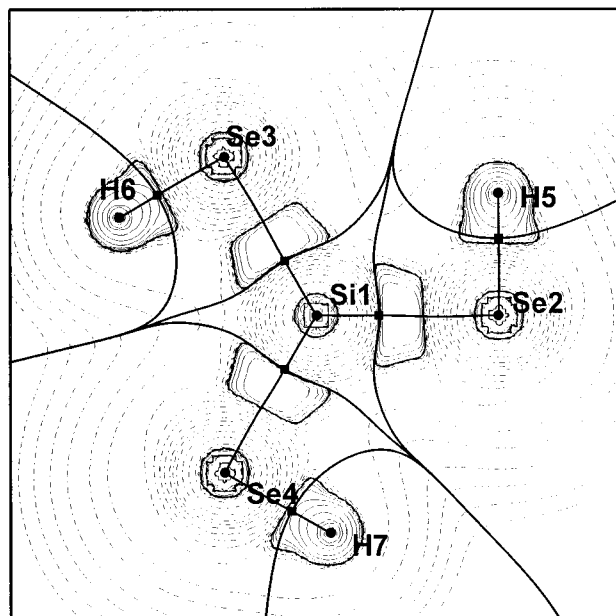
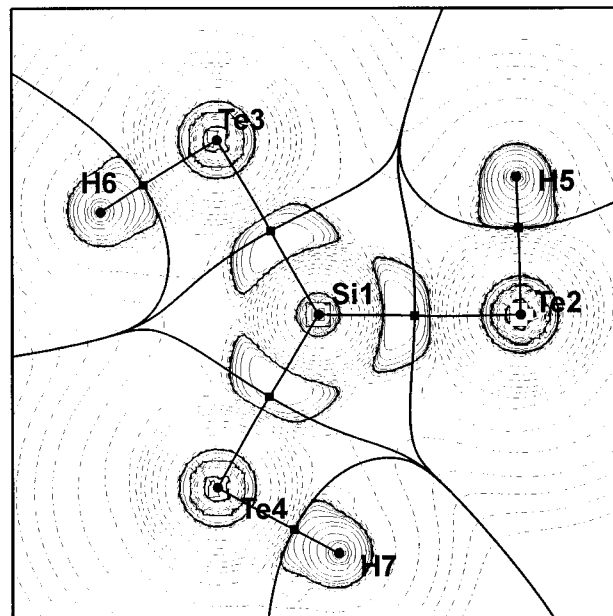
(a) $[\text{Si}(\text{OH})_3]^+$ **1a**(b) $[\text{Si}(\text{SH})_3]^+$ **2a**(c) $[\text{Si}(\text{SeH})_3]^+$ **3a**(d) $[\text{Si}(\text{TeH})_3]^+$ **4a**

Figure 3. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ at MP2/DZP(AE) of **1a–4a**. Dashed lines indicate charge depletion ($\nabla^2\rho(\mathbf{r}) > 0$), and solid lines indicate charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$). The solid lines connecting the atomic nuclei are the bond paths, and the solid lines separating the atomic nuclei indicate the zero-flux surfaces in the plane. The crossing points of the bond paths and zero-flux surfaces are the bond critical points \mathbf{r}_b .

Table 5. Calculated Total Charges q and $p(\pi)$ Population at the Si Atom and Total $\text{Si} \rightarrow \text{XH}$ σ -Donation in the Silylium Cations

X	$[\text{Si}(\text{XH})_3]^+$			$[\text{HSi}(\text{XH})_2]^+$			$[\text{H}_2\text{Si}(\text{XH})]^+$		
	q	$p(\pi)$	σ	q	$p(\pi)$	σ	q	$p(\pi)$	σ
O	2.45	0.35	1.81	2.12	0.28	1.40	1.77	0.19	0.95
S	0.98	0.60	0.58	1.05	0.49	0.53	1.17	0.32	0.49
Se	0.67	0.65	0.32	0.82	0.53	0.35	1.04	0.36	0.40
Te	0.16	0.76	-0.08	0.47	0.80	0.27	0.84	0.43	0.27

the formally empty $p(\pi)$ valence orbital of Si acquires significant electronic charge through $p(\pi)$ donation from the chalcogen lone-pair electrons. Table 5 shows that the $p(\pi)$ occupation at Si in the silylium cations is rather high, particularly in the heavier chalcogen substituted species. There is 0.76 electron

in the silicon $p(\pi)$ valence orbital of $[\text{Si}(\text{TeH})_3]^+$ (Table 5). As expected, the occupation of the silicon $p(\pi)$ orbital is lower in the singly and doubly substituted silylium cations.

Table 5 also shows the total σ -donation from Si to the XH substituents. Silicon is a strong σ -donor in the oxygen-

Table 6. Results of the Topological Analysis of the Charge Distribution in $[\text{Si}(\text{XH})_3]^+$ ^a

bond	$\text{Si}-r_b$ [Å]	ρ_b [e·Å ⁻³]	$\nabla^2\rho_b$ [e·Å ⁻³]	$H(r_b)$ [hartree·Å ⁻³]	ϵ_b
1a Si–O	0.646	1.061	33.867	−0.216	0.168
2a Si–S	0.726	0.804	4.104	−0.540	0.227
3a Si–Se	0.759	0.723	0.579	−0.507	0.246
4a Si–Te	1.161	0.642	−2.462	−0.317	0.306

^a $\text{Si}-r_b$ gives the distance from Si to the bond critical point. ρ_b and $\nabla^2\rho_b$ give the electron density and second derivative at the bond critical point; $H(r_b)$ gives the energy density at the bond critical point; ϵ_b = ellipticity at the bond critical point.

substituted silylium cations. The σ -donation becomes weaker when the chalcogen atom becomes heavier and is even reversed in $[\text{Si}(\text{TeH})_3]^+$, where the calculations give a small $\text{Te}\rightarrow\text{Si}$ σ -donation of 0.08 electron (Table 5). The strong $X\rightarrow\text{Si}$ π -donation of the heavier chalcogen substituted silylium cations indicates a substantial degree of double-bond character of the Si–X bonds. The calculated Wiberg bond orders shown in Table 4 support the conclusion. All silylium cations with sulfur, selenium, or tellurium substituents have bond orders > 1.

Table 5 shows that the $X\rightarrow\text{Si}$ π -donation increases and the $\text{Si}\rightarrow\text{XH}$ σ -donation decreases from $X = \text{O}$ to Te . It can be argued that the $\text{Si}\rightarrow\text{XH}$ σ -donation is more important for the stability of the silylium cations because the decrease in the σ -donation is steeper than the increase of the $X\rightarrow\text{Si}$ π -donation, particularly for $[\text{Si}(\text{XH})_3]^+$ from $X = \text{O}$ to Te (Table 5). Clearly, both factors stabilize the silylium cation. That the $X\rightarrow\text{Si}$ π -donation is more important than the $\text{HX}\rightarrow\text{Si}$ σ -donation becomes obvious by a comparison of the chalcogen-substituted silylium ions with the parent $[\text{SiH}_3]^+$ cation. $[\text{SiH}_3]^+$ has a positive charge of +0.64 at Si. It follows that there is total σ -donation of 0.36 e from hydrogen to Si. Nevertheless, $[\text{SiH}_3]^+$ is less stable than $[\text{Si}(\text{XH})_3]^+$ (Table 3). It follows that the higher stability of the heavier chalcogen-substituted silylium cations is mainly due to the increase of the $X\rightarrow\text{Si}$ π -donation. Because the $X\rightarrow\text{Si}$ π -donation increases and the $\text{HX}\rightarrow\text{Si}$ σ -bond becomes less polar from $X = \text{O}$ to Te , the covalent character of the X–Si bond increases. This is indicated by the increase of the calculated bond order (Table 4).

The trend in the nature and the polarity of the Si–X bonds becomes visible in Figure 3, where the Laplacians of the electron density distribution of $[\text{Si}(\text{XH})_3]^+$ in the molecular plane are shown. The shape of the areas of electron concentration ($\nabla^2\rho(\mathbf{r}) < 0$, solid lines) for the Si–X bond and the location of the bond critical point r_b shows clearly the change in the polarity from Si–O to Si–Te, where the bond critical point is nearly in the center of the charge concentration. The calculated energy densities at the bond critical points of the Si–X bonds (Table 6) support the classification as polar covalent bonds. The $H(r_b)$ values are negative, which has been suggested as a criterion for the covalent character of a bond.²⁷ The $H(r_b)$ value for the Si–S bond is more negative than that for the Si–O bond, but

it becomes less negative for Si–Se and particularly Si–Te (Table 6). The trend of the $H(r_b)$ values appears to be in conflict with the steady increase of the bond orders. However, the $H(r_b)$ values indicate energies, not charges. Because the valence electrons of the heavier atoms are more weakly bonded than those of the lighter atoms, the energetic effects dominate the $H(r_b)$ values of the Si–Se and Si–Te bond. The bond ellipticity ϵ_b ²¹ shows that the double bond character of the Si–X bond increases from **1a** ($X = \text{O}$) to **4a** ($X = \text{Te}$). The position of the bond critical point given by the distance from the silicon atom $\text{Si}-r_b$ is a further proof that the Si–X bond becomes less polar when X becomes heavier. The bond critical point of the Si–Te bond is nearly in the middle of the Si–Te bond (Table 6 and Figure 3).

Conclusion

The chalcogen-substituted silylium cations $[\text{Si}(\text{XH})_3]^+$ are strongly stabilized by π -donation from the chalcogen lone-pair electrons into the formally empty p(π) valence orbital of Si. The $X\rightarrow\text{Si}$ π -donation increases from $X = \text{O}$ to Te . The calculated reaction energies of isodesmic reactions give a stabilization of 28.6 kcal/mol for $X = \text{oxygen}$ and 50.8 kcal/mol for $X = \text{tellurium}$ relative to SiH_3^+ . The same trend toward higher stability of the heavier chalcogen substituted silylium cation is given by the calculated complexation energies of the water complexes. The stability order of the $[\text{Si}(\text{XH})_3]^+$ cations $X = \text{O} < \text{S} < \text{Se} < \text{Te}$ is caused by the increase in the $X\rightarrow\text{Si}$ π -donation. The calculations show the same trend for the singly and doubly chalcogen-substituted silylium cations $[\text{HSi}(\text{XH})_2]^+$ and $[\text{H}_2\text{Si}(\text{XH})]^+$. The substituent effects of the chalcogens on the stability of the silylium cations is very different from that of the carbenium cations. The chalcogens stabilize carbenium cations much more than silylium cations, but the strength of the stabilization changes little from oxygen to tellurium. The performance of the chalcogens as stabilizing substituents is also very different from that of the halogens. Chalcogens stabilize silylium cations and carbenium cations more than the halogen of the same row of the periodic system.

The experimentally most relevant result of this study of silylium cations is the prediction that tellurium-substituted species $[\text{Si}(\text{TeR})_3]^+$ are the most stable chalcogen-substituted silylium cations.

Acknowledgment. This work was supported by the Swiss National Science Foundation, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie. U.P. thanks the Fonds der Chemischen Industrie for a doctoral stipend. We acknowledge excellent service and a generous allotment of computer time from the HRZ Marburg, HHLR Darmstadt, and the HLRZ Jülich.

Supporting Information Available: Figure with geometries of all calculated energy minima of the silylium cations and neutral compounds **1–28** (7 pages). See any current masthead page for ordering and Internet access instructions.

(27) Cremer, D.; Kraka, E. *Angew. Chem.* **1984**, *96*, 612; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 627.