Ionization Energies of Linear and Cyclic Polysilanes. Application of the Green's Function Method Coupled with Semiempirical Molecular Orbital Calculations

Yitzhak Apeloig* and David Danovich†

Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

Received July 26, 1995⊗

The ionization energies of the parent and permethylated linear $[R_3Si(SiR_2)_nSiR_3]$ ($n = 1-3$; R = H, CH_3) and cyclic $[(c\text{-}SiR_2)_n]$ ($n = 3-6$; R = H, CH_3) polysilanes have been calculated with the outer valence Green's function (OVGF) technique, using as the zeroth order approximation the wave functions obtained with semiempirical AM1, PM3, and MNDO methods. It is found that the OVGF(AM1) method gives significantly better agreement with the experimental ionization potentials than semiempirical calculations using Koopmans' theorem. Furthermore, the OVGF(AM1) results are of comparable quality to those of OVA and EPT *ab initio* calculations. The mean deviation, for all the studied molecules, between the experimental and the OVGF(AM1) values is only 0.21 eV. The ionization energies of the studied polysilanes behave as follows: (1) The first ionization energies of the permethylated polysilanes are significantly (by 1−1.7 eV) lower than those of the corresponding parent polysilanes. (2) In the cyclic silanes the first IP is higher when the number of silicon atoms in the polysilane increases, while in the open-chain silanes the first IP decreases with the number of silicon atoms. The crossover between the two series occurs between the Si_4 and Si_5 polysilanes.

Introduction

Photoelectron spectroscopy (PES) has developed during the last decade into an extremely useful experimental technique for studying the electronic structure of atoms and molecules and, in particular, for analyzing the bonding characteristics of orbitals and their mutual interactions.[1] In order to interpret a PE spectrum and to fully exploit the information contained in it, a theoretical determination of the ionization potentials (IPs) is required. Usually Koopmans' theorem,[2] equating the IP with the negative value of the energy of the molecular orbital from which the electron is removed, is used in the interpretation.

A large number of theoretical methods and techniques, semiempirical as well as *ab initio*, are now available for calculating the energies of molecular orbitals. However, in some cases these theoretical methods fail to give the correct quantitative IPs or even to reproduce the correct orbital ordering. Cederbaum and his co-workers have shown recently for a variety of systems that the combination of *ab initio* techniques with Green's function methods can improve significantly the ability of theoretical calculations to accurately predict IPs.[3] In this method the many-body perturbation theory is used to obtain equations that calculate ionization potentials which include corrections for electron correlation and for relaxation effects.[3] Hartree−Fock solutions obtained from *ab initio* calculations serve as the zeroth approximation in the perturbation series.

Unfortunately, at present the application of *ab initio*-Green's function methods is practical only for relatively small- or medium-size molecules,[3] i.e. containing up to 10 non-hydrogen atoms. To overcome this difficulty, one of us has suggested recently[4,5] to couple the outer-valence Green's function (OVGF) approach with semiempirical methods such as AM1[6] (denoted in this paper as OVGF(AM1)). The OVGF(AM1) method was recently applied successfully to calculate the IPs of a variety of nitrogen-containing heterocycles, such as substituted pyridines (30 compounds), pyrimidines, pyridazines, and azoles.[4,5] More recently we applied the semiempirical Green's function method to calculate the IPs of a series of substituted triazines and tetrazines[7a] as well as for calculating the IPs of radicals and the electron affinities of various neutral compounds.[7b] In general it was found that inclusion of the Green's function method in the calculations improved substantially the quantitative theoretical−experimental agreement.[4,5,7] Furthermore, this agreement was better than that obtained with the HAM/3 method,[8] which was specifically designed for calculating ionization potentials.[4,5] In cases where

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† Present address: The Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel. E-mail: chrapel@tx.technion.ac.il and dodik@yfaat.ch.huji.ac.il.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) From the numerous reviews and monographs available, see for example: (a) Heilbronner, E.; Mailer, J. P. In *Electron Spectroscopy: Theory, Techniques and Applications*; Brundle, C. R., Baker, A. D., Eds.; Academic Press: London, 1977; Vol. 1, p 205. (b) Bock, H.; Ramsey, B. G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 734. (c) Martin, H.-D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 283. (d) *Molecular Photoelectron Spectroscopy*; Turner, D. W., Baker, C., Baker, A. D., Brundle, C. R., Eds.; Wiley-Interscience: London, 1970.

(2) Koopmans, T. *Physica* **1933**, *1*, 104.

(3) (a) Cederbaum, L. S.; Domcke, W. *Adv. Chem. Phys.* **1977**, *36*, 206. (b) Von Niessen, W.; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57.

(4) Danovich, D.; Zakrzewski, V.; Domnina, E. *J. Mol. Struct. (Theochem)* **1989**, *188*, 159.

(5) (a) Danovich, D.; Turchaninov, V. K.; Zakrzewski, V. G. *J. Mol. Struct. (Theochem)* **1990**, *209*, 77. (b) Danovich, D.; Zakrzewski, V.; Domnina, E. *J. Mol. Struct. (Theochem)* **1989**, *187*, 297.

(6) Dewar, M. J. S.; Zoebish, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(7) (a) Danovich, D.; Apeloig, Y. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1865. (b) Danovich, D.; Apeloig, Y.; Shaik, S. *J. Chem. Soc., Perkin Trans. 2* **1993**, 321.

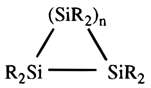
0276-7333/96/2315-0350$12.00/0

comparisons were available the OVGF(AM1) and the OVGF (*ab initio* with polarized basis sets) calculations gave results of comparable quality.[4,5] A computer program combining the outer-valence Green's function formalism with the AM1,[6] MNDO,[9] MNDOC,[10] and PM3[11] semiempirical methods is now available from QCPE,[12a] and it was also incorporated in the new MOPAC-93 package.[12b]

Polysilanes are attracting considerable attention during the last decade because of their many interesting chemical and physical properties.[13−19] A variety of possible new applications of polysilanes, such as photoconducting polymers in photocopying processes, silicon carbide precursors, self-developing photoresists in photolithography, and as photoinitiators in radical-assisted polymerization, have raised widespread interest in these novel polymers.[13a−d] Polysilane dentrimers have also been synthesized recently.[13e,f] Many of these technological applications are directly connected to the electronic structure of these organosilane polymers and to their ionization potentials,[13a−d] and there is therefore a need for developing better theoretical approaches for these molecules.

The current theoretical understanding of the spectroscopy of polysilanes relies on a series of semiempirical and *ab initio* calculations on their ground state and their excited singlet states.[14−27] Previous theoretical studies in this area have included *ab initio* studies of small di- and trisilanes[19] as well as semiempirical calculations on larger oligomers and polymers.[18] Two recent reviews have summarized the previous theoretical studies of the electronic structure polysilanes.[13b,15] A recent review by Bock and Solouki has summarized the known PES of linear and cyclic polysilanes as well as their assignments using the semiempirical CNDO method.[14,20] A study of the PES of several small polysilanes using *ab initio* methods was reported recently.[21−24] Ortiz and Mintmire showed that Koopmans' theorem is not a good approximation for describing the ionization potentials of short linear polysilanes, $H_3Si-(SiH_2)_n-SiH_3$ (n = 1−3).[23,24] On the other hand, using the electron-propagator theory (EPT) with the outer-valence approximation [EPT(OVA)] excellent agreement with the experimental PES of these polysilanes was achieved.[23] More recently, Ortiz and Rohlfing have expanded successfully these calculations to $Si_{10}H_{22}$,[24f] but very large computational resources were required. Unfortunately, at present, with *ab initio* calculations as zeroth approximation, the OVA and EPT techniques can be used only for relatively small- or medium-size molecules and with the computer resources available to us even relatively short permethylated polysilanes (e.g., Si_4Me_8) are too large for such calculations.

Chart 1

$R_3Si(SiR_2)_nSiR_3$	
1a, n=1, R=H	**4a**, n=1, R=H
1b, n=1, R=CH_3	**4b**, n=1, R=CH_3
2a, n=2, R=H	**5a**, n=2, R=H
2b, n=2, R=CH_3	**5b**, n=2, R=CH_3
3a, n=3, R=H	**6a**, n=3, R=H
3b, n=3, R=CH_3	**6b**, n=3, R=CH_3
	7a, n=4, R=H
	7b, n=4, R=CH_3

In this paper we report OVGF calculations coupled with the semiempirical MNDO, AM1, and PM3 methods for a number of linear and cyclic polysilanes and for their permethylated compounds, containing up to six silicon atoms **1**−**7** (see Chart 1). We compare our computational results for **1**−**7** with the available experimental ionization potentials, as well as with previous semiempirical and *ab initio* calculations. Although the major focus of this paper is to evaluate the suitability of the OVGF(semiempirical) method for the study of the PES of the linear and cyclic polysilanes, we also discuss briefly the AM1 geometries and the electronic structure of these molecules. A more detailed discussion of these aspects can be found elsewhere.[14,15]

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(8) Asbrink, L.; Fridh, C.; Lindholm, E. *Chem. Phys. Lett.* **1977**, *52*, 63.

(9) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(10) Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1413.

(11) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(12) (a) Danovich, D. *OVGF(SEMI): molecular orbital package for outer-valence Green's function calculations coupled with the MNDO, MNDOC, AM1, PM3 semiempirical approximations*; Program No. 602, Quantum Chemistry Program Exchange (QCPE): Indiana University, Bloomington, IN 47405. (b) Stewart, J. J. P. MOPAC-93, A Semiempirical Molecular Orbital Program; Stewart, J. J. P. and Fujitsu Limited, Tokyo, Japan, 1993. (c) AMPAC 4.5, Semichem, 12715 W. 66th Terrace, Shawnee, KS 66216, 1993.

(13) For reviews on polysilanes see: (a) West, R. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 19. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (c) West, R. In *Ultrastructure Processing of Ceramics, Glasses and Composites*; Hench, L., Ulrich, D. L., Eds.; John Wiley and Sons: New York, 1984. (d) Hofer, D. C.; Miller, R. D.; Wilson, C. G.; Neurather A. *Proc. SPIE, Adv. Resist Technol.* **1984**, *469*, 108. For recent papers on polysilane dentrimers see: (e) Lambert, J. B.; Pflung, J. L.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98. (f) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 4195.

(14) For a review on the photoelectron spectra of polysilanes, see: Bock, H.; Solouki, B. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; Chapter 9.

(15) For a general theoretical review, see: Apeloig, Y. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 2.

(16) (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) French, R. H.; Meth, J. S.; Thorne, J. R. G.; Hochstrasser, R. M.; Miller, R. D. *Synth. Met.* **1992**, *50*, 499.

(17) Fujino, M. *Chem. Phys. Lett.* **1987**, *136*, 451.

(18) For semiempirical calculations of polysilanes, see: (a) Dewar, M. J. S.; Coaxian, J. *Organometallics* **1987**, *6*, 1486. (b) Bigelow, R. W. *Organometallics* **1986**, *5*, 1502. (c) Bigelow, R. W.; McGrane, K. M. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1239. (d) Crespo, R.; Paqueras, M. C.; Orti, F.; Bredas, J. L. *Synth. Met.* **1991**, *42*, 3457. (e) Crespo, R.; Paqueras, M. C.; Orti, F.; Tomas, F. *Synth. Met.* **1993**, *54*, 173.

(19) For *ab initio* calculations of silane and polysilanes, see: (a) Sax, A. F. *J. Comput. Chem.* **1985**, *6*, 469. (b) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M. B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 260. (c) Plitt, H. S.; Michl, J. *Chem. Phys. Lett.* **1992**, *198*, 400. (d) Balaji, V.; Michl, J. *Polyhedron* **1991**, *10*, 1265. (e) Grev, R. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1987**, *109*, 6569. (f) Albinsson, B.; Downing, J. W.; Goss, L.; Schmidbaur, H.; Michl, J. Presented at the American Chemical Society, Division of Organic Chemistry, 209th ACS National Meeting, Anaheim, CA, April 2−6, 1995; Abstract 316.

(20) Bock, H.; Ensslin, W.; Feher, F.; Freund, R. *J. Am. Chem. Soc.* **1976**, *98*, 668.

(21) (a) Stuger, H.; Hengge, E.; Janoschek, R. *Phosphorus Sulfur Silicon* **1990**, *48*, 189. (b) Hengge, E.; Janoschek, R. *Chem. Rev.* **1995**, *95*, 1495.

(22) Nelson, J. T.; Pietro, W. J. *J. Phys. Chem.* **1988**, *92*, 136.

(23) Ortiz, J. V.; Mintmire, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 4522.

(24) (a) Ortiz, J. V. *J. Chem. Phys.* **1991**, *94*, 6064. (b) Ortiz, J. V.; Mintmire, J. W. *Adv. Chem. Ser.* **1988**, *No. 224*, 551. (c) Ortiz, J. V. *Polyhedron* **1991**, *10*, 1285. (d) Ortiz, J. V.; Mintmire, J. W. *J. Phys. Chem.* **1991**, *95*, 8609. (e) Ortiz, J. V. *Macromolecules* **1993**, *26*, 2989. (f) Ortiz, J. V.; Rohlfing, C. M. *Macromolecules* **1993**, *26*, 7282.

Computational Methods

The OVGF method is described in detail in ref 3. The application of this method for the case of semiempirical wave functions was discussed in refs 4, 5, and 7, and a computer program implementing the method is available from QCPE[12a] and is also incorporated in the new MOPAC-93 package.[12b] Here we repeat briefly some of the main points about the computational method, and the interested reader is referred to refs 3–5 and 7 for more details.

The OVGF technique was used with the self-energy part extended to include third-order perturbation corrections.[3] The higher order contributions were estimated by the renormalization procedure. The actual expression used to calculate the self-energy part, $\sum_{pp}(\omega)$, chosen in the diagonal form, is given in eq 1, where $\sum^{(2)}_{pp}(\omega)$ and $\sum^{(3)}_{pp}(\omega)$ are the second- and third-order corrections and A is the screening factor accounting for all the contributions of higher orders.

$$\sum\nolimits_{pp}(\omega) = \sum\nolimits^{(2)}_{pp}(\omega) + (1 + A)^{-1}\sum\nolimits^{(3)}_{pp}(\omega) \qquad (1)$$

The particular expression which was used for the second-order corrections is given in eq 2.

$$\sum\nolimits^{(2)}_{pp}(\omega) = \sum_{a}\sum_{i,j} \frac{(2V_{paij} - V_{paji})V_{paij}}{\omega + \epsilon_a - \epsilon_i - \epsilon_j} + \sum_{a,b}\sum_{i} \frac{(2V_{piab} - V_{piba})V_{piab}}{\omega + \epsilon_i - \epsilon_a - \epsilon_b} \qquad (2)$$

$$V_{pqrs} = \int\int \phi^{*}_{p}(1)\, \phi^{*}_{q}(1)(1/r_{12})\phi_{r}(1)\phi_{s}(1)\, d\tau_1\, d\tau_2$$

In eq 2, i, j denote occupied orbitals, a, b denote virtual orbitals, p denotes orbitals with unspecified occupancy, ϵ denotes the orbital energy, and ω is the corrected ionization potential. The equations were solved by an iterative procedure which is given in eq 3.

$$\omega^{i+1}_{p} = \epsilon_p + \sum\nolimits_{pp}(\omega^{i}) \qquad (3)$$

The SCF energies and the corresponding integrals, which were calculated by a particular semiempirical method (MNDO, AM1, or PM3), were taken as the zeroth order approximation for the Green's function expansion, and all MOs were included in the active space for the OVGF calculations. The expressions used for $\sum^{(3)}_{pp}(\omega)$ and A are given in ref 3b.

Results and Discussion

The geometries of all compounds under consideration were fully optimized with the specified semiempirical methods, i.e., AM1, PM3, and MNDO, using the MOPAC[12b] or slightly modified AMPAC-4.5[12c] programs. The AM1 optimized geometries are presented in Figure 1. The ionization potentials were calculated using the above-mentioned semiempirical methods with either Koopmans' theorem or outer valence Green's function methods[12] (denoted as OVGF(SEMI), e.g. OVGF(AM1)), and the computational results are presented in the tables.

The main criteria which will be used to compare the experimental and the computational data and to compare the performance of the various computational methods is the mean deviation $\bar{\Delta}$ between the experimental and theoretical ionization potentials, either for a particular orbital or for all the orbitals of a particular polysilane. Special attention will be given to cases where the qualitative ordering of the orbitals calculated with the semiempirical methods is different from that calculated with *ab initio* methods. When discussing atomic contributions to various molecular orbitals, we use data from AM1 calculations (the corresponding PM3 and MNDO results are very similar).

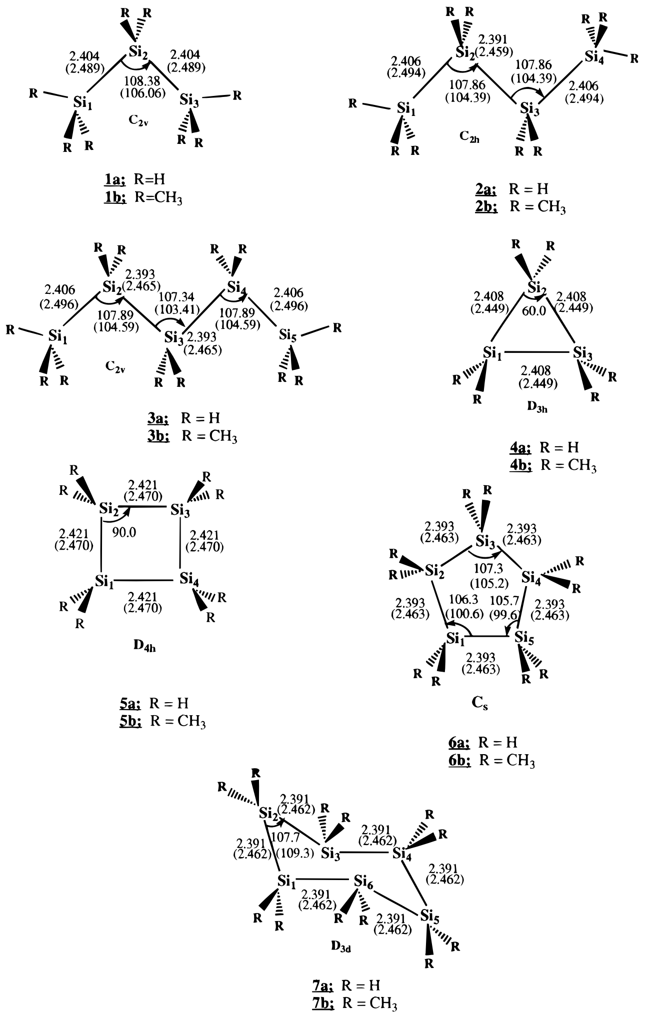

Figure 1. Selected geometrical parameters calculated by the AM1 method for linear and cyclic polysilanes (**1a**–**7a**) and for the corresponding permethylpolysilanes (**1b**–**7b**). Values in parentheses correspond to the permethylated polysilanes.

A. Linear Tri-, Tetra-, and Pentasilanes. 1. Linear Trisilanes. a. Si_3H_8 (1a). The PES of linear polysilanes with up to 5 silicon atoms shows absorptions in the range 9.0–12.5 eV, and it is composed of two well-separated regions: (a) ionizations from the σ(Si–Si) orbitals which appear in the range 9–11 eV; (b) ionizations from the σ(Si–H) orbitals which appear in the range 11.5–12.5 eV. The calculated ionization potentials for Si_3H_8 by the SCF(MNDO), SCF(AM1), SCF(PM3), OVGF(MNDO), OVGF(AM1), and OVGF(PM3) methods, as well as previous computational[23,24] and experimental[20] data, are summarized in Table 1. The C_{2v} structure (see Figure 1), which is the most stable conformation of Si_3H_8 at all these levels of theory,[23,24] was used in the calculations.

At the SCF level, with either the *ab initio* or the semiempirical methods, the calculated ionization energies exhibit substantial deviations from the experimental data. At the SCF level all the semiempirical methods give smaller mean deviation values $\bar{\Delta}$ than the SCF/6-31G* *ab initio* calculations. For **1a** the smallest

Table 1. Experimental and Calculated Ionization Energies (eV) of Trisilapropane (1a), Tetrasilabutane (2a), and Pentasilapentane (3a)

molecule	MO	sym	expt[a]	SCF (ab initio)[b]	OVA (ab initio)[b]	AM1	OVGF (AM1)	PM3	OVGF (PM3)	MNDO	OVGF (MNDO)
Si_3H_8	σ(Si−Si)	b_2	9.87	10.45	9.73	10.41	10.27	9.50	9.46	9.48	9.34
(**1a**)[c]	σ(Si−Si)	a_1	10.72	11.48	10.61	10.92	10.74	10.04	9.96	10.18	10.01
	σ(Si−H)	b_1	11.65	12.77	11.78	11.79	11.52	10.81	10.57	11.71	11.43
	σ(Si−H)	a_2	12.02	13.18	12.26	12.41	12.15	11.71	11.45	12.14	11.84
	σ(Si−H)	b_1	12.17			12.44	12.19	11.84	11.57	12.14	11.85
	$\bar{\Delta}$[d]			0.91	0.16	0.31	0.14	0.51	0.69	0.23	0.39
Si_4H_{10}	σ(Si−Si)	a_g	9.62	10.03	9.27	10.14	9.97	9.07	9.03	9.13	8.99
(**2a**)[e]	σ(Si−Si)	a_g	10.30	11.42	10.46	10.89	10.64	9.94	9.83	10.27[f]	10.05[f]
	σ(Si−Si)	b_u	10.85	11.60	10.73	11.24	11.03	10.70	10.58[f]	10.04[f]	9.86[f]
	σ(Si−H)	b_g	11.60	12.73	11.67	11.73	11.43	10.74	10.48[f]	11.73	11.39
	σ(Si−H)	a_u	11.80	12.97	11.97	12.09	11.81	11.23	10.95	11.98	11.66
	σ(Si−H)	b_u	12.00			12.47	12.19	11.88	11.60	12.13	11.82
	$\bar{\Delta}$[d]			0.92	0.17	0.40	0.21	0.44	0.64	0.29	0.40
Si_5H_{12}	σ(Si−Si)	b_2	9.36	9.85[g]	9.12[g]	9.99	9.79	8.79	8.74	9.21	9.02
(**3a**)[c]	σ(Si−Si)	a_1	10.10	11.28[g]	10.36[g]	10.76	10.51	9.80	9.69	9.81	9.62
	σ(Si−Si)	a_1	10.60	11.64[g]	10.76[g]	11.20	10.94	10.69[f]	10.58[f]	10.30	10.08
	σ(Si−Si)	b_2	10.90	11.71[g]	10.84[g]	11.21	10.97	10.47[f]	10.31[f]	10.34	10.08
	σ(Si−H)	b_1	11.80			11.68	11.37	10.71	10.43[f]	11.71	11.37
	$\bar{\Delta}$[d]			0.87	0.18	0.46	0.34	0.50	0.61	0.28	0.52

[a] From ref 20. [b] From ref 23. [c] C_{2v} symmetry. [d] Mean deviation for all MOs between the calculated and the experimental ionization energies. [e] C_{2h} symmetry, *anti*-conformer. [f] The relative ordering of these orbitals is different from the ordering according to the OVA (ab initio) calculations. [g] From ref 24a.

$\bar{\Delta}$ between the experimental and the theoretical ionization potentials for the five highest occupied orbitals of 0.23 eV is obtained using SCF(MNDO). The SCF(AM1) calculations are also quite successful, the overall $\bar{\Delta}$ being only 0.31 eV. At SCF/6-31G* $\bar{\Delta}$ is much larger, 0.91 eV.[23] Ortiz and Mintmire have shown recently for several silicon-containing compounds that application of the OVA technique lowers the *ab initio* SCF/6-31G* calculated IPs by about 1 eV, improving considerably the theoretical−experimental agreement.[23,24] For the four lowest ionization energies of **1a** $\bar{\Delta}$ decreases from 0.91 eV at SCF/6-31G* to only 0.16 eV with the OVA method.[23] For the individual orbitals the deviations are in the range 0.11−0.24 eV.[23]

The addition of Green's function improves $\bar{\Delta}$ significantly for the AM1 calculations but not for the PM3 or the MNDO calculations (see Table 1); with OVGF(AM1) $\bar{\Delta}$ decreases to only 0.14 eV for the five highest occupied MOs of **1a**. Only for the HOMO the deviation from the experimental IP remains relatively high at 0.4 eV. For the other occupied MOs the deviations are only ca. 0.1 eV, within the experimental error bars. Thus, for **1a** the OVGF(AM1) method gives excellent quantitative agreement with the experimental IPs, similar (except for the HOMO) to that of the much more elaborate and costly OVA(6-31G*) calculations.[23] On the other hand, $\bar{\Delta}$ is actually higher (i.e., 0.69 eV for the OVGF(PM3) calculations and 0.39 eV for OVGF(MNDO)) than for the corresponding SCF calculations (Table 1). Note, that the orbital ordering which we find here is the same as given by *ab initio* calculations.[19d,23,24]

According to both the *ab initio* and the semiempirical calculations the two highest occupied MOs of **1a** are σ-(Si−Si)-type orbitals. According to AM1 the HOMO is nearly a pure σ(Si−Si) orbital with contributions of only ca. 7% from the hydrogen atomic orbitals (AOs). For the HOMO-1 the hydrogen contributions are larger, ca. 20%.

b. Si_3Me_8 (1b). The calculated first five IPs of the permethylated trisilapropane **1b** are presented in Table 2 together with the available experimental data.[14] The reported calculations are for the C_{2v} structure (see Figure 1), which is the most stable conformer of **1b**.

Methyl substitution lowers significantly the IPs of **1b** (i.e., by 1−1.7 eV) relative to the unsubstituted **1a**. This general phenomena applies also to other permethylated polysilanes (see below). According to the calculations the two highest bands in **1b** are in the range 8.0−9.5 eV and they correspond to ionization from the σ(Si−Si) bonds. According to the AM1 calculations the contributions of the AOs on the carbons and the hydrogens to the HOMO and HOMO-1 are 16% and 24%, respectively. The bands in the range 10−11.5 eV correspond to ionization from the σ(Si−C) bonds (according to the calculations ionization from the σ(C−H) bonds are in the range 12−14.5 eV). The experimental PES of **1b** shows two peaks at 8.19 and 9.14 eV and strongly overlapping bands in the 10.4−11.1 eV range.[14] According to the calculations and in analogy to **1a** the 10.4−11.1 eV band is composed of three overlapping bands peaking at 10.4, 10.7, and 11.0 eV. Using this interpretation the mean deviations $\bar{\Delta}$ of the SCF calculations from the experimental data for the five highest occupied MOs are 0.03 eV with PM3, 0.50 eV with AM1, and 1.09 eV with MNDO (the largest deviations are for the HOMO and HOMO-1). With both **1a**,**b** the OVGF-(AM1) calculations provide a very good quantitative agreement between the theoretical and the experimental values, with $\bar{\Delta}$ of only ca. 0.15 eV for each MO in either **1a** or **1b**. Application of the OVGF method improves $\bar{\Delta}$ significantly also in conjugation with MNDO but not for PM3 (although $\bar{\Delta}$ remains low (0.20 eV) also with OVGF(PM3)). Note that for both **1a**,**b** the OVGF-(AM1) results agree better with the experimental PES than *ab initio* calculations which used a modified STO-3G basis set.[21a]

2. Linear Tetrasilane. a. Si_4H_{10} (2a). Four rotational conformers of the tetrasilane **2a** were considered, the *anti* conformer (C_{2h} symmetry), where the dihedral angle ϕ between the planes defined by Si_1−Si_2−Si_3 and Si_2−Si_3−Si_4 (see Figure 1) is 180°, the *syn*-conformer ($\phi = 0$, C_{2v}), and two *gauche* conformers with

Table 2. Experimental and Calculated Ionization Energies (eV) of Permethylated Trisilapropane (1b), Tetrasilabutane (2b), and Pentasilapentane (3b)

molecule[a]	MO	sym	expt[b]	SCF (ab initio)[c]	AM1	OVGF (AM1)	PM3	OVGF (PM3)	MNDO	OVGF (MNDO)
Si_3Me_8	σ(Si−Si)	b_2	8.19	7.94	8.68	8.35	8.18	8.07	9.35	9.05
(**1b**)[d]	σ(Si−Si)	a_1	9.14	8.88	9.50	9.11	9.12	8.95	10.32	9.95
	σ(Si−C)	b_1	≈10.4−11.1	10.36	11.01	10.49	10.40	10.12	11.34	10.88
	σ(Si−C)	b_2	≈10.4−11.1		11.12	10.62	10.51	10.19	11.48	11.04
	σ(Si−C)	a_2	≈10.4−11.1		11.18	10.68	10.61	10.30	11.50	11.05
	$\bar{\Delta}$[e]			≈0.19	≈0.50	≈0.10	≈0.03	≈0.20	≈1.09	≈0.72
Si_4Me_{10}	σ(Si−Si)	a_g	7.98		8.50	8.14	7.73	7.61	9.02	8.69
(**2b**)[f]	σ(Si−Si)	b_u	8.76		9.38	8.98	9.25	9.05	9.87	9.50
	σ(Si−Si)	a_g	9.30		9.68	9.21	9.37	9.15	10.31	9.88
	σ(Si−C)	b_g	≈10.50		11.03	10.46	10.39	10.07	11.42	10.93
	σ(Si−C)	a_u	≈10.60		11.11	10.58	10.44	10.12	11.46	10.99
	$\bar{\Delta}$[e]				≈0.51	≈0.11	≈0.22	≈0.34	≈0.99	≈0.57
Si_5Me_{12}	σ(Si−Si)	b_1			8.40	8.02	7.59	7.44	9.04	8.70
(**3b**)[d]	σ(Si−Si)	a_1			9.15	8.76	8.90	8.71	9.70	9.33
	σ(Si−Si)	b_1			9.66	9.20	9.31	9.08	10.30	9.87
	σ(Si−Si)	a_1			9.74	9.22	9.38	9.12	10.46	9.99
	σ(Si−C)	b_2			11.03	10.44	10.42	10.08	11.36	10.86
	σ(Si−C)	a_2			11.08	10.52	10.45	10.12	11.40	10.91
	σ(Si−C)	a_1			11.18	10.64	10.62	10.30	11.49	11.03

[a] Me = CH_3. [b] From ref 14. [c] From ref 21a. [d] C_{2v} symmetry. [e] Mean deviation for all MOs between the calculated and the experimental ionization energies. [f] C_{2h} symmetry (*anti*-conformer).

Table 3. Relative Energies (kcal/mol) of Different Conformers of Tetrasilabutane (2a) and of the Permethylated Tetrasilabutane (2b) Calculated with Different Theoretical Methods

	Si_4H_{10} (**2a**)			Si_4Me_{10} (**2b**)[a]
conformation[b]	6-31G* [c]	MP2/6-31G*	AM1	AM1
syn, ϕ = 0°	1.49	1.47	0.07	4.34
gauche, ϕ = 60°	0.19	−0.05	−0.01	1.23
gauche, ϕ = 120°	0.87	0.68	0.24	0.82
anti, ϕ = 180° [d]	0.0	0.0	0.0	0.0

[a] Me = CH_3. [b] Geometry was fully optimized for each conformer, except for ϕ, which was kept at the indicated value. Full geometry optimization for the *gauche*-60° conformer (**2a**) lowers the energy by only 0.01 kcal/mol leading to ϕ = 54.5°. [c] From ref 23, geometry optimized at 3-21G*. [d] Fully optimized.

ϕ = 60° and 120° (C_2). At the HF/6-31G*//3-21G* and the MBPT(2)/6-31G*//3-21G* levels of theory, as well as at SCF(AM1), these conformers have similar energies, i.e., within 1.5 kcal/mol (see Table 3), with the *gauche*-60° and *anti*-conformer being the most stable and lying very close in energy, i.e., within 0.2 kcal/mol. According to MP2/6-31G** calculations Si_4H_{10} has *gauche*- and *anti*-conformers with a Si−Si−Si−Si dihedral angle of 57 and 180°, respectively.[19f]

Because the different conformers of **2a** are so close in energy, the PES of **2a** at room temperature reflects a thermal average of all rotational isomers. We have therefore carried out calculations of the IPs for the four conformers of tetrasilane **2a** using the OVGF(AM1) method which performed the best for **1a**,**b**, and the results together with the available experimental[20] and *ab initio*[23] EPT(OVA) data are collected in Table 4. The dependence of the ionization potentials of **2a** on the dihedral angle ϕ as calculated by the EPT(OVA)[23] and the OVGF(AM1) methods are also presented in Figure 2. Such calculations, in which the ionization energies are calculated as a function of the dihedral angle ϕ, can serve as a useful model for studying the influence of the conformation on the spectra of longer polysilanes. In general, the semiempirical methods and the *ab initio* calculations show a similar dependence of the ionization potentials on the dihedral angle ϕ (Figure 2).

Figure 2 shows that the ionization energies of Si_4H_{10} change quite significantly as a function of the dihedral angle ϕ. For example, the $4b_2$ orbital drops in energy by ca. 0.8 eV, when ϕ is changed from 0 to 180°. According to EPT(OVA) calculations the ordering of the energy levels for the *syn* (ϕ = 0) and the *anti* (ϕ = 180) conformers is not identical (i.e., $5a_g > 4a_g > 4b_u > 2b_g > 2a_u$ for the *anti*-conformer[25] and $5a_1 > 4b_2 > 4a_1 > 2a_2 > 3b_2$ for the *syn*-conformer). According to OVGF(AM1) the ordering of the energy levels for the *syn*-conformer is different ($4b_2 > 5a_1 > 4a_1 > 2a_2 > 3b_2$), but the difference between the HOMO ($4b_2$) and the HOMO-1 ($5a_1$) levels is small, only 0.04 eV (0.3 eV according to EPT(OVA)). According to both methods the HOMO−HOMO-1 gap increases significantly on going from the *syn*- to the *anti*-conformer; i.e., in the *anti*-conformer this gap is 0.67 eV at OVGF(AM1) and 1.19 eV at EPT(OVA). The best agreement between the calculated and the experimental PES of **2a**, both with the EPT(OVA) and the OVGF(AM1) calculations, is obtained for the *gauche*-60° conformer ($\bar{\Delta}$ being 0.16 and 0.15 eV for the five and six highest occupied MOs, respectively). This is consistent with the fact that the *gauche*-60° conformer of **2a** is calculated to be the most stable conformer. However, also for the other conformers $\bar{\Delta}$ is smaller than 0.25 eV. The full assignment of the ionization energies for the *syn*, *anti*, *gauche*-60°, and *gauche*-120° conformers and the mean deviation of the theoretical values from the experimental ionization potentials are presented in Table 4. For a systematic comparison with the other polysilanes and with permethylated polysilanes we will use the calculated ionization potentials for the *anti*-conformer which is the most stable conformer for most polysilanes studied here. These data are collected in Table 1.

The experimental PES of **2a** shows broadened peaks at 9.62, 10.3, and 10.85 eV,[20] which according to the calculations correspond to ionization from the σ(Si−Si) bonds. Three other strongly overlapping bands at 11.6, 11.8, and 12.0 eV correspond according to the calculations to ionization from the σ(Si−H) bonds. According

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(25) The same orbital ordering was found according to *ab initio* calculations using a double-ζ basis set.[19d]

Table 4. Ionization Energies (eV) of Different Conformers of Tetrasilabutane (2a) Calculated Using the OVA (ab Initio)[a] and OVGF(AM1) Methods

		syn-0° [b]			*gauche*-60° [c]			*gauche*-120° [c]			*anti*-180° [d]		
MO	expt[e]	sym	OVA	OVGF	sym	OVA	OVGF	sym	OVA	OVGF	sym	OVA	OVGF
σ(Si−Si)	9.62	a_1	9.56	10.27	a	9.49	10.19	a	9.33	10.05	a_g	9.27	9.97
σ(Si−Si)	10.30	b_2	9.86	10.23	b	10.05	10.35	b	10.44	10.70	a_g	10.46	10.64
σ(Si−Si)	10.85	a_1	11.04	11.22	a	10.81	10.91	a	10.57	10.70	b_u	10.73	11.03
σ(Si−H)	11.60	a_2	11.57	11.34	a	11.87	11.73	b	11.78	11.62	b_g	11.67	11.43
σ(Si−H)	11.80	b_1	12.10	11.91	b	11.92	11.73	a	11.97	11.80	a_u	11.97	11.81
σ(Si−H)	12.00			11.97			12.05			12.18			12.19
$\bar{\Delta}^f$			0.20	0.25		0.16	0.15		0.21	0.20		0.17	0.21

[a] From ref 23. [b] C_{2v} symmetry. [c] C_2 symmetry. [d] C_{2h} symmetry. [e] From ref 20. [f] Mean deviation between the calculated and the experimental ionization energies (for all MOs).

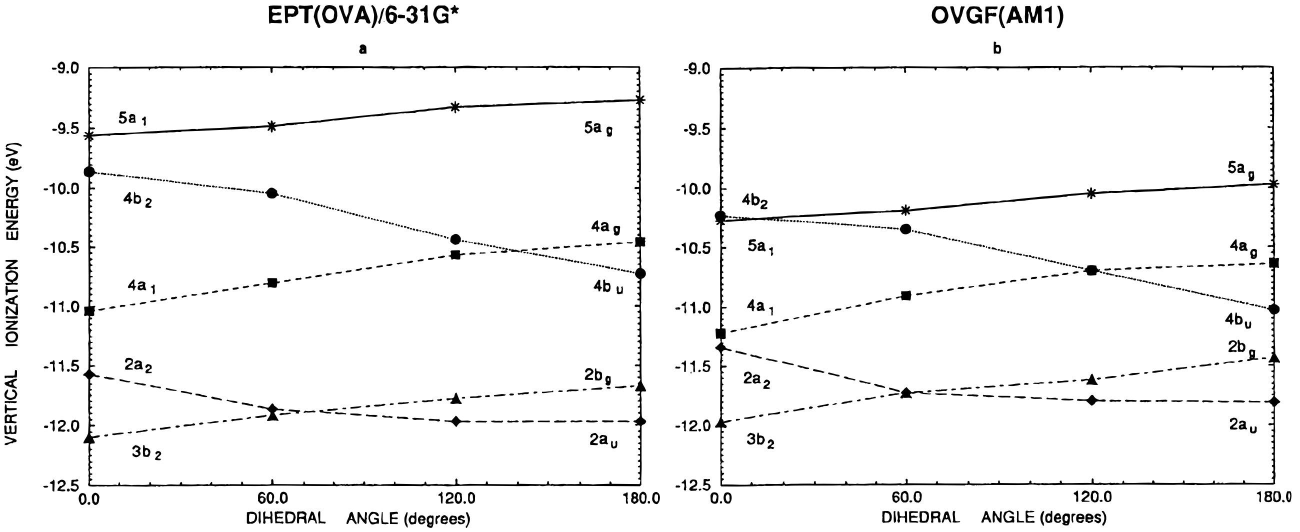

Figure 2. Calculated vertical ionization potentials for Si_4H_{10} (**2a**) as a function of the dihedral angle (ϕ) between the Si_1−Si_2−Si_3 and the Si_2−Si_3−Si_4 planes at (a) EPT(OVA)/6-31G*[23] and (b) OVGF(AM1). Numbering of the orbitals is according to Gaussian-92 (valence orbitals) and MOPAC-93 calculations, respectively.

to AM1 the HOMO and HOMO-2 orbitals of **2a** are almost pure σ(Si−Si) orbitals with contributions from the hydrogens AOs of only 5% and 7%, respectively, but the hydrogens' contribution increases to 23% in the HOMO-1 (PM3 and MNDO give similar results).

As for **1a** and also for **2a** the calculated ionization potentials at the SCF level (excluding the MNDO method with $\bar{\Delta} = 0.29$ eV) are unsatisfactory . The SCF-(*ab initio*) and SCF(AM1) ionization potentials are generally by ca. 1.0 and 0.4 eV, respectively, higher than the experimental values while the SCF(PM3) values are by ca. 0.5 eV lower than the experimental ionization energies. Inclusion in the calculations of Green's function improves substantially the agreement between the theoretical and the experimental ionization potentials both in the *ab initio*[23] and in the semiempirical (AM1) calculations. The mean deviation $\bar{\Delta}$ of the five highest occupied MOs decreases from 0.92 to 0.17 eV for the electron-propagator theory [EPT(OVA)] and from 0.4 to 0.21 eV for the OVGF(AM1) calculations (for the six highest occupied MOs). As for **1a** and also for **2a** the OVGF methods do not improve $\bar{\Delta}$ in conjugation with the MNDO and the PM3 methods.

b. Si_4Me_{10} (2b). For the decamethyltetrasilabutane (**2b**) the *anti*-conformer is for steric reasons favored over the other conformers (see Table 3). The second most stable conformer is the *gauche*-120° conformer, which lies 1.2 kcal/mol (AM1, 0.8 kcal/mol *ab initio*[19c]) higher in energy. The calculated ionization energies for the *anti*-conformer of decamethyltetrasilabutane (**2b**) are presented in Table 2 together with the experimental data.[14] The three highest occupied MOs of **2b** correspond mainly to σ(Si−Si) orbitals, but they include significant contributions from the carbons' and hydrogens' AOs: ca. 20% for the HOMO and 35% for the HOMO-1 and HOMO-2 orbitals.

The experimental PES of **2b** shows three peaks at 7.98, 8.76, and 9.30 eV corresponding to ionization from σ(Si−Si) bonds. As in the case of **1b**, the bands arising from ionization from the σ(Si−C) orbitals are strongly overlapping and they lie in the range 10.5−11.0 eV.[14] As for **1b** also for **2b** the SCF(MNDO) results are poor, the mean deviation for the five highest occupied MOs is 0.99 eV ($\bar{\Delta} = 1.09$ eV for **1b**). On the other hand, very good agreement is obtained for both **1b** and **2b** with the SCF(PM3) method ($\bar{\Delta} = 0.22$ eV). However, SCF-(PM3) gives quite poor results ($\bar{\Delta}$ ca. 0.5 eV) for the ionization potentials of the corresponding unsubstituted polysilanes **1a** and **2a** (see Tables 1 and 4).

The OVGF(AM1) calculations provide a very good quantitative correspondence between the theoretical and the experimental ionization potentials of **2b** ($\bar{\Delta} = 0.11$ eV for the five highest occupied MOs), as well as for **1a**,**b** and **2a**. In the case of **2b** the OVGF method improves significantly the computational results for MNDO but not for PM3.

The changes in the ionization energies of **2b** as a function of the dihedral angle ϕ (Figure 3) are similar to those found for **2a** (Figure 2), but the ordering of the HOMO-1 and HOMO-2 orbitals is slightly different for

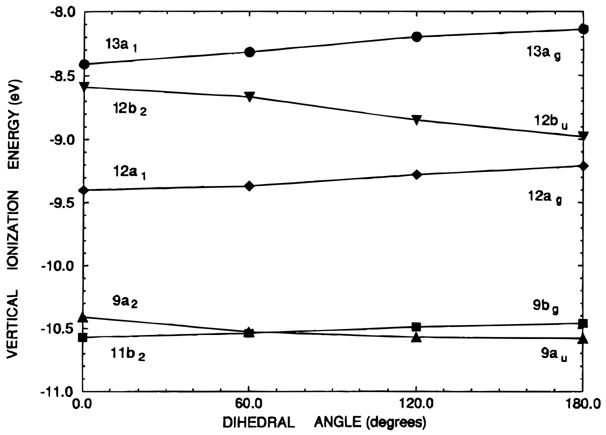

Figure 3. Calculated vertical ionization potentials (using OVGF(AM1)) for Si_4Me_{10} (**2b**) as a function of the dihedral angle ϕ between the $Si_1-Si_2-Si_3$ and $Si_2-Si_3-Si_4$ planes. Numbering of orbitals is according to MOPAC-93 calculations.

Table 5. Ionization Energies (eV) of Different Conformers of the Parent Pentasilane (3a) and the Permethylated Pentasilapentane (3b) as Calculated by the OVA (ab Initio) (for 3a) and OVGF(AM1) Methods

		60,60[a]		180,60[b]		180,180[c]	
MO	expt[d]	OVA[e]	OVGF	OVA[e]	OVGF	OVA[e]	OVGF
			Si_5H_{12} (**3a**)				
σ(Si−Si)	9.36	9.58	10.16	9.33	9.94	9.12	9.79
σ(Si−Si)	10.10	9.87	10.22	10.02	10.31	10.36	10.51
σ(Si−Si)	10.60	10.37	10.47	10.63	10.74	10.76	10.94
σ(Si−Si)	10.90	11.06	11.09	10.95	10.99	10.84	10.97
σ(Si−H)	11.80		11.61		11.51		11.37
$\bar{\Delta}$[f]		0.21	0.29	0.05	0.26	0.18	0.34
			Si_5Me_{12} (**3b**)				
σ(Si−Si)			8.30		8.15		8.02
σ(Si−Si)			8.47		8.66		8.76
σ(Si−Si)			8.95		9.11		9.20
σ(Si−Si)			9.53		9.36		9.22
σ(Si−C)			10.51		10.49		10.44
σ(Si−C)			10.61		10.49		10.52
σ(Si−C)			10.62		10.63		10.64

[a] C_2 symmetry. [b] C_1 symmetry. [c] C_{2v} symmetry. [d] From ref 20. [e] From ref 24a. [f] Mean deviation for all MOs between the calculated and the experimental ionization energies.

the two molecules (i.e, $13a_g > 12b_u > 12a_g$ for *anti*-**2b** compared to $5a_g > 4a_g > 4b_u$ for *anti*-**2a**). According to OVGF(AM1) the energy gap between the HOMO and the HOMO-1 increases from 0.2 eV in the *syn*-conformer to 0.8 eV in the *anti*-conformer.

3. Linear Pentasilanes. a. Si_5H_{12} (3a). Three conformers of the pentasilane **3a** were considered: the fully extended *anti,anti* conformer of C_{2v} symmetry, where the dihedral angles between the $Si_1-Si_2-Si_3$ and the $Si_2-Si_3-Si_4$ planes (ϕ_1) and between the $Si_2-Si_3-Si_4$ and the $Si_3-Si_4-Si_5$ planes (ϕ_2) are both 180°; the *gauche,gauche* conformer (C_2), where $\phi_1 = \phi_2 = 60°$ and the *anti,gauche* conformer, where $\phi_1 = 180°$ and $\phi_2 = 60°$ (C_1). At SCF(AM1) the most stable conformer of **3a** is the 60°,60° conformer, but the 60°,180° and 180°,180° conformers are only 0.1 and 0.5 kcal/mol, respectively, higher in energy. Thus, as for **2a** and also for **3a** the relatively small energy difference between the conformations suggests that the experimental PES is obtained from a thermal mixture of the rotational isomers of **3a**. The ionization potentials of the *anti,anti* conformer of **3a**, as calculated by the various semiempirical and the *ab initio* EPT(OVA) methods,[24a] are presented in Table 1 together with the available experimental data.[20] We choose to present in Table 1 the results for the *anti,anti* conformer of **3a** because of its higher symmetry, which facilitates the comparison between different calculations. In any case, the difference in the ionization potentials between the conformers is not very large, as shown by the OVGF(AM1) and EPT(OVA) calculations presented in Table 5.

The experimental PES of **3a** shows a well-separated peak at 9.36 eV and three strongly overlapping peaks at 10.1, 10.6, and 10.9 eV.[14,20] According to the AM1 calculations all the four highest occupied MOs have mainly σ(Si−Si) character with the contributions from the hydrogens' AOs being ca. 15%, 20%, 10%, and 20% for the HOMO to HOMO-3 orbitals, respectively. The results of the MNDO and PM3 calculations are essentially the same.

SCF calculations, either *ab initio*[23] or semiempirical, do not reproduce well the ionization potentials of **3a** (Table 1), except for MNDO (as was the case with **1a** and **2a**). However, MNDO does not predict correctly the IPs of permethyl-substituted polysilanes including those of **1b**, **2b**, and **3b** (see below). Also for **3a**, the addition of Green's function improves substantially the agreement between the calculated and the experimental ionization potentials, both for the *ab initio* and for the SCF(AM1) calculations. With both methods, the best experimental−theoretical agreement was obtained for the *gauche,anti* conformer with $\bar{\Delta} = 0.05$ and 0.26 eV for the EPT(OVA) and the OVGF(AM1) calculations, respectively (see Table 5). For the *anti,anti* conformer, $\bar{\Delta}$ was 0.18 eV for EPT(OVA) and 0.34 eV for OVGF-(AM1).

b. Si_5Me_{12} (3b). The *anti,anti* conformer of the permethyl pentasilane (**3b**) is favored over the other conformers probably due to steric reasons. However, the two other conformers, the C_2 *gauche,gauche* conformer ($\phi_1 = \phi_2 = 60°$) and the C_1 *anti,gauche* conformer ($\phi_1 = 180°$, $\phi_2 = 60°$), are only 1.0 and 1.5 kcal/mol, respectively, higher in energy, suggesting that the experimental PES of **3b** is obtained from a thermal mixture of the rotational isomers. The calculated IPs for the *anti,anti* conformer of **3b** by the different semiempirical methods are given in Table 2. The ionization energies of the other conformations of **3b** calculated with the OVGF(AM1) method are presented in Table 5. Unfortunately, according to the best of our knowledge, the PES of **3b** is not available, and therefore we cannot test the reliability of the theoretical predictions in this case. According to our experience with the other permethyl linear polysilanes the OVGF(AM1) and the SCF(PM3) methods are expected to be the best semiempirical methods for calculating the ionization potentials of **3b**. We indeed find that for **3b** these methods give very similar results except for the first ionization potential where the difference between the two methods is ca. 0.6 eV. The same trend has been observed also for **1b** and **2b**. On the basis of the above experience, we predict that the first ionization potential of **3b** lies between the OVGF(AM1) and SCF(PM3) values, i.e., around 7.8 eV.

The four highest occupied MOs of **3b** have predominantly σ(Si−Si) character, but the contributions from the C−Si orbitals are significant: i.e., 20%, 30%, 35%,

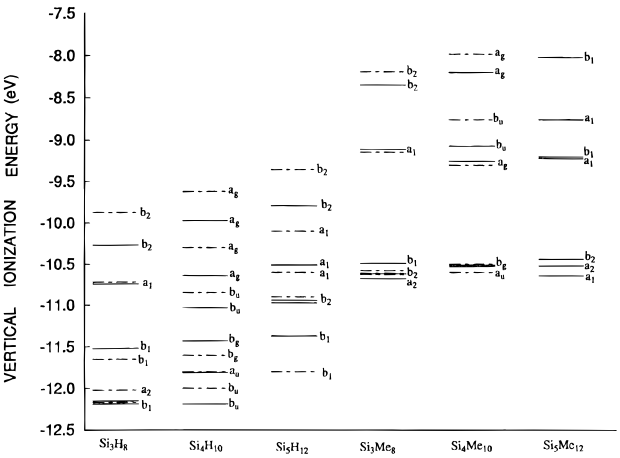

Figure 4. Experimental (- - -) and OVGF(AM1) (—) calculated vertical ionization potentials of linear polysilanes Si_nH_{2n+2}, $n = 3-5$, and of the corresponding permethylpolysilanes Si_nMe_{2n+2}, $n = 3-5$.

and 37% for the HOMO to the HOMO-3 orbitals, respectively (AM1). It is our general observation that as the silicon chain gets longer there are higher contributions to the higher lying orbitals from the Si−H or Si−C bonds.

To conclude our discussion of linear polysilanes we have collected in Figure 4 the experimental and the OVGF(AM1) calculated IPs for all the linear polysilanes studied. Figure 4 shows a general very good agreement (within ca. 0.1 eV) between the calculated and the experimental IPs of $R_3Si-(SiR_2)_n-SiR_3$ (R = H, CH_3; $n = 1-3$), except for the HOMO where there is a considerable difference between the theoretical and the experimental values. The calculated first IPs are too high by approximately 0.4 eV for the parent linear polysilanes and by 0.2 eV for the permethyl polysilanes. The most important conclusions from Figure 4 are (1) the first IP of linear polysilanes decreases as the chain length increases and (2) the permethylated polysilanes have IPs which are by 1−1.5 eV lower than the corresponding hydrogen-substituted systems. This might be due, at least partially, to the significantly longer Si−Si bonds in the permethylated polysilanes compared to the corresponding polysilanes (Figure 1), e.g., r(Si−Si) = 2.404 Å in $H_3SiSiH_2SiH_3$ and 2.489 Å in $Me_3SiSiMe_2SiMe_3$.

B. Cyclic Polysilane. 1. Parent Cyclic Polysilanes. The calculated ionization energies for the parent cyclic polysilanes **4a**−**7a** are presented in Table 6 together with the experimental data which are available only for **6a** and **7a**.[26]

For trisilacyclopropane **4a**, the ordering of the energy levels is the same, i.e., $e' > e'' > a_1'$, using either the semiempirical SCF(AM1), SCF(PM3), OVGF(AM1), and OVGF(PM3) methods or SCF *ab initio* calculations.[27] With SCF(MNDO) and OVGF(MNDO) the ordering of the a_1', and e'' orbitals is reversed.[28] The contribution of the hydrogens AOs to the e-type orbitals is small, only 3% (AM1), but it increases to 52% and 31% for the e'' and a_1' orbitals, respectively. The e-type degenerate orbitals are substantially higher in energy than the other orbitals.

In tetrasilacyclobutane **5a** the highest MO is not so well separated from the next lower orbitals as in the case for **4a** and different computational methods predict different ordering of the σ(Si−Si) energy levels. According to AM1 and PM3 the two degenerate e_u orbitals lie above b_{1g}. On the other hand, according to both 6-31G* *ab initio* and MNDO calculations the ordering is reversed with the b_{1g} orbital lying by 0.6−1.1 eV higher in energy than the degenerate e_u orbitals. On the basis of our experience, we believe that the AM1 and PM3 methods, even with Green's function, are not adequate for describing quantitatively the ionization potentials of **5a**. *Ab initio* calculations augmented with Green's function are needed to resolve the discrepancy and to establish the correct ordering of the MOs of **5a**. According to AM1 calculations for both linear and cyclic (see also section B2 below) polysilanes the contribution of the hydrogens' AOs to the HOMO is usually very small but it increases for the lower occupied orbitals. **5a** is an exception; the two degenerate HOMO orbitals contain 7% contributions from the hydrogens' AO, and this contribution vanishes in the b_{1g} orbital.

For pentasilacyclopentane **6a** (C_s, with a dihedral angle of 16° between the $Si_5-Si_4-Si_1$ and the $Si_4-Si_1-Si_2$ planes according to AM1), all the SCF semiempirical methods and the corresponding Green's function calculations predict the same ordering of the energy levels, with the highest four orbitals having mainly σ(Si−Si) character. The experimental PES of **6a** shows two broadened peaks at 9.4 and 10.35 eV[26] which correspond to ionization from the σ(Si−Si) bonds, a peak at 11.4 eV, and a wide peak in the range 12−13 eV, corresponding to ionization from σ(Si−H) bonds. The smallest mean deviation between the experimental and the theoretical ionization potentials for the six highest occupied orbitals of **6a** was obtained with MNDO ($\bar{\Delta}$ = 0.23 eV). However, as discussed below this method does not reproduce properly the ionization energies of the permethylated cyclic polysilanes. Using AM1 and PM3 $\bar{\Delta}$ is 0.55 eV. Incorporation of the OVGF method improves $\bar{\Delta}$ only for AM1, and at OVGF(AM1) $\bar{\Delta}$ = 0.30 eV. Yet, for the two lowest ionization potentials even this method produces significant differences (ca. 0.8 eV) between the experimental and the theoretical values.

Hexasilacyclohexane **7a** is most stable in a *chair* conformation (D_{3d} symmetry, Figure 1, with a dihedral angle of 31° between the $Si_1-Si_2-Si_3$ and $Si_1-Si_3-Si_4$ planes, AM1). SCF(MNDO) and OVGF(MNDO) calculations predict that the a_{1u} orbital lies above the two degenerate e_g orbitals, but AM1 and PM3 calculations both at the SCF and at the OVGF levels of theory give a reversed order. Experimentally, these three levels are practically degenerate. As found for all the other linear and cyclic parent polysilanes that we have studied, the OVGF(AM1) method provides the best quantitative agreement with the experimental data; the mean deviation for the eight highest occupied MOs is only 0.19 eV. As observed in the other cases and also for **7a** the OVGF(AM1) method overestimates somewhat the first IP (by ca. 0.4 eV).

2. Permethylated Cyclic Polysilane. The calculated and experimental IPs of the permethylated cyclic

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[26] Janoschek, R.; Hengge, E.; Stuger, H.; Nyulaszi, L. *Monatsh. Chem.* **1991**, *122*, 31.

[27] Schoeller, W. W.; Dabisch, T. *Inorg. Chem.* **1987**, *26*, 1081.

[28] Also for the larger cyclic polysilanes we find that the MNDO method predicts that the a-type orbital, corresponding to ionization mainly from Si−H bonds, lies above the e-type orbitals, while with the other semiempirical methods and the *ab initio* calculations the orbital ordering is reversed (see Table 6).

Table 6. Experimental and Calculated Ionization Energies (eV) of Trisilacyclopropane (4a), Tetrasilacyclobutane (5a), Pentasilacyclopentane (6a), and Hexasilacyclohexane (7a)[a]

molecule	MO	sym	expt[b]	SCF (ab initio)[c]	AM1	OVGF (AM1)	PM3	OVGF (PM3)	MNDO	OVGF (MNDO)
c-Si_3H_6	σ(Si−Si)	e′		9.2	9.76	9.61	8.88	8.88	8.48	8.34
(**4a**)[d]	σ(Si−Si)	e′		9.2	9.76	9.61	8.88	8.88	8.48	8.34
	σ(Si−H)	e″		13.1	12.16	11.80	11.46	11.17	11.89	11.51
	σ(Si−H)	e″		13.1	12.16	11.80	11.46	11.17	11.89	11.51
	σ(Si−H)	a_1'		13.5	12.47	12.10	12.38	12.12	11.29	10.97
c-Si_4H_8	σ(Si−Si)	e_u		10.4 (10.23)[e]	10.22	9.98	9.12	9.08	9.60	9.38
(**5a**)[f]	σ(Si−Si)	e_u		10.4 (10.23)[e]	10.22	9.98	9.12	9.08	9.60	9.38
	σ(Si−Si)	b_{1g}		*9.8 (9.52)*[e]	10.39	10.17	9.98	9.92	*8.54*	*8.39*
	σ(Si−H)	b_{1u}		12.6 (12.59)[e]	11.65	11.31	10.58	10.30	11.75	11.36
	σ(Si−H)	e_g		13.2 (13.20)[e]	12.47	12.10	11.84	11.52	12.13	11.74
	σ(Si−H)	e_g		13.2 (13.20)[e]	12.47	12.10	11.84	11.52	12.13	11.74
	σ(Si−H)	a_{1g}		13.6 (13.45)[e]	12.64	12.27	12.77	12.50	11.48	11.16
c-Si_5H_{10}	σ(Si−Si)	a″	9.4	9.37[g]	10.44	10.19	9.63	9.55	9.13	8.93
(**6a**)[h]	σ(Si−Si)	a′	9.4	*9.10*[g]	10.48	10.23	9.63	9.55	9.13	8.93
	σ(Si−Si)	a″	10.35	10.86[g]	10.66	10.38	9.67	9.58	10.20	9.93
	σ(Si−Si)	a′	10.35	10.53[g]	10.66	10.38	9.67	9.58	10.20	9.93
	σ(Si−H)	a′	11.4	11.95[g]	11.66	11.31	10.67	10.37	11.51	11.18
	σ(Si−H)	a″	11.4	12.07[g]	11.71	11.35	10.68	10.37	11.82	11.43
	σ(Si−H)	a′	12−13	12.91[g]	12.81	12.43	12.81	12.59	11.82	11.43
	σ(Si−H)	a″	12−13	13.03[g]	12.82	12.43	12.46	12.10	12.34	11.94
	$\bar{\Delta}$[i]			0.37	0.55	0.30	0.55	0.65	0.23	0.34
c-Si_6H_{12}	σ(Si−Si)	e_g	9.6	9.52[g]	10.28	10.03	9.13	9.03	9.53	9.30
(**7a**)[j]	σ(Si−Si)	e_g	9.6	9.52[g]	10.28	10.03	9.13	9.03	9.53	9.30
	σ(Si−Si)	a_{1u}	9.6	*9.41*[g]	10.55	10.28	9.89	9.79	*9.15*	*8.93*
	σ(Si−Si)	e_u	10.8	11.10[g]	11.12	10.80	10.29	10.15	10.54	10.24
	σ(Si−Si)	e_u	10.8	11.10[g]	11.12	10.80	10.29	10.15	10.54	10.24
	σ(Si−H)	a_{1g}	10.9	11.62[g]	11.25	10.91	10.27	10.05	11.17	10.83
	σ(Si−H)	e_u	11.7	12.69[g]	12.20	11.80	11.40	11.06	12.08	11.67
	σ(Si−H)	e_u	11.7	12.69[g]	12.20	11.80	11.40	11.06	12.08	11.67
	$\bar{\Delta}$[i]			0.46	0.49	0.19	0.46	0.60	0.27	0.32

[a] The italicized values indicate the lowest ionization potential when the order is different from the order of the enteries. [b] Experimental data from ref 26. [c] From ref 27 (basis set consists of Gaussian lobe functions). [d] D_{3h} symmetry. [e] 6-31G*. [f] D_{4h} symmetry. [g] STO-3G from ref 26. [h] C_s symmetry. [i] Mean deviation for all MOs between the calculated and the experimental ionization energies. [j] D_{3d} symmetry.

polysilanes Me_6Si_3 to $Me_{12}Si_6$ (**4b**−**7b**) are reported in Table 7. Similarly to the open chain polysilanes and also in the cyclic series, methyl substitution lowers significantly (by up to 1.7 eV) the first IPs of cyclic polysilanes.

For Me_6Si_3 (**4b**) all the semiempirical methods give the same orbital ordering. The contribution from non-silicon AOs in the practically degenerate HOMO is quite significant (17%, AM1), and it increases to 27% for the next lower two degenerate levels. The theoretically predicted IPs obtained by OVGF(AM1), OVGF(PM3), and OVGF(MNDO) are similar. The calculations predict that the IP of c-Si_3Me_6 should be the lowest among the cyclic silanes, and we estimate it to be around 7.45 eV. Recent HF/6-31G* calculations predicts a value of 7.9 eV.[29] Unfortunately, an experimental PES for **4b** is not yet available.

For the permethylated tetrasilacyclobutane **5b**, all the available semiempirical and *ab initio*[21a] calculations predict that the first ionizations occur from b_{2g} and e_u orbitals which have mainly σ(Si−Si) character although the contribution from non-silicon AOs is quite significant, ca. 20% (AM1). This is in agreement with the experimental PE spectrum,[21a] if the Jahn−Teller splitting of the degenerate e_u orbitals is taken into account. The bands corresponding to ionization from Si−C-type orbitals strongly overlap in the experimental PES[21a] and lie significantly lower in energy, in the range 10.5−11.2 eV. The SCF(AM1), SCF(MNDO), and OVGF(MNDO) methods do not reproduce satisfactory the observed IPs of **5b**. The mean theoretical−experimental deviation $\bar{\Delta}$ for the five highest occupied MOs is 0.69 eV for SCF-(AM1), 1.07 eV for SCF(MNDO), and 0.65 eV for OVGF-(MNDO). *Ab initio* calculations[21a] with a modified STO-3G basis set give a $\bar{\Delta}$ value of 0.38 eV. As in previous cases, significant improvement of the agreement between the experimental and the theoretical results is achieved with the OVGF(AM1) method ($\bar{\Delta}$ = 0.29 eV), but $\bar{\Delta}$ is found again to be relatively low for the SCF-(PM3) and the OVGF(PM3) methods ($\bar{\Delta}$ = 0.31 and 0.28 eV, respectively).

All the SCF methods and also OVGF(PM3) and OVGF(MNDO) predict the same orbital ordering for c-Si_5Me_{10} (**6b**) (C_s symmetry, Figure 1, with a dihedral angle of 31° between the Si_5−Si_4−Si_1 and Si_4−Si_1−Si_2 planes, AM1), but the quantitative theoretical−experimental agreement is rather poor. The mean deviation $\bar{\Delta}$ for the seven highest occupied MOs is 0.69 eV for SCF(AM1), 0.57 eV for SCF(PM3), 0.53 eV for OVGF-(PM3), 1.11 eV for SCF(MNDO), and 0.65 eV for the OVGF(MNDO) method. Significant improvement of the agreement between the experimental and the theoretical results is achieved with the OVGF(AM1) method, for which the mean deviation for the seven highest MOs is only 0.25 eV. However, even with OVGF(AM1) the first IP is by 0.38 eV too high. According to AM1 calculations the HOMO is practically degenerate and it has a 21% contribution from non-silicon AOs. Ab initio calculations for **6b** are not yet available.

For the permethylated cyclohexasilahexane (**7b**), which exists in a chair conformation (D_{3d} symmetry, Figure 1), $\bar{\Delta}$ for the seven highest occupied MOs is 0.77 eV for SCF(AM1), 0.26 eV for OVGF(AM1), 1.29 eV for SCF-(MNDO), 0.80 eV for OVGF(MNDO), 0.27 eV for SCF-

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(29) Nagase, S.; Kobayashi, K.; Nagashima, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1302.

Table 7. Experimental and Calculated Ionization Energies (eV) of Permethylated Trisilacyclopropane (4b), Tetrasilacyclobutane (5b), Pentasilacyclopentane (6b), and Hexasilacyclohexane (7b)[a]

molecule[b]	MO	sym	expt	ab initio	AM1	OVGF (AM1)	PM3	OVGF (PM3)	MNDO	OVGF (MNDO)
c-Si_3Me_6	σ(Si−Si)	e′		7.9[c]	8.43	8.12	7.89	7.82	8.65	8.36
(**4b**)[d]	σ(Si−Si)	e′			8.43	8.12	7.89	7.82	8.65	8.36
	σ(Si−C)	a_1'			10.70	10.18	10.66	10.37	11.15	10.67
	σ(Si−C)	e″			11.35	10.76	10.87	10.56	11.50	11.01
	σ(Si−C)	e″			11.35	10.76	10.87	10.56	11.50	11.01
	σ(Si−H)	a_2''			11.79	11.18	11.72	11.34	11.89	11.38
c-Si_4Me_8	σ(Si−Si)	b_{2g}	7.60[e]	(6.92)[e]	8.62	8.25	8.39	8.25	8.56	8.25
(**5b**)[f]	σ(Si−Si)	e_u	8.15[e]	(7.94)[e]	9.04	8.63	*8.30*	*8.18*	9.73	9.33
	σ(Si−Si)	e_u	8.50[e]	(7.94)[e]	9.04	8.63	*8.30*	*8.18*	9.73	9.33
	σ(Si−C)	a_{1g}	10.50[e]	(10.94)[e]	10.83	10.30	10.86	10.55	11.26	10.77
	σ(Si−C)	b_{2u}	10.50[e]	(10.31)[e]	11.11	10.52	10.44	10.13	11.33	10.82
	σ(Si−C)	e_g		(10.76)[e]	11.39	10.80	10.93	10.60	11.60	11.08
	σ(Si−H)	e_g		(10.76)[e]	11.39	10.80	10.93	10.60	11.60	11.08
	$\bar{\Delta}$[g]			(0.38)	0.69	0.29	0.31	0.28	1.07	0.65
c-Si_5Me_{10}	σ(Si−Si)	a″	7.94[h]		8.73	8.32	8.16	8.01	9.00	8.63
(**6b**)[i]	σ(Si−Si)	a′	7.94[h]		8.83	8.41	8.36	8.20	9.03	8.66
	σ(Si−Si)	a′	8.91[h]		9.54	9.06	8.86	8.68	10.30	9.83
	σ(Si−Si)	a″	8.91[h]		9.56	9.07	8.89	8.71	10.30	9.84
	σ(Si−C)	a′	9.80[h]		10.65	10.09	10.21	9.92	11.17	10.65
	σ(Si−C)	a″	10.7[h]		11.13	10.52	10.50	10.15	11.39	10.85
	σ(Si−C)	a′	10.7[h]		11.40	10.79	11.02	10.63	11.51	10.98
	$\bar{\Delta}$[g]				0.69	0.25	0.57	0.53	1.11	0.65
c-Si_6Me_{12}	σ(Si−Si)	a_{1u}	7.79[h]		8.80	8.35	8.31	8.13	8.93	8.54
(**7b**)[j]	σ(Si−Si)	e_g	8.16[h]		8.95	8.49	*8.27*	*8.10*	9.43	9.01
	σ(Si−Si)	e_g	8.16[h]		8.95	8.49	*8.27*	*8.10*	9.43	9.01
	σ(Si−Si)	e_u	9.12[h]		9.79	9.27	9.27	9.05	10.62	10.11
	σ(Si−Si)	e_u	9.12[h]		9.79	9.27	9.27	9.05	10.62	10.11
	σ(Si−C)	a_{1g}	9.78[h]		10.40	9.83	9.92	9.61	11.03	10.49
	σ(Si−C)	e_u	10.40[h]		11.30	10.66	10.71	10.33	11.52	10.95
	$\bar{\Delta}$[g]				0.77	0.26	0.27	0.15	1.29	0.80

[a] The italicized values indicate the lowest ionization potential when the order is different from the order of the entries. [b] Me = CH_3. [c] HF/6-31G* from ref 29. [d] D_{3h} symmetry. [e] From ref 21a. [f] D_{4h} symmetry. [g] The mean deviation for all MOs between the calculated and the experimental ionization energies (eV). [h] From ref 14. [i] C_s symmetry. [j] D_{3d} symmetry.

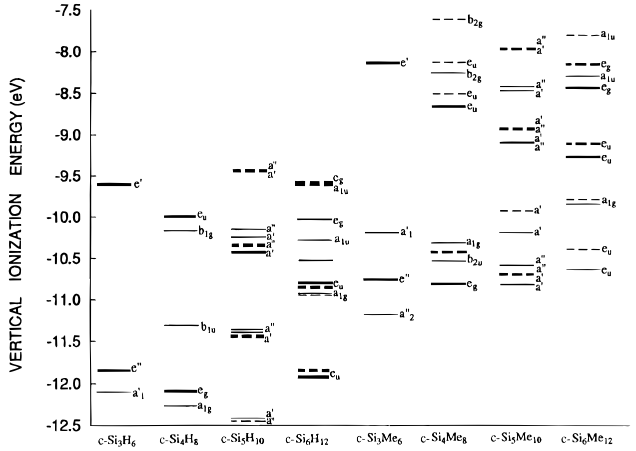

Figure 5. Experimental (- - -) and OVGF(AM1) (—) calculated vertical ionization potentials of cyclic polysilanes Si_nH_{2n}, $n = 3-6$, and of the corresponding cyclic permethylsilanes Si_nMe_{2n}, $n = 3-6$ (bold lines correspond to degenerate orbitals).

(PM3), and 0.15 eV for OVGF(PM3). Thus, as with c-Si_4Me_8 (**5b**) and c-Si_5M_{10} (**6b**), also with c-Si_6Me_{12} (**7b**) we find that the SCF(AM1), SCF(MNDO), and OVGF-(MNDO) methods give poor results, while the SCF-(PM3), OVGF(PM3), and OVGF(AM1) methods give good agreement with experiment. Also for **7b** *ab initio* calculations are not yet available due to the prohibitive cost of such calculations. On the basis of the experience of this work, we conclude that the *most reliable method for calculating the ionization energies of permethyl cyclic polysilanes is the OVGF(AM1) method*.

Figure 5 displays the OVGF(AM1) calculated ionization potentials of the Si_3−Si_6 cyclic polysilanes and of the corresponding permethylated cyclic polysilanes. The experimental data (where available) are also shown in dashed lines. Comparison of Figure 5 with Figure 4 reveals an interesting contrast in the change of the first IP as a function of the polysilane length between the chain and the cyclic polysilanes. Thus, *in the cyclic silanes the first IP is higher when the number of Si atoms in the polysilane increases, while in the open-chain silanes the first IP decreases with the number of silicon atoms*. This interesting contrast between the two families probably results from the fact that three- and four-membered ring silanes are “irregular” in the sense that in these silanes there are strong repulsive electronic interactions between the Si−Si bond electrons, pushing the HOMO to higher energies. These interactions become less important as the ring becomes larger. In cyclosilapentane the trend reverses, and the IP of cyclosilahexane is lower than that of cyclosilapentane. Janoschek and his co-workers explained the unusual stability of the HOMO in Si_6H_{12} compared to Si_5H_{10} in terms of the smaller ring strain in the six-membered ring.[26] In the open-chain silanes repulsive interactions between the Si−Si bonds can be relieved by rotation to *anti*- or *gauche*-conformers and the observed trend is therefore “regular”, i.e., a lower IP for a longer silane.

The opposite behavior of the first IP of cyclic and of linear silanes generates an interesting crossover between the two series. Thus, the IP of c-Si_3Me_6 is lower than that of the open-chain Si_3Me_8, but the reverse is true for the pentasilanes where the calculated IP of c-Si_5Me_{10} is higher than that of the corresponding open chain Si_5Me_{12}. We predict that for polysilanes having more than 6 silicon atoms the first IP of the cyclopolysilane is higher than that of its open chain analogue.

Conclusions

We have studied the ability of semiempirical calculations coupled with OVGF techniques to correctly predict the PE spectra of the valence electrons of linear and cyclic polysilanes containing 3−6 silicon atoms and of the corresponding permethylated compounds.

The SCF(MNDO) method is found to produce reliable results only for open-chain polysilanes, but it fails for the cyclic systems and for the permethylated compounds (both linear and cyclic). OVGF(MNDO) calculations fail for all the investigated species. The reverse is observed with the SCF(PM3) and OVGF(PM3) methods; these methods give poor results for the IPs of the open-chain parent polysilanes but produce excellent results for the corresponding permethylated linear polysilanes as well as for the cyclic polysilanes ($\bar{\Delta} \approx 0.30$ eV). The best and most balanced results for *all* the molecules which we have studied are obtained with the OVGF(AM1) method which produces much improved results over the SCF(AM1) calculations. For the 10 linear and cyclic polysilanes studied, the OVGF(AM1) method gives a mean deviation from the experimental ionization potentials of only 0.21 eV which is similar to that achieved (for fewer systems) with the much more costly *ab initio* outer-valence Green's function approximations (OVA) with the 6-31G* basis set. All methods including the OVGF(AM1) method calculate the first IP to be too high by up to 0.4 eV (this is especially pronounced for SCF(MNDO) and OVGF(MNDO)). This implies that even at this level of theory the magnitude of the destabilizing interactions between the σ(Si−Si) bonds are underestimated. We suggest that the lowest IP of polysilanes can be estimated reliably by subtracting an empirical correction of 0.4 eV for the parent polysilanes and 0.2 eV for the corresponding permethylated polysilanes from the OVGF(AM1) calculated value for the desired molecule. *We conclude that the OVGF technique coupled with the semiempirical AM1 and PM3 methods as the zeroth approximation is a very reliable computational method for predicting the ionization potentials of linear and cyclic polysilanes.* These methods can therefore be very useful in studying the electronic properties of larger polysilanes and probably also of segments of polysilane polymers, a topic which attracts considerable contemporary interest. We are currently applying these methods to study the electronic properties of other interesting groups of silicon compounds.

We have shown previously that these methods, in particular the OVGF(AM1) method, reproduce reliably also the ionization potentials of heterocyclic molecules with one to four nitrogen atoms[4,5,7a] and of organic radicals and anions.[7b] We therefore believe that the combination of the OVGF technique with semiempirical computational methods is very useful for routine calculations of the ionization potentials of relatively large molecules, for which the corresponding *ab initio* procedures are prohibitively expensive or are entirely outside the computational capabilities of most research laboratories.

Regarding the ionization energies of the Si_3−Si_6 polysilanes that were studied, the major conclusion are the following: (1) The first ionization energies of the permethylated polysilanes are significantly (by 1−1.7 eV) lower than those of the corresponding parent polysilanes. (2) In the cyclic silanes the first IP is higher when the number of silicon atoms in the polysilane increases, while in the open-chain silanes the first IP decreases with the number of silicon atoms. The crossover between the two series occurs between the Si_4 and Si_5 polysilanes.

Acknowledgment. This research was supported by the Israel Science Foundation administered by the Israel Academy of Sciences and Humanities and by the Fund for Promotion of Research at the Technion and the Technion VPR Fund-Loewengart Research Fund. D.D. acknowledges a scholarship from the Center of Absorption in Science, Israel Ministry of Immigrant Absorption, the State of Israel. Y.A. acknowledges a research Award from the Alexander von-Humboldt Foundation and the warm hospitality of Prof. H. Schwarz at the Technische Universität, Berlin, where this work was completed. We thank Professors Janoschek and Hengge for a preprint of ref 21b.

OM950583Z