Semiempirical SCF-MO Modeling of Polysilanes Using AM1 and PM3 Methods

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AM1 and PM3 semiempirical SCF-MO methods have been used to calculate structures and properties of model polysilanes. Bond lengths and molecular orbital energies of poly(hydrosilanes) calculated by both methods are in good agreement with ab initio results, but bond angles deviate slightly. Our studies of molecular geometry and electronic properties of polysilane models show similar behavior for the AM1 and PM3 methods in most cases, but the PM3 method appears to be superior in predicting bandgaps. The PM3 method predicts that the anti conformer of $Si_4(CH_3)_{10}$ lies ≈1.0 kcal/mol lower in energy than the gauche conformer. Studies evaluating polysilanes bearing substituent groups with different steric requirements and electronic properties (Me, Et, F, Cl, and OCH_3) were instructive. Compared to the unsubstituted model, all of the substituted polysilanes have larger Si–Si bond angles, in agreement with experiment. Our calculations suggest that substituents may have a significant effect on Si–Si–Si bond angles pushing them to well above the 120° value estimated for the hexyl derivative from X-ray data. The effect of substitution on electronic properties is predicted to be complicated. For calculation of structure and properties of polysilane models overall, the AM1 and PM3 methods are judged to provide excellent agreement with experimental data and ab initio methods.

Introduction

Polysilanes represent an important class of σ-conjugated polymers showing extensive delocalization of electrons through the σ-bonded network. These polymers have attracted attention because of the many interesting chemical and physical properties that they exhibit.[1] The photochemical properties of polysilanes provide them with potential applications in the many technological areas including lithography[2] and use as wave guides.[3] These applications depend intimately on the electronic or optical properties of these materials. Unlike most polymers whose absorption properties are due to the side chain, the polysilanes are a member of a small class of polymers where the backbone itself constitutes the chromophore. Hence, the spectral properties may be dependent on conformation. Since the polysilanes are σ-bonded polymers, they are unique in this regard.

With decreasing temperature, several dialkyl-substituted polysilanes in solution, in particular poly(di-*n*-hexylsilane), exhibit a red shift of λ_{max} up to about 40 nm with a concomitant narrowing of the absorption line shape occurring at roughly −30 °C.[4-6] A similar red shift is observed for the polymer as a solid film. These bathochromic shifts are attributed to order–disorder transitions of substituted polysilanes, although in solution aggregation effects may complicate the interpretation. Nevertheless in the solid state the transition is a result of conformational changes.[7]

X-ray diffraction and other spectroscopic measurements suggest that the room-temperature phase of poly(di-*n*-hexylsilane), PDHS, in solid films is a highly crystalline, all-trans conformation with a silicon backbone bond angle of roughly 120°.[5] Raman studies[8] show that the structure of poly(di-*n*-pentylsilane), PDPS, is significantly different from that of PDHS. There are significant differences in the silicon–silicon stretching region, which indicate that the backbone of PDPS is no longer planar. The structure of PDPS as determined by WAXD demonstrates that the backbone dihedrals are about 155° rather than 180° resulting in a helical structure. This torsional twisting may account for the strong blue shift in the electronic absorption spectrum,[8] but our calculations (vide infra) suggest that the HOMO–LUMO energy gap is not that sensitive in the 135–180° range. Other factors such as the Si–Si–Si bond angle changes, which we show to be highly susceptible to steric effects (vide infra), cannot be excluded.

On the basis of valence photoelectron spectra, Ensslin et al.[9] estimate that the anti conformer of tetrasilane is lower in energy than the gauche conformer by 0.4 kcal/mol. Similarly, NMR and vibrational spectroscopic measurements on the oligomer decamethyltetrasilane, $Si_4(CH_3)_{10}$, indicate that the anti conformer lies roughly 0.5 kcal/mol lower than the gauche conformer.[10]

Because of the strong influence of the silicon backbone conformation on the electronic properties, theoretical in-

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vestigation of the stable conformations may be highly instructive. Molecular mechanics calculations[12] suggest stabilization of the gauche conformer relative to the anti conformers of 0.09 and 0.70 kcal/mol for tetrasilane and pentasilane, respectively. In contrast, semiempirical MO calculations using the MNDO method predict that the all-trans conformer of *n*-Si_7H_{16} should be lower in energy by roughly 2.5 kcal/mol than the all-gauche conformer.[13] Full relaxation empirical force field calculations, as contained in the MM2 program, have been reported for various conformations of PDHS.[14] These calculations suggest that the all-trans backbone conformation is lowest in energy and average Si–Si–Si bond angles of 110.4° and a Si–Si bond lengths of 2.355 Å are predicted. On the other hand, X-ray diffraction results indicate a substantially larger Si–Si–Si bond angle of 120°, assuming a standard Si–Si bond length of 2.35 Å.[5]

Empirical force field calculations by Farmer and coworkers[15] suggest that the most stable conformation for oligomers is slightly helical as found experimentally in the solid state for PDPS. Considering the nature of all semiempirical calculations and the assumptions involved, the similar conformational energies for the trans and gauche are computed to be too close to allow for an absolute assignment of the molecules preference.

Calculations on polysilane models by ab initio methods are restricted to small molecules.[16–18] The calculated total energies of the tetrasilane conformers using 3-21G* and 6-31G* basis sets indicate that the anti conformer is lower in energy by 0.17 and 0.19 kcal/mol, respectively, compared to the gauche conformer.[17] However, inclusion of second-order Møller–Plesset perturbation theory (MP2) corrections changes the relative ordering of the conformational energies.[17]

Our study of polysilanes is a result of our interest in polymers that have potentially useful nonlinear optical properties. While our earlier efforts have focused on π-conjugative systems, in particular polydiacetylenes, σ-conjugated systems, such as the polysilanes, are of interest to us because they absorb in the UV, thus avoiding practical problems associated with visible light absorption from intense laser sources which may cause polymer degradation.

The present study focuses on two main goals. Primarily, we are interested in determining the best semiempirical MO methods for prediction of the electronic properties and molecular geometries of silicon polymers. We are especially interested in comparing our calculations to data in the literature to see if our calculations can provide insight into interesting experimental observations. Secondarily, we are interested in examining the effect of substitution on polysilane conformation.

To evaluate two of the most recent semiempirical SCF-MO methods, i.e., AM1[19] and PM3,[20] we have calculated the molecular structures and electronic properties of some polysilanes and compared these results with available ab initio and experimental data. Also, the substituent effects are investigated systematically. Two alkyl substituents (R = Me, Et) and three substituents having nonbonding electrons on the silicon-bonding atom (R = Cl, F, OCH_3) are used as side-chain substituents.

Table I. Anti S_4H_{10} Molecular Geometry, C_{2h} Symmetry

	bond lengths, Å		
	AM1	PM3	ab initio[a]
Si_1–Si_2	2.406	2.391	2.344
Si_2–Si_3	2.391	2.380	2.348
Si_1–H (H's in Si plane)	1.467	1.488	1.477
Si_1–H (H's out of Si plane)	1.466	1.488	1.477
Si_2–H	1.471	1.488	1.481
	bond angles, deg		
	AM1	PM3	ab initio
Si–Si–Si	108.0	109.0	111.7
Si_2–Si_1–H (H's in Si plane)	109.3	109.7	111.2
Si_2–Si_1–H (H's out of Si plane)	109.7	110.0	109.8
Si_1–Si_2–H	109.7	109.2	109.7
	dihedral angles, deg		
	AM1	PM3	ab initio
Si_3–Si_2–Si_1–H (H's out of Si plane)	60.2	60.2	59.6
Si_1–Si_2–Si_3–H	60.1	60.3	59.0

[a] Ab initio results are taken from ref 18.

Methodology

All calculations were carried out on a CRAY X-MP/24 computer using the MOPAC (version 5.04)[21] and AMPAC (version 2.11)[22] packages. SCF convergence and energy minimization criterion were limited to the program default values. Computations were restricted to an s and p atomic valence orbital basis set as set forth in MOPAC. Inclusion of d-type basis functions would be expected to give more accurate geometries for silicon-containing chains,[18] but such basis sets are beyond the scope of the MOPAC and AMPAC methods. Even so, we show below that the agreement of these semiempirical methods with ab initio calculations and experimental data is remarkably good.

The polysilanes are soluble linear polymers with minimal cross-linking between chains and are well suited for study assuming a model with one-dimensional periodicity. The model compounds used for representing the polymer chains in the calculations are represented by the formula $H_3Si(SiX_2)_nSiH_3$, where X is H, CH_3, C_2H_5, Cl, F, or OCH_3 groups. For all substituents except for the ethyl group, *n* is chosen to be 5. For the ethyl group, *n* is chosen to be 4 due to computational limitations. For these model compounds the SiH_3 group represents the end group, and its bond lengths and angles are fixed and taken from previous ab initio calculations.[18] The Si–H bond length is assumed to be 1.477 Å, bond angles for the hydrogens in plane and hydrogens out of the plane of the backbone are fixed at 111.2° and 109.8°, respectively, and the Si–Si bond length for the end group is fixed at 2.344 Å.[18] All other bond lengths and bond angles within the polymer chains are fully optimized. The SYMMETRY option within the MOPAC package is used to ensure the D_{2h} symmetry for optimized structures. Model structures were examined for both substituent and conformational effects. The anti conformer, which has been found to be the most stable conformer, is used for the determination of substitution effects.

Results and Discussion

Since our primary goal was to test the reliability of the AM1 and PM3 methods for calculation of molecular and

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Table II. Comparison of Semiempirical Calculated Koopmans Ionization Energies (eV) of Disilane with the ab Initio and Experimental Values

	CNDO[a]	AM1[b]	PM3[b]	ab initio[c]	exptl[d]
$^2A_1{}^g$	12.74	10.65	9.90	10.97	10.53
^2E_g	15.46	11.94	11.02	12.87	11.9, 12.1
^2E_u	16.07	13.02	12.77	13.61	12.73, 13.08
$^1A_{2u}$	20.03	15.40	15.58		16.50

[a] These results are taken from ref 23. [b] This work. [c] Koopman's energies are calculated with the 6-31G* basis; see ref 18. [d] From refs 9 and 23.

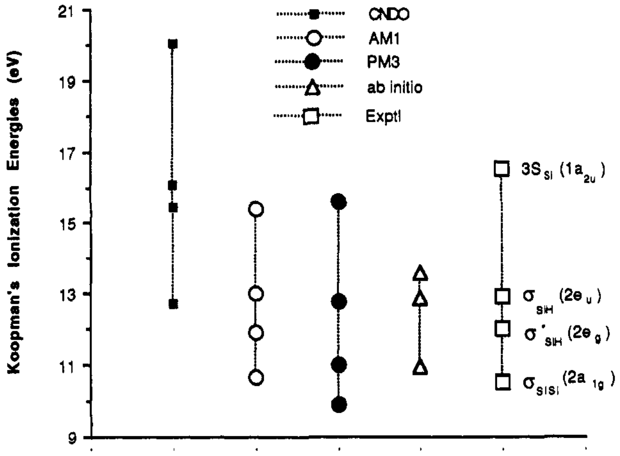

Figure 1. Comparison of semiempirical calculated Koopmans ionization energies (eV) of disilane with ab initio and experimental results.

Table III. Comparison of AM1 and PM3 Calculated Relative Energies (kcal/mol) for Different Conformers of Si_4H_{10} with ab Initio Results

			ab initio[a]		
conformation	AM1	PM3	3-21G*	6-31G*	MP2/ 6-31G*
anti	0.00	0.00	0.00	0.00	0.00
eclipsed (120°)	+0.47	+0.47	+0.75	+0.62	+0.58
gauche	−0.01	+0.28	+0.17	+0.19	−0.04
eclipsed (0°)	+0.07	+0.32	+1.26	+1.65	+1.25

[a] Results are taken from ref 18.

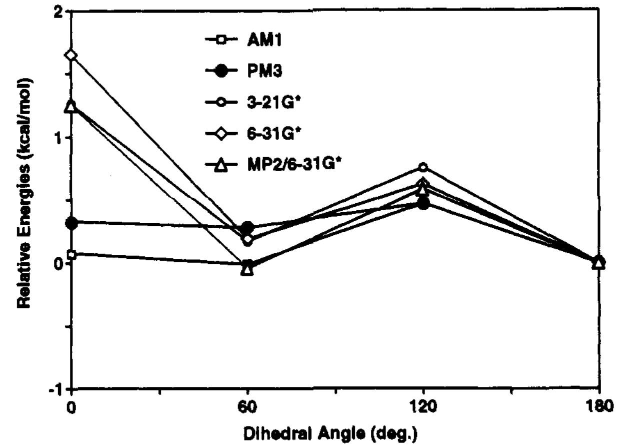

Figure 2. Comparison of calculated relative energies for different conformations of tetrasilane.

electronic properties of silicon polymers and since both tetrasilane and disilane have been the subjects of a number of ab initio studies,[16-18] we initially selected oligohydrosilanes for evaluation. We have carried out full geometry optimization for the anti conformer of tetrasilane by using AM1 and PM3 methods and have compiled the results in Table I. Inspection of these data reveals that the Si-Si bond lengths calculated by AM1 and PM3 are in reasonable agreement with the ab initio results. AM1 and PM3 methods tend to overestimate this bond length by 0.05 and 0.04 Å, respectively. The Si-H bond lengths calculated by AM1 and PM3 are close to the ab initio data. The average AM1 and PM3 Si-H bond lengths are 0.02 Å shorter and 0.01 Å longer, respectively, than those obtained by ab initio calculations. Bond angles, in general, show a larger deviation. The Si-Si-Si bond angles calculated by AM1 and PM3 methods are smaller than the corresponding ab initio calculated values by 3.7° and 2.7°, respectively.

Photoelectron spectra of linear silanes, Si_nH_{2n+2}, are available in the literature.[23] To test ability of AM1 and PM3 to reproduce the electronic properties of polysilanes, the ionization energies for the four highest molecular orbitals of disilane are given in Table II and are depicted in Figure 1. Also, for comparison purposes, some CNDO[23] and ab initio[18] results are included in Table II and Figure 1. The ionization energies are based on the validity of the Koopmans theorem, $IP_n = -E_j{}^{SC}{}_F$. For comparison purposes, Koopmans ionization potentials (IPs) computed by ab initio methods are included. Ortiz and Mintmire[18] used the electron propagator theory to calculate the vertical ionization energies, which are in good agreement with experiment. Although the CNDO energies are obtained using a CNDO version reparametrized to improve correlations between differences in PE ionization potentials, they still deviate significantly from the experimental results. Both the AM1 and PM3 data, especially for the three highest states, are in excellent agreement with experiment. These methods also predict a lower ionization energy for the $^1A_{2u}$ state, for which there are no ab initio data available for comparison.

Both the AM1 and PM3 eigenvectors of disilane indicate that σ_{SiSi} makes a considerable contribution to the $^2A_{1g}$ state. For the ^2E_g and ^2E_u states, σ_{SiH} makes the largest contribution, and finally the silicon's 3s orbital makes a large contribution to both the $^1A_{2u}$ and $^1A_{2g}$ states. This rationalizes the approximate classification into σ_{SiSi}, σ_{SiH}, and $3s_{Si}$ ionization regions in the silane photoelectron spectra proposed by Bock and co-workers.[23]

Experimental studies[7] on polysilanes have demonstrated the strong conformational dependence of UV absorption. Therefore, as another test of the reliability of the AM1 and PM3 methods, the relative energies for four conformations of tetrasilane, Figure 2, are compared in Table III. Again, tetrasilane was studied because of the availability of ab initio data for comparison. The four conformations are the anti conformer with a Si-Si-Si-Si dihedral angle of 180°, a gauche conformer with a dihedral angle of 60° and two eclipsed conformers with dihedral angles of 120° and 0°, respectively. In contrast to the ab initio results, both AM1 and PM3 methods predict the 0° eclipsed conformer to be more stable than the 120° eclipsed conformer. However, the core–core repulsions play a significant role in the case of the 0° eclipsed conformer, and the partition of the total energies reveal that both AM1 and PM3 methods may underestimate these sort of repulsions. Both the AM1 and ab initio calculations,[17] using a 6-31G*/MP2, indicate that the gauche structure is more stable than the anti conformer. On the other hand, on the basis of photoelectron spectroscopy,[9] it was concluded that the anti conformer of Si_4H_{10} is 0.4 kcal/mol lower in energy than the gauche conformer. This is in reasonable agreement

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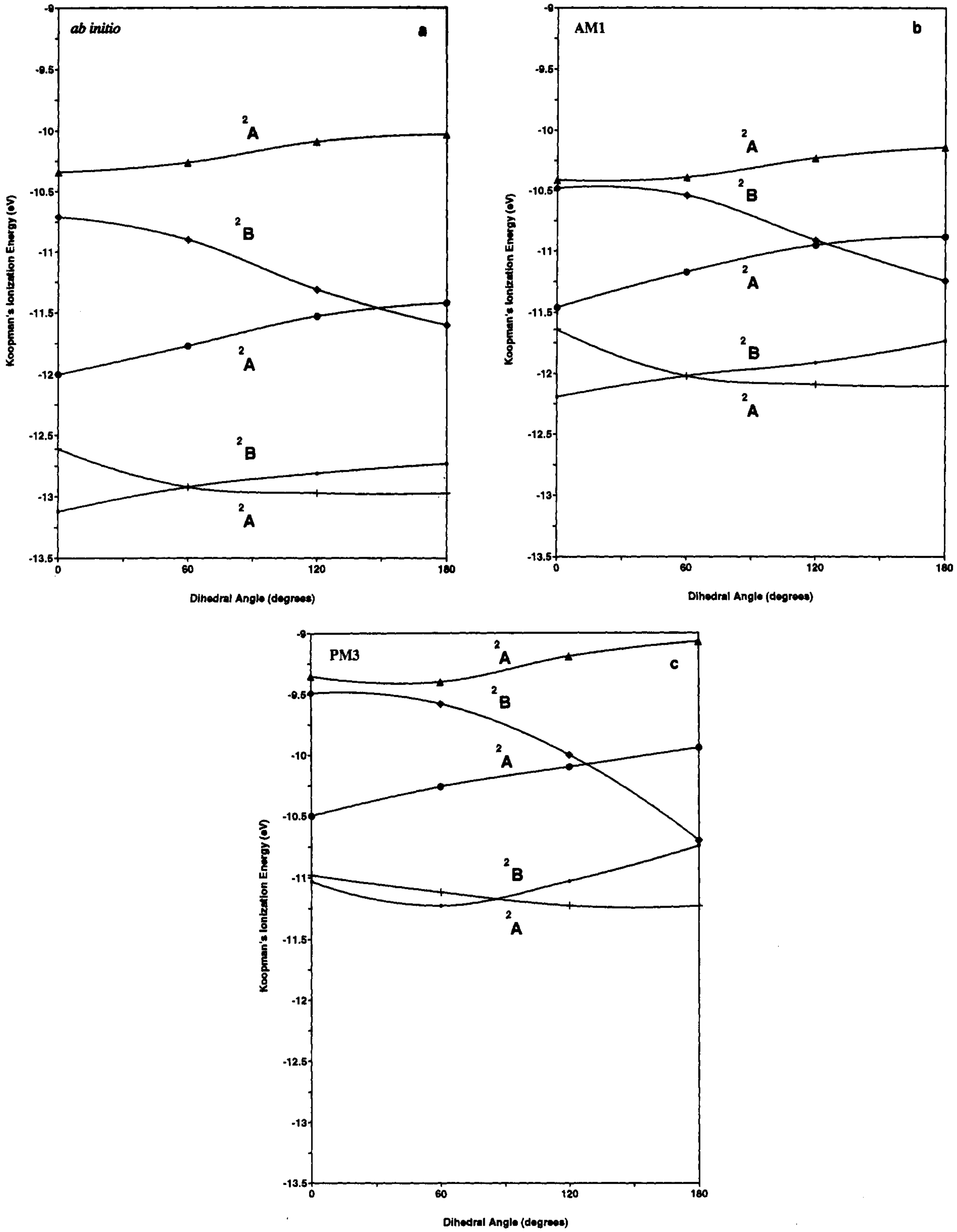

Figure 3. Variation of Koopmans ionization energies for tetrasilane as a function of dihedral angle: (a) *ab inito*; (b) AM1; (c) PM3.

with the PM3 calculated steric energy, ($E_{\text{gauche}} - E_{\text{anti}}$), of 0.28 kcal/mol. Steric energies calculated using ab initio at the 3-21G* and 6-31G* levels are 0.17 and 0.19 kcal/mol, respectively. One can conclude from Table III and Figure 2 that most theoretical methods, in general, predict small energy differences between conformers.

Figure 3 demonstrates how the computed Koopmans ionization energies of five final states vary with the Si–Si–Si–Si dihedral angle for tetrasilane. The ab initio results are from the study by Ortiz and Mintmire.[18] In most of the computed cases, the AM1 method shows good agreement with the ab initio data, while the PM3 method predicts significantly lower ionization energies. By comparing these results with those included in Table III, one may conclude that changes of molecular orbital energies are much more dependent on conformational variation than total energy changes. The energy level of the highest occupied molecular orbital with "A" symmetry decreases in going from the anti to the gauche conformer. This trend is opposite to that observed for those molecular orbitals with "B" symmetry. Our calculations, which are in agreement with ab initio calculations,[17] support the sug-

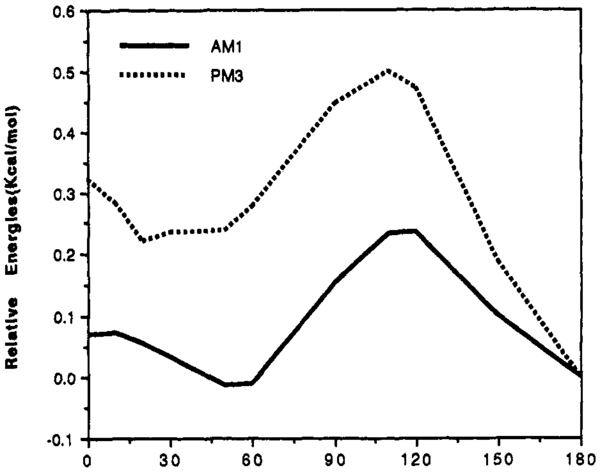

Figure 4. Relative energies (kcal/mol) vs dihedral angles (deg).

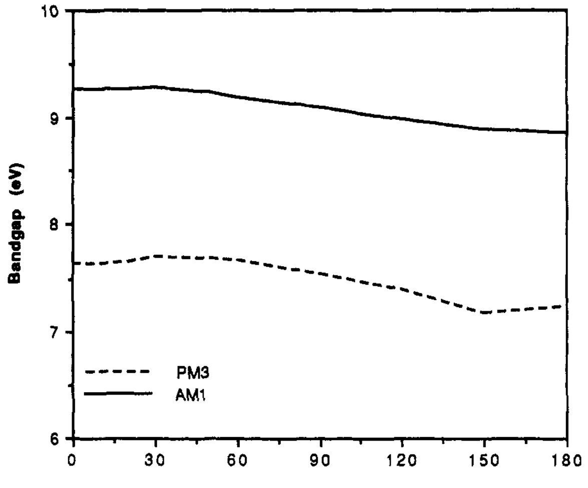

Figure 5. Bandgap (eV) of tetrasilane with respect to the dihedral angle (deg).

Table IV. Changes of AM1 and PM3 Calculated Bandgaps (eV) of Tetrasilane as a Function of Variations of the Dihedral Angle[a]

		dihedral angle, deg			
		0	60	120	180
LUMO	AM1	-1.15	-1.19	-1.25	-1.29
	PM3	-1.71	-1.73	-1.79	-1.82
HOMO	AM1	-10.41	-10.39	-10.23	-10.14
	PM3	-9.35	-9.40	-9.19	-9.07
bandgap	AM1	9.26	9.19	8.98	8.85
	PM3	7.64	7.68	7.40	7.25
ΔE_g	AM1	0.41	0.34	0.13	0.00
	PM3	0.40	0.43	0.15	0.00

[a] Bandgap changes, ΔE_g, are given with respect to the anti conformer.

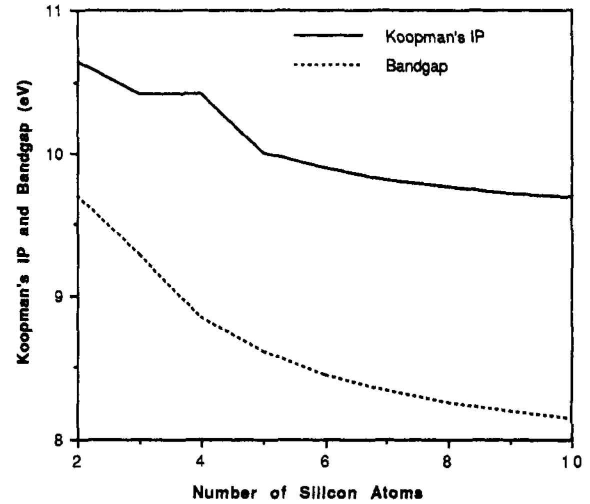

Figure 6. AM1 calculated bandgap and Koopmans IP as a function of the chain length for polysilanes.

gestion by Michl and co-workers that long-range through-bond interactions are responsible for the conformationally dependent spectral properties of polysilanes.[24]

To predict the rotational barriers for Si_4H_{10}, the relative energies are plotted against the dihedral angle (see Figure 4). The calculated total energies are plotted versus rotation about a central Si-Si bond over the range 0-180° in increments of 30° with increments of 10° near energy extrema. The AM1 method predicts the conformer with a dihedral angle 50° to be the most stable and that with a dihedral angle of 120° to be least stable. In the case of the PM3 method, the anti conformer is the most stable, and the highest energy conformation occurs at a dihedral angle of 110°. The AM1 and PM3 calculated rotational barriers are 0.25 and 0.5 kcal/mol, respectively.

Obviously, changes in the HOMO-LUMO gap or bandgap (i.e., $E_{LUMO} - E_{HOMO}$) could be a cause of the thermochromic shift. The AM1 and PM3 calculated HOMO-LUMO gaps with respect to the Si-Si-Si-Si dihedral angle of tetrasilane are depicted in Figure 5. The HOMO and LUMO energies and the bandgaps for tetrasilane at four dihedral angles (0°, 60°, 120°, and 180°) are also summarized in Table IV. PM3 shows the largest difference between trans and gauche rotamers, but AM1 shows the largest difference between dihedral angles of 180° and 0°. These differences are 0.41 and 0.43 eV for AM1 and PM3 methods, respectively. These results are in excellent agreement with the experimentally observed shift of $\approx$0.5 eV for PDHS.[8]

Mintmire[25] has recently calculated the one-dimensional band structure of polysilanes using a linear combination of atomic orbital local-density-functional (LCAO-LDF) method and has found that the bandgap increases by roughly 2 eV as the backbone is twisted from the all-trans conformation to an all-gauche conformation. This large value is apparently due to sensitivity of the first principles approach to choice of parameters and lack of a suitable parameter set. Teramae and Takeda's ab initio calculations[16] also show a bandgap difference of 2.96 eV for polysilanes, which seems to be far from that observed experimentally. In spite of the absolute values, this study as well as all previous theoretical studies[16,25] show increases in the bandgap as the dihedral angle changes from 180°.

The long-wavelength excitation energies of alkylsilanes also decrease with increasing silicon chain length.[26] Since these energies are defined by the HOMO-LUMO gap, we investigated both the bandgaps and the ionization potentials as a function of the chain length. Figures 6 and 7 summarize this study for poly(hydrosilanes) using the AM1 and PM3 methods, respectively. Both methods reproduce the experimentally observed shift of the maximum peak location with increasing catenation. In going from disilane

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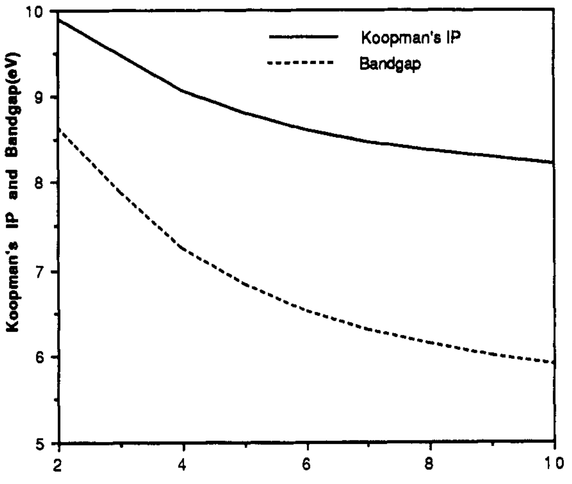

Figure 7. PM3 calculated Koopmans IP and bandgap (eV) as a function of the chain length for polysilanes.

Table V. PM3 Calculated Relative Energies (kcal/mol) and Bandgaps (eV) for Different Conformers of $Si_4(CH_3)_{10}$

	rel energies, kcal/mol	bandgap, eV	ΔE_g, eV
anti	0.00	6.47	0.00
eclipsed (120°)	0.84	6.61	0.14
gauche	1.01	6.88	0.41
eclipsed (0°)	2.88	7.03	0.56

to decasilane, the AM1 method predicts a reduction of 0.96 eV in ionization potential and 1.55 eV for the bandgap. The PM3 method suggests larger changes, e.g., 1.69- and 2.75-eV reduction of the ionization potential and the bandgap, respectively. Less sophisticated MO methods also predict a leveling of the gap with increasing catenation.[24] These large variations suggest that one should be very careful in theoretical modeling of electronic properties of polymeric silanes using small molecules. However, since more than 80% of the changes in the bandgap and ionization energies occur by the seventh silicon atom in the chain, e.g., heptasilane, modeling of polysilanes with seven or more silicon atoms in the backbone may be reasonable. Organopolysilanes absorb in the ultraviolet at energies in the 3-4-eV range. Therefore, it seems that AM1 overestimates the bandgap and the PM3 method is more reasonable in this respect.

Our studies of molecular geometry and electronic properties of polysilanes generally show similar trends for AM1 and PM3 calculations. Since we concluded above that the PM3 method may be superior in predicting bandgaps, we have used only the PM3 method to investigate the effects of substitution for polysilanes.

PM3 calculated relative energies and bandgaps for four conformations of $Si_4(CH_3)_{10}$ are given in Table V. We find that the addition of methyl substituents leads to a decrease in the bandgap from 7.25 to 6.46 eV. The PM3 calculated bandgap for the most stable conformer of decamethyltetrasilane (i.e., anti conformer) is 6.46 eV. This value is larger than the experimental value (5.3 eV) for decamethyltetrasilane.[27]

The relative energies for different conformers of $Si_4(CH_3)_{10}$ show much larger differences than those of the unsubstituted analogue (tetrasilane). This implies that steric factors may be the dominant factor in the relative energies of substituted rotamers. The PM3 method predicts that the anti conformer of $Si_4(CH_3)_{10}$ lies ≈1.0 kcal/mol lower in energy than the gauche conformer. Although it is risky to make too much of comparisons of "gas-phase" calculations with solution-phase experimental data, the latter prediction is in qualitative agreement with 0.5 kcal/mol value obtained by NMR spectroscopic measurements.[10] Tables VI and VII show the effects of substitution on molecular geometries and electronic properties for polysilane model compounds, $H_3Si(SiX_2)_5SiH_3$. All of the substituted model compounds have longer Si-Si bond lengths than comparable unsubstituted polysilanes. However, a comparison of the Si-Si bond length for the methyl and ethyl groups suggests that steric effects are important in elongation of this bond. Steric effects may not be solely responsible as indicated by the effect of the small electronegative fluorine groups, which increase the Si-Si bond length by 0.14 Å.

Table VI. Substitution Effects on Molecular Geometries of the Trans Planar Conformation of Polysilane Model Compounds, $H_3Si-(SiX_2)_5-SiH_3$[a]

substituent (X)	Si-Si length, Å	Si-Si-Si angle, deg
H	2.38	108.5
CH_3	2.39	98.4
C_2H_5	2.46	104.8
OCH_3	2.54	114.5
Cl	2.47	111.6
F	2.52	107.2

[a] For X = $-C_2H_5$, polysilane model compound is $H_3Si-(SiX_2)_4-SiH_3$.

The interplay between Si-Si-Si bond angle and bond length is interesting. For the hydrogen-substituted structure, the Si-Si-Si bond angle may be wide because of the absence of steric interference by the hydrogen atoms. However, as bulkier substituents are used, these tend to influence both the bond angles and lengths causing an intial drop in the angle with methyl groups. The interplay between angles and lengths is apparently complex. Thus, our calculations show that the Si-Si-Si bond angle shows a large variation upon substitution.

The calculation of several ethyl conformations demonstrates that steric effects play the dominant role in variation of bond angle. Structural and bandgap data for four minimum energy conformations (e.g., 1-4, Chart I) of ethyl-substituted hexasilane are included in Table VIII. While all structures are essentially trans planar, the most stable structure, 1, has a Si-Si-Si bond angle that fits nicely in the trend of values shown in Table VI. What may appear to be subtle rotational differences in the conformations produces large differences in structures and properties. For example, the most crowded conformer shows a large Si-Si-Si angle, 121°, confirming that the very large Si-Si-Si angle estimated for PDHS by Miller et al.[5] from X-ray data (assuming Si-Si distances of 2.35 Å) is reasonable for such a crowded molecule. This conclusion has been reached independently by Farmer et al.[28] using molecular mechanics calculations.

It can be seen from Table VII that the HOMO-LUMO gap decreases upon substitution for hydrogen. Substitution of hydrogen by ethyl groups has a small effect on the bandgap, while fluorine reduces this number by ≈1.5 eV. Therefore, one may conclude that substitution plays an important role in determining electronic properties. The effect of substitution on ionization potentials, HOMOs and LUMOs, is complicated. For example, a bulky electron-donating group such as ethyl and an electronegative group

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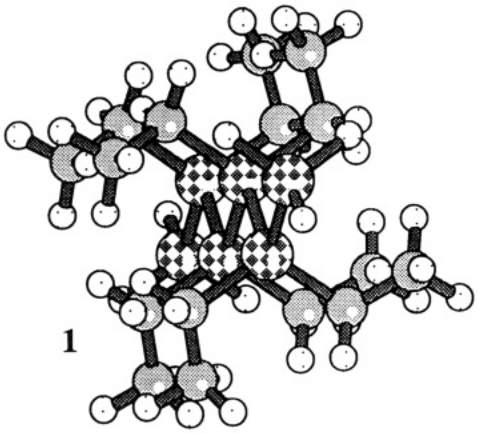
(28) Chapman, B. R.; Patnaik, S. S.; Farmer, B. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (No. 2), 265.

Chart I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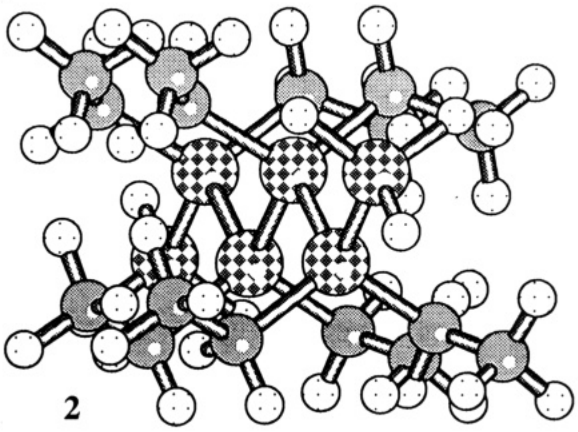
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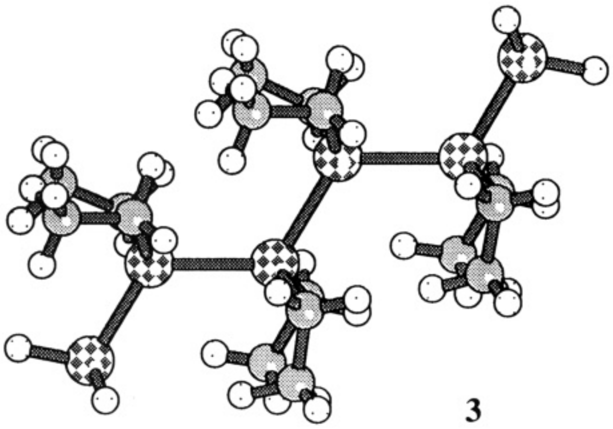
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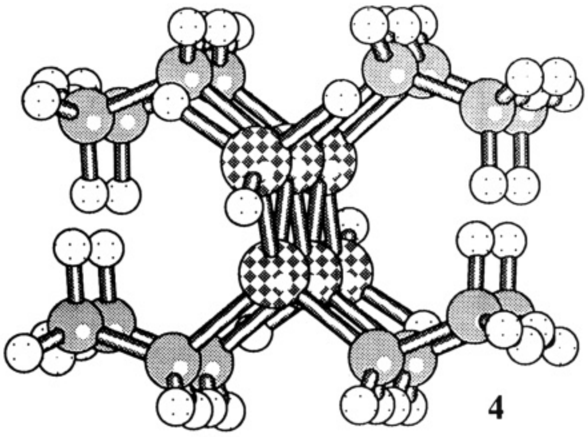
4

Table VII. Substitution Effects on Koopmans IP, HOMO, LUMO, and Bandgap of the Trans Planar Conformation of Polysilane Model Compounds, $H_3Si-(SiX_2)_5-SiH_3$[a,b]

substituent (X)	IP, eV	ΔIP, eV	HOMO, eV	LUMO, eV	bandgap, eV	ΔE_g, eV
H	8.49	0.00	−8.49	−2.17	6.32	0.00
CH_3	7.27	−1.22	−7.27	−1.72	5.54	−0.77
C_2H_5	7.86	−0.62	−7.86	−1.85	6.01	−0.30
OCH_3	7.29	−1.20	−7.29	−1.78	5.59	−0.81
Cl	8.50	+0.02	−8.50	−3.65	4.86	−1.46
F	7.66	−0.83	−7.66	−2.88	4.79	−1.53

[a] For X = $-C_2H_5$, polysilane model compounds is $H_3Si-(SiX_2)_4-SiH_3$. [b] Changes in Koopmans IP and bandgaps are given with respect to the unsubstituted model compound.

Table VIII. Heats of Formation, Bond Lengths, Bond Angles and HOMO–LUMO Gaps of Selected Conformers of Polysilane Model Compound $H_3Si-(Si(C_2H_5)_2)_4-SiH_3$

conformer	ΔH_f, kcal/mol	Si–Si length, Å	Si–Si–Si angle, deg	bandgap, eV
1	−153.5	2.46	104.8	6.01
2	−148.2	2.51	114.4	6.25
3	−140.0	2.55	121.1	6.31
4	−139.1	2.42	95.2	5.62

such as chlorine both have a small influence on ionization potential. It is apparent, however, that while the HOMO–LUMO gap (bandgap) is reduced more significantly by electron-withdrawing rather than electron-donating groups, the bandgap seems to track Si–Si–Si angle (e.g., see Tables VI–VIII).

In summary, the AM1 and PM3 methods are found to be especially useful in computing structures and properties of polysilanes. Our studies predict that Si–Si–Si bond lengths and angles may vary widely with structure and that electronic properties tend to follow structural variation in an orderly fashion. Our studies suggest some interesting new directions for synthetic approaches to molecules that may have useful electronic and optical properties.

Registry No. Si_2H_6, 1590-87-0; Si_4H_{10}, 7783-29-1; $Si_4(CH_3)_{10}$, 865-76-9; $H_3Si-(SiH_2)_5-SiH_3$, 14693-65-3; $H_3Si-(Si[CH_3]_2)_5-SiH_3$, 135975-08-5; $H_3Si-(Si[C_2H_5]_2)_4-SiH_3$, 135975-09-6; $H_3Si-(Si[OCH_3]_2)_5-SiH_3$, 135975-10-9; $H_3Si-(SiCl_2)_5-SiH_3$, 135975-11-0; $H_3Si-(SiF_2)_5-SiH_3$, 135975-12-1.