Conformers of n-Si_6Me_{14}: Ab Initio, Molecular Mechanics, and Additive Increment Methods

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The stable backbone conformers of n-Si_6Me_{14} have been identified through geometry optimizations with the HF/3-21G(d), MM2, and MM3 methods. With the exception of the MM2 method, their relative potential energies, and also single-point energies calculated by the HF/6-31G(d) and MP2/6-31G(d) methods at HF/3-21G(d) optimized geometries (E_{calc}), agree with energies E^0_{incr}, obtained using additive increment sets previously derived from results for n-Si_4Me_{10} and n-Si_5Me_{12}, with mean deviations of 0.11−0.15 kcal/mol. The energy E^0_{incr} is a simple function of the number of gauche, ortho, and transoid Si backbone bond conformations and of SiSi adjacent bond interactions. With the MM2 method the deviations from additivity are larger; E^0_{incr} and E_{calc} agree only with a mean deviation of 0.52 kcal/mol. Improved increment sets were obtained by a simultaneous least-squares treatment of data for n-Si_4Me_{10}, n-Si_5Me_{12} and n-Si_6Me_{14}, including a few increments for interaction between next-nearest bond conformations. This yields energies E''_{incr} that reproduce E_{calc} with mean deviations of 0.05, 0.03, 0.05, and 0.03 kcal/mol at the HF/3-21G(d), HF/6-31G(d), MP2/6-31G(d), and MM3 levels of theory. With the MM2 method a similar agreement between E_{calc} and E''_{incr} was obtained only after inclusion of 12 increments for interaction between next-nearest bond conformations. The energies E_{calc} of selected low-energy conformers of n-Si_7Me_{16} and n-Si_8Me_{18} obtained by geometry optimization at HF/3-21G(d) and MM3 levels are reproduced by E''_{incr} with mean (maximum) deviations of 0.04 (0.11) and 0.07 (0.26) kcal/mol. We conclude that the HF/3-21G(d), HF/6-31G(d), MP2/6-31G(d), and MM3 potential energies of all stable conformations of permethylated oligosilane conformers of any length except those with folded chains can now be estimated accurately from a small increment set, and the MP2-based results represent the best current estimates for conformer energies in the gas phase. It is likely that future more accurate computed or measured energies of the three conformers of n-Si_4Me_{10}, the eight or nine conformers of n-Si_5Me_{12}, and approximately 10 specifically chosen conformers of n-Si_6Me_{14} will automatically provide improved increment sets and thus more accurate prediction of stable conformation energies for permethylated oligosilane chains of all lengths. Relative energies of conformers in solution are not predicted well by the MP2 calculations and will probably require an explicit consideration of solvent effects. In the meantime, they are best approximated by the HF calculations.

Introduction

The past decades have witnessed rising interest in oligosilanes and polysilanes (n-Si_nR_{2n+2}), polymers which have a σ-conjugated Si backbone and in some respects resemble polyenes.[1] Sigma conjugation reflects an interplay between vicinal, geminal, and perivalent interactions,[2,3] and depends strongly on the conformation of the Si backbone. Therefore, the electronic structure and excited state properties of oligosilanes[4−8] and polysilanes[9] are expected to depend not only on chain length but on conformation as well, and this dependence is believed to be responsible for polysilane piezochromism,[10] solvatochromism,[11] ionochromism,[12] and thermochromism.[13] A direct demonstration of the conformational dependence of photoelectron and UV absorption spectra of peralkylated tetrasilanes was provided by the comparison of a series of tetrasilanes with constrained SiSiSiSi backbone dihedral angle ω.[6,7] While the energy of the transitions to the first three excited states is almost independent of ω, their relative intensity varies dramatically,[4,5,7,8] in excellent agreement with the trends expected theoretically.[4,5,8]

A detailed understanding of the optical properties of polysilanes therefore requires a knowledge of the structures of their various conformers, their relative free energies, and their spectral properties. These will clearly depend on the nature of the lateral substituents. We started our combined experimental and computational effort with permethylated oligosilanes,[5,14−17] which represent the simplest case. In the present paper we examine the conformers of n-Si_6Me_{14}. We have now adopted the recently proposed[1b] nomenclature according to which the term anti is reserved for ω values within a few degrees of 180°, whereas conformations with $\omega \simeq \pm 165°$ are referred to as transoid.

Three enantiomeric pairs of conformers have been computed for n-Si_4Me_{10}, corresponding to the gauche minimum ($g_\pm$) at $\omega \simeq \pm 55°$, the ortho minimum ($o_\pm$) at $\omega \simeq \pm 90°$, and the transoid minimum ($t_\pm$) at $\omega \simeq \pm 165°$.[5,18] The distortion of the transoid minimum from the ideal value, $\omega = 180°$, to $\omega \simeq 165°$ is due to steric repulsion between the methyl groups on silicon atoms 1 and 3, whereas the ortho minimum results from a splitting of an anticipated gauche minimum by repulsion between methyl groups on Si atoms 1 and 4. It has been predicted[18,19] that the ortho conformer will exist in any A_nX_{2n+2} chain with substituents X of a reduced crystallographic van der Waals radius size (i.e., size in units of backbone bond length) in the range 0.8−1.0, and separate spectra of three conformers have actually been observed for n-C_4F_{10}[20] and n-Si_4Cl_{10}[21].

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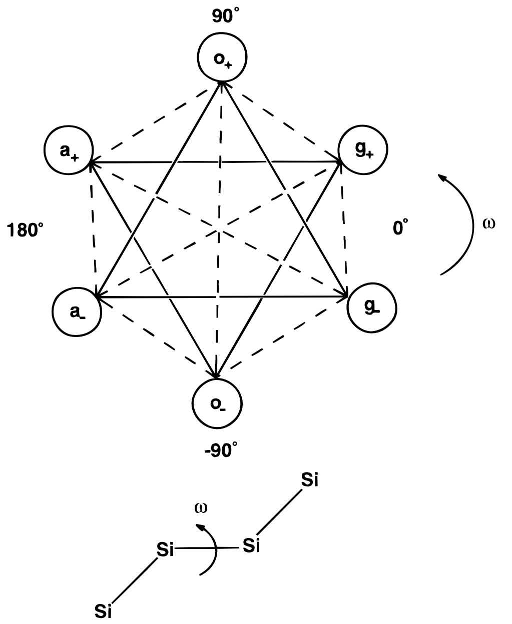

Figure 1. Diagrammatic representation of adjacent bond interactions in n-Si$_n$Me$_{2n+2}$ chains. Solid lines: favorable interactions, dashed lines: unfavorable interactions.

Temperature dependence of solution spectra showed that the $t_\pm$ conformer of n-Si$_4$Me$_{10}$ is lowest in energy by 0.5−1.0 kcal/mol,[22] and this agrees with HF/6-31G(d) and MM2 calculations. Its $o_\pm$ conformer has not been observed. At the MP2/6-31G(d) and MM3 levels the energy difference between the $t_\pm$ and $g_\pm$ conformations is very small (0.03−0.15 kcal/mol), in better agreement with experimental estimates from the gas phase, which are close to zero.[5] The relative energies obtained by the MM2 method resemble the HF values, whereas MM3 energy differences are similar to the MP2 values.

For longer oligosilanes and polysilanes the number of possible combinations of Si backbone dihedral angles $t_\pm$, $g_\pm$, and $o_\pm$ increases rapidly. Solution spectroscopic studies at low temperature, including comparison with model compounds with fixed dihedral angles, have shown[14,15] that the most stable conformers of n-Si$_5$Me$_{12}$ and n-Si$_6$Me$_{14}$ are of the all-transoid type, but the relative energies of the other conformers are not known. It is not likely that they could be estimated accurately from a simple count of the numbers of transoid, ortho and gauche bonds in the backbone, because it is known from both calculations and qualitative considerations that certain combinations of adjacent dihedral angles are more compatible than others.[16,19] The dihedral angles t_+ and g_+ in the backbone combine preferably with an adjacent t_+ or g_+ dihedral angle, while combinations with t_- or g_- lead to less stable conformers or to structures that do not correspond to potential energy minima at all. In contrast, the o_+ bond conformation combines favorably with another o_+ conformation or with a t_- or g_- conformation. The 15 possible combinations of two adjacent dihedral angles are summarized in Figure 1. Favorable combinations are shown in solid and unfavorable ones in dashed lines.

The existence of these relations suggested the feasibility of an additive procedure[16] for predicting the relative stabilities of all conformers of permethylated oligosilanes of all lengths from a more complicated set of empirical increments, still in the spirit of the rotational isomeric state (RIS) model[23] of polymer chain structure. In this procedure, a sum of bond conformation increments $E(\alpha)$ is refined by adding a sum of adjacent bond interaction increments $E(\alpha,\beta)$ as shown in eq 1. The energy of an arbitrary conformer n-Si$_n$Me$_{2n+2}$, characterized by $n - 3$ dihedral angles $\alpha_1, \alpha_2, \alpha_3, ..., \alpha_{n-3}$ relative to the energy of the all-transoid conformer with a constant helical sense, $E(\alpha_1,\alpha_2,\alpha_3,...,\alpha_{n-3}) - E(t_+,t_+,t_+...,t_+)$, is expressed as a sum of bond conformation increments $E(\alpha)$ plus a sum of adjacent bond pair conformation increments $E(\alpha,\beta)$. Since α and β can each acquire six values ($t_\pm$, $o_\pm$, $g_\pm$) there are three distinct increments $E(\alpha)$ and 12 distinct increments $E(\alpha,\beta)$ (mirror images have equal energies and the order in which the bonds are taken is immaterial). The values of the 12 increments are uniquely determined if the energies of the three enantiomeric conformer pairs in n-Si$_4$Me$_{10}$ and the nine enantiomeric conformer pairs in n-Si$_5$Me$_{12}$ are known [$E(t_+) = E(t_+,t_+) = 0$ by definition]. If some dihedral angle combinations do not correspond to potential energy minima, there will be fewer available energy values, but also fewer increments to determine. Increment values could in principle be determined from measurements or calculations.

$$E_{\mathrm{incr}}(\alpha_1,\alpha_2,...,\alpha_{n-3}) - E(t_+,t_+,...,t_+) = \sum_{i=1}^{n-3} E(\alpha_i) + \sum_{i=1}^{n-4} E(\alpha_i,\alpha_{i+1}) \quad (1)$$

Since there is not much hope that experimental values will be available any time soon, we deduced approximate values from calculations.[16] In principle, this permits the determination of increments even at combinations that do not correspond to potential energy minima, i.e., to stable conformers. Five different increment sets were obtained at the HF/3-21G(d), HF/6-31G(d)//HF/3-21G(d), MP2/6-31G(d)//HF/3-21G(d), MM2, and MM3 levels of calculation.

There is no guarantee that increments deduced from the computed energies of conformers of Si$_4$Me$_{10}$ and Si$_5$Me$_{12}$ using eq 1 will reproduce well the computed energies of the conformers of Si$_6$Me$_{14}$ and longer chains, and this needs to be tested next. Such test calculations have already been performed for the MM3 increment set for a few selected conformers and the results were encouraging.[16]

Presently, we report (i) geometry optimization of all the stable backbone conformers of n-Si$_6$Me$_{14}$ at the MM2, MM3, and HF/3-21G(d) levels (in principle there might be additional conformers differing by methyl rotations, but we have not found any), (ii) use of their energies to test all five increment sets derived earlier from calculations on n-Si$_4$Me$_{10}$ and n-Si$_5$Me$_{12}$, (iii) a refinement of the increment sets by a least-squares optimization on the overdetermined set of results for n-Si$_4$Me$_{10}$, n-Si$_5$Me$_{12}$ and n-Si$_6$Me$_{14}$, (iv) a test of the MM2, MM3 and HF/3-21G(d) refined increment sets on selected low-energy conformers of the next longer permethylated chains, n-Si$_7$Me$_{16}$ and n-Si$_8$Me$_{18}$, (v) an optimized increment set [MM2, MM3, HF/3-21G(d), HF/6-31G(d) and MP2/6-31G(d)] based on results for n-Si$_4$Me$_{10}$, n-Si$_5$Me$_{12}$ and n-Si$_6$Me$_{14}$ that includes a few increments $E(\alpha,\beta,\gamma)$ for next-nearest bond interactions, and (vi) a test of this increment set on a series of selected conformers of n-Si$_7$Me$_{16}$ and n-Si$_8$Me$_{18}$.

We propose that energy increments for even more distant interactions, such as $E(\alpha,\beta,\gamma,\delta)$, are negligible except as needed for chain folding and self-avoidance. If this is correct, it is now possible to predict the MM2, MM3, HF/3-21G(d), HF/6-31G(d), and MP2/6-31G(d) energies of all low-energy conformers of all permethylated oligosilanes of any length with trivial ease until a length is reached at which hairpin-like folding sets in and permits van der Waals interactions that are topologically of long range. This probably never happens in solution in good solvents that provide adequate intermolecular van der Waals stabilization, but may well happen in poor

TABLE 1: Classification of n-Si_6Me_{14} Conformers

	bond interactions		
dihedral angles	two favorable (**A**)	one favorable (**B**)	none favorable (**C**)
only transoid (**1**)	$t_+t_+t_+$ (**1A**)	$t_+t_+t_-$ (**1B**)	$t_+t_-t_+$ (**1C**)
two transoid and one twisted (**2**)	$t_+t_+g_+$, $t_+g_+t_+$, $t_+t_+o_-$, $t_+o_-t_+$ (**2A**)	$t_+t_-g_-$, $t_+t_+g_-$, $t_+g_+t_-$, $t_+t_+o_+$, $t_+t_-o_+$, $t_+o_+t_-$ (**2B**)	$t_+t_-g_+$, $t_+g_-t_+$, $t_+t_-o_-$, $t_+o_+t_+$ (**2C**)
one transoid and two twisted (**3**)	$t_+g_+g_+$, $g_+t_+g_+$, $t_+o_-o_-$, $o_+t_-o_+$ (**3A**)	$t_+g_-g_-$, $t_+g_+g_-$, $g_+t_+g_-$, $t_+o_+o_+$, $t_+o_-o_+$, $o_+t_+o_-$ (**3B**)	$t_+g_-g_+$, $g_+t_-g_+$, $t_+o_+o_-$, $o_+t_+o_+$ (**3C**)
one transoid, one gauche, and one ortho (**4**)	$t_+g_+o_-$, $t_+o_-g_+$, $o_+t_-g_-$ (**4A**)	$t_+g_+o_+$, $t_+g_-o_+$, $t_+o_-g_-$, $t_+o_+g_-$, $o_+t_+g_+$, $o_+t_-g_+$ (**4B**)	$t_+g_-o_-$, $t_+o_+g_+$, $o_+t_+g_-$ (**4C**)
two gauche and one ortho (**5**)	$o_+g_-g_-$, $g_+o_-g_+$ (**5A**)	$o_+g_-g_+$, $o_+g_+g_+$, $g_+o_+g_-$ (**5B**)	$o_+g_+g_-$, $g_+o_+g_+$ (**5C**)
two ortho and one gauche (**6**)	$o_+o_+g_-$, $o_+g_-o_+$ (**6A**)	$o_+o_-g_+$, $o_+o_+g_+$, $o_+g_+o_-$ (**6B**)	$o_+o_-g_-$, $o_+g_+o_+$ (**6C**)
only gauche (**7**)	$g_+g_+g_+$ (**7A**)	$g_+g_+g_-$ (**7B**)	$g_+g_-g_+$ (**7C**)
only ortho (**8**)	$o_+o_+o_+$ (**8A**)	$o_+o_+o_-$ (**8B**)	$o_+o_-o_+$ (**8C**)

solvents and in the solid, and is guaranteed to happen in the gas phase, but it is not known at which chain length.

Computational Methods

Ab initio computations were performed at the Hartree−Fock (HF) and second-order Møller−Plesset perturbation theory (MP2) levels with the 3-21G(d)[24] or the 6-31G(d)[25] basis set on an IBM RS6000-590 or an HP Exemplar computer with the Gaussian94[26a] and Gaussian98[26b] program packages. The MM2[27] and MM3[28] molecular mechanics calculations used the MM2-(92)[29] and MM3(96)[30] programs by Allinger and co-workers and an IBM RS6000 workstation.[31]

Ab initio geometry optimizations were started at the HF/3-21G(d) level and at the gauche, ortho, and transoid dihedral angles that had been optimized[5] at this level for n-Si_4Me_{10} (53.7°, 92.0°, and 163.5°, respectively). When a particular combination of the three backbone dihedral angles in n-Si_6Me_{14} did not correspond to a minimum on the potential energy surface, we made partial optimizations with these dihedral angles fixed to the corresponding optimal values in n-Si_4Me_{10} found at the respective level of theory (HF/3-21G(d), MM2, and MM3), and all other geometry parameters optimized. Possible presence of symmetry elements was verified by frequency calculations at the respective level of theory (HF/3-21G(d) and MM3). Vibrational spectra were calculated for low-energy conformers to aid with their future experimental identification (the scaling factor 0.9085 was used, as reported optimal for HF/3-21G [32]). Single-point HF/6-31G(d) and MP2/6-31G(d) (frozen core) energy calculations were performed at the HF/3-21G(d) optimized geometries.

Optimized increment sets were found by least-squares fitting[33] to the energies of all stable conformers of n-Si_4Me_{10}, n-Si_5Me_{12}, and n-Si_6Me_{14} (14 unknowns and 46 equations for the ab initio methods, and 38 and 48 equations for the MM2 and MM3 methods, respectively). Further improvement of the increment sets was obtained by adding increments $E(\alpha,\beta,\gamma)$ for conformers for whose energies the initial unimproved increments gave values that differed by 0.20 kcal/mol or more from the computed ones.

Density Functional Calculations. Density functional theory (DFT)[34] computations with an empirically adjusted exchange and correlation potential frequently yield results numerically equivalent to those of more expensive electron-correlated ab initio methods, but they have a reputation for not doing very well for van der Waals interactions.[35] We have performed B3LYP/6-31G(d) calculations on the three conformers of n-Si_4Me_{10}, where fully optimized MP2/6-31G(d) geometries and energies are available, and found the dihedral angles to be 163.1° ($t_\pm$), 87.5° ($o_\pm$), and 57.2° ($g_\pm$), in only fair agreement with the MP2/6-31G(d) values of 161.7°, 91.4°, and 52.6°, respectively. The B3LYP energies of the $o_\pm$ and $g_\pm$ conformers were 0.50 and 0.45 kcal/mol above the $t_\pm$ conformer, respectively, while the MP2 values lie 0.65 and 0.09 kcal/mol above, respectively. With the smaller basis set 3-21G(d), B3LYP gives $\omega = 170°$ for the transoid conformer, which is wrong, and the relative energies are 0.79 kcal/mol for $o_\pm$ and 0.43 kcal/mol for $g_\pm$. These results are not encouraging, and it seems that as a minimum, in DFT calculations larger basis sets are required for proper description of conformer stabilities in oligosilanes than at HF and MP2 levels. We have therefore refrained from further use of DFT in the present investigation.

Results and Discussion

For each enantiomeric pair of conformers we only discuss the conformer with the first dihedral angle positive, and we rank the angles in the order t_+, o_+, g_+. E.g., only the $t_+g_+o_+$ conformer is mentioned in the text and the equivalent forms $t_-g_-o_-$, $o_+g_+t_+$, and $o_-g_-t_-$ are ignored.

In Table 1, we group the 63 possible combinations of the $t_\pm$, $o_\pm$, and $g_\pm$ dihedral angles in n-Si_6Me_{14} into eight classes. Table 2 contains their relative energies optimized at all these angle combinations, of which many correspond to stable conformers. Table 3 (Supporting Information) lists the stability orders as obtained from computations and from increment addition, limited to conformers with energies less than 3 kcal/mol above the most stable one. Optimized backbone dihedral angles in the stable conformers are listed in Table 4. Table 5 gives the increment sets. Conformer energies of n-Si_4Me_{10} and n-Si_5Me_{12} derived from increment sets are collected in Table 6. Selected conformer energies for n-Si_7Me_{16} and n-Si_8Me_{18} are contained in Table 7 (Supporting Information). Finally, IR and Raman frequencies and intensities calculated at the HF/3-21G(d) level for the 10 n-Si_6Me_{14} conformers of lowest energy are listed in Table 8 (Supporting Information).

Figure 2 compares the conformer energies and Figure 3 the dihedral angles computed by the ab initio and the molecular mechanics methods. In Figure 4, the molecular structures and essential geometry parameters for a few n-Si_6Me_{14} conformers are given. Figures 5−9 show the plots of conformer energies of n-Si_6Me_{14} derived from increments (E_{incr}) against those computed (E_{calc}). Figure 10 shows the corresponding information for selected n-Si_7Me_{16} and n-Si_8Me_{18} conformers. Schematic plots of the IR and Raman spectra of n-Si_6Me_{14} conformers whose energies are less than 2 kcal/mol above the most stable conformer based on HF/3-21G(d) calculations are shown in Figures 11 and 12 (Supporting Information).

TABLE 2: Conformer Energies of n-Si_6Me_{14} Relative to the $t_+t_+t_+$ Conformer[a]

		HF/3-21G(d)				HF/6-31G(d)//HF/3-21G(d)				MP2(fc)/6-31G(d)// HF/3-21G(d)				MM2[b]				MM3			
conformer	ν_1[c]	E_{calc}	E^0_{incr}	E'_{incr}	E''_{incr}	E_{calc}	E^0_{incr}	E'_{incr}	E''_{incr}	E_{calc}	E^0_{incr}	E'_{incr}	E''_{incr}	E_{calc}	E^0_{incr}	E'_{incr}	E''_{incr}	E_{calc}	E^0_{incr}	E'_{incr}	E''_{incr}
$t_+t_+t_+$ (**1A**)	19.3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$t_-g_+t_-$ (**2A**)	20.7	0.78	0.72	0.88	0.87	0.84	0.75	0.92	0.87	0.29	0.23	0.37	0.33	0.44	0.38	0.48	0.46	−0.07	−0.11	−0.06	−0.04
$t_+o_-t_+$ (**2A**)	19.6	1.02	1.05	1.01	1.07	0.78	0.83	0.77	0.82	0.69	0.75	0.62	0.68	0.91	0.89	0.81	0.88	0.38	0.43	0.30	0.39
$t_+t_+g_+$ (**2A**)	22.2	0.74	0.71	0.76	0.78	0.76	0.72	0.72	0.76	0.21	0.19	0.24	0.25	0.55	0.63	0.67	0.65	−0.06	−0.04	−0.04	−0.03
$t_+t_+o_-$ (**2A**)	20.1	1.00	0.97	1.00	0.99	0.74	0.72	0.73	0.72	0.67	0.66	0.63	0.62	0.88	0.85	0.91	0.83	0.37	0.39	0.42	0.36
$t_+g_+g_+$ (**3A**)	20.9	2.00	1.91	2.01	1.98	1.70	1.62	1.75	1.70	0.78	0.77	0.83	0.81	1.51	1.47	1.62	1.53	0.14	0.12	0.16	0.11
$g_+t_+g_+$ (**3A**)	21.9	1.51	1.42	1.53	1.55	1.49	1.44	1.44	1.52	0.45	0.38	0.48	0.50	1.17	1.26	1.34	1.30	−0.10	−0.08	−0.08	−0.06
$t_+o_-o_-$ (**3A**)	21.5	2.06	2.08	2.08	2.12	1.55	1.55	1.53	1.57	1.36	1.38	1.32	1.38	2.19	2.14	2.13	2.14	0.92	0.97	0.87	0.92
$o_+t_-o_+$ (**3A**)	17.0	1.93	1.94	1.99	1.97	1.47	1.44	1.47	1.44	1.15	1.32	1.26	1.24	1.60	1.70	1.83	1.66	0.72	0.78	0.85	0.72
$t_+g_-o_-$ (**4A**)	17.6	2.75	2.51	2.77	2.75	2.28	2.02	2.42	2.28	1.79	1.47	1.72	1.79	3.05	2.73	3.13	3.05	1.17	1.13	1.44	1.18
$o_+t_-g_-$ (**4A**)	20.3	1.77	1.68	1.76	1.76	1.51	1.44	1.45	1.48	0.94	0.85	0.87	0.87	1.68	1.48	1.58	1.68	0.37	0.35	0.38	0.33
$t_+o_-g_+$ (**4A**)	16.2	2.64	2.58	2.66	2.57	2.19	2.10	2.25	2.11	1.50	1.52	1.58	1.39	3.18	3.02	3.23	3.14	1.13	1.24	1.34	1.22
$o_+g_-g_-$ (**5A**)	14.2	4.07	3.70	3.89	4.07	3.17	2.89	3.24	3.17	2.42	2.01	2.18	2.42	5.12	3.82	4.28	5.12	2.03	1.36	1.66	2.03
$g_+o_-g_+$ (**5A**)		8.03	4.11	4.31	4.07	7.45	3.37	3.73	3.40	5.77	2.29	2.54	2.10	(4.92)	(5.15)	(5.64)	(5.40)	2.09	2.05	2.37	2.06
$o_+o_+g_-$ (**6A**)	15.6	3.50	3.61	3.73	3.62	2.82	2.82	3.02	2.86	1.96	2.15	2.29	2.09	4.45	4.27	4.54	4.40	1.83	1.78	1.90	1.76
$o_+g_-o_-$ (**6A**)	17.6	4.84	4.30	4.66	4.84	4.12	3.29	3.91	4.12	3.47	2.71	3.07	3.47	7.78	5.08	5.79	7.78	3.72	2.37	2.94	3.72
$g_+g_+g_+$ (**7A**)	24.2	3.13	3.10	3.13	3.08	2.70	2.49	2.57	2.70	1.35	1.31	1.29	1.28	2.31	2.56	2.76	2.31	0.27	0.35	0.37	0.26
$o_+o_+o_-$ (**8A**)	21.7	3.22	3.11	3.15	3.18	2.35	2.27	2.30	2.31	2.16	2.01	2.03	2.07	3.49	3.39	3.44	3.40	1.44	1.51	1.43	1.46
$t_-t_+t_-$ (**1B**)		0.85	0.73	0.70	0.71	0.94	0.70	0.69	0.69	0.82	0.85	0.85	0.85	1.02	1.08	0.55	0.85	0.39	0.66	0.46	0.56
$t_-t_-g_-$ (**2B**)		1.63	1.44	1.46	1.48	1.60	1.42	1.41	1.45	1.20	1.04	1.09	1.10	1.86	1.71	1.22	1.50	0.45	0.62	0.42	0.54
$t_-g_+t_-$ (**2B**)		2.69	1.51	1.60	1.62	2.45	1.29	1.55	1.39	2.28	1.14	1.12	1.14	4.20	3.56	2.04	3.38	1.95	0.90	0.92	0.95
$t_-t_+g_-$ (**2B**)	8.8	1.52	1.50	1.48	1.53	1.31	1.26	1.35	1.28	1.12	1.10	0.99	1.06	3.78	3.81	2.23	3.57	0.97	0.97	0.94	0.96
$t_-t_+o_-$ (**2B**)	9.4	1.58	1.70	1.67	1.68	1.21	1.30	1.27	1.26	1.26	1.35	1.32	1.33	(1.55)	(2.12)	(1.65)	(1.76)	0.93	0.63	0.79	0.93
$t_-t_-o_-$ (**2B**)		1.64	1.70	1.70	1.69	1.40	1.42	1.43	1.41	1.48	1.51	1.48	1.48	1.44	1.93	1.46	1.44	0.72	1.05	0.88	0.72
$t_-o_+t_-$ (**2B**)		1.95	1.78	1.68	1.76	1.54	1.41	1.30	1.35	1.58	1.44	1.31	1.39	1.71	2.16	1.55	1.82	0.77	0.67	0.66	0.70
$t_-g_+g_-$ (**3B**)		5.58				5.23				4.22				9.77				5.17			
$t_-g_-g_-$ (**3B**)	14.4	2.62	2.70	2.72	2.73	2.21	2.16	2.37	2.22	1.50	1.68	1.58	1.62	3.16	4.65	3.18	3.16	1.06	1.13	1.13	1.10
$g_-t_+g_-$ (**3B**)	12.7	2.29	2.21	2.24	2.30	2.02	1.98	2.07	2.04	1.36	1.29	1.23	1.31	(4.08)	(4.44)	(2.90)	(4.22)	1.07	0.93	0.90	0.93
$t_-o_-o_+$ (**3B**)		4.05	3.98	3.90	3.94	3.25	3.25	3.23	3.26	3.01	2.45	2.61	2.42	5.65	5.70			2.75	3.69	3.56	3.67
$t_-o_+o_-$ (**3B**)		3.01	2.81	2.75	2.81	2.31	2.13	2.07	2.10	2.34	2.07	2.02	2.09	2.73	3.41	2.86	2.73	1.22	1.21	1.23	1.23
$o_-t_+o_-$ (**3B**)	8.2	2.61	2.67	2.67	2.66	1.88	2.02	2.00	1.98	1.90	2.01	1.95	1.95	(2.36)	(2.97)	(2.57)	(2.59)	1.26	1.02	1.21	1.26
$t_-g_+o_-$ (**4B**)	11.5	2.70	2.51	2.63	2.62	2.05	1.87	2.05	1.98	1.80	1.63	1.70	1.71	(2.82)	(3.81)	(2.55)	(3.71)	1.27	1.14	1.12	1.20
$t_-g_-o_-$ (**4B**)	14.8	3.39	3.30	3.49	3.34	3.39	2.56	3.04	3.39	2.23	2.38	2.48	2.23	6.82	5.91	4.70	5.82	3.62	2.14	2.42	2.17
$t_-o_-g_-$ (**4B**)	13.8	2.63	2.58	2.52	2.60	1.96	1.95	1.89	1.98	1.72	1.68	1.55	1.69	(2.49)	(4.10)	(2.64)	(3.95)	1.25	1.25	1.01	1.24
$t_-o_+g_-$ (**4B**)		3.54	3.31	3.33	3.26	2.97	2.68	2.79	2.64	2.24	2.21	2.27	2.10	3.62	4.29	3.96	3.62	1.50	1.48	1.70	1.53
$o_-t_+g_-$ (**4B**)	8.4	2.51	2.41	2.43	2.45	2.11	2.02	1.99	2.02	1.68	1.54	1.56	1.58	2.73	2.75	2.32	2.41	0.95	0.59	0.74	0.64
$o_-t_-g_+$ (**4B**)	7.7	2.50	2.47	2.48	2.51	2.03	1.98	2.08	2.00	1.65	1.76	1.62	1.68	4.57	4.66	3.15	4.40	1.22	1.36	1.36	1.32
$o_-g_-g_-$ (**5B**)		8.62				7.91				6.24				15.74				5.98			
$o_-g_+g_+$ (**5B**)	12.6	3.59	3.70	3.75	3.72	2.83	2.74	2.88	2.82	1.97	2.17	2.16	1.97	3.78	4.90	3.70	3.78	1.32	1.37	1.33	1.35
$g_-o_+g_-$ (**5B**)	7.4	4.00	4.11	4.17	4.10	3.24	3.22	3.37	3.27	2.33	2.45	2.51	2.40	5.18	6.23	5.06	5.18	2.07	2.06	2.05	2.08
$o_-o_+g_-$ (**6B**)	14.9	3.68	3.61	3.59	3.65	2.73	2.67	2.65	2.73	2.40	2.31	2.26	2.39	(3.51)	(5.35)	(3.96)	(5.22)	1.72	1.79	1.58	1.78
$o_-o_-g_+$ (**6B**)		6.88	5.51	5.55	5.44	6.02	4.52	4.71	4.55	4.49	3.22	3.57	3.13	8.81	7.83			4.20	4.50	4.60	4.50
$o_-g_+o_-$ (**6B**)		4.01	4.30	4.51	4.33	3.19	3.14	3.55	3.23	2.48	2.87	3.05	2.80	4.94	6.16	5.21	4.94	2.18	2.38	2.62	2.18
$g_-g_+g_-$ (**7B**)		8.03				7.21				5.72				10.74				5.58			
$o_-o_+o_-$ (**8B**)		5.08	5.01	4.97	4.99	4.05	3.97	3.99	4.01	3.77	3.08	3.32	3.11	6.96	6.95			3.38	4.23	4.13	4.20
$t_-t_-t_+$ (**1C**)		2.03	1.46	1.40	1.41	1.96	1.40	1.38	1.38	2.20	1.70	1.70	1.71	2.48	2.16	1.10	1.70	1.80	1.32	0.91	1.13
$t_-t_-g_-$ (**2C**)		3.31	2.23	2.18	2.23	2.96	1.96	2.04	1.97	2.79	1.95	1.84	1.91	5.17	4.89	2.78	4.42	2.17	1.63	1.39	1.53
$t_-g_-t_-$ (**2C**)		4.27	2.30	2.32	2.37	3.63	1.83	2.17	1.91	3.54	2.05	1.88	1.95	5.13	6.74	3.60	6.30	3.06	1.91	1.89	1.93
$t_-t_-o_-$ (**2C**)		3.04	2.43	2.37	2.38	2.51	2.00	1.96	1.95	2.73	2.20	2.17	2.18	2.96	3.20	2.20	2.61	1.97	1.29	1.24	1.23
$t_-o_+t_-$ (**2C**)		2.65	2.51	2.36	2.45	2.18	1.99	1.84	1.89	2.38	2.13	2.00	2.10	2.87	3.43	2.29	2.76	1.76	0.91	1.02	1.00

$t_-g_-g_-$ **(3C)**		6.80				6.23				5.26				9.54				4.77			
$g_+t_-g_-$ **(3C)**		4.35	3.00	2.96	3.05	3.90	2.52	2.69	2.57	3.26	2.20	1.99	2.12	7.46	7.62	4.46	7.14	2.71	1.94	1.87	1.92
$t_-o_+o_-$ **(3C)**		4.47	4.71	4.57	4.63	3.53	3.83	3.77	3.79	3.50	3.14	3.31	3.13	6.48	6.97			3.16	3.93	3.92	3.97
$o_+t_+o_-$ **(3C)**		3.83	3.40	3.34	3.35	2.84	2.60	2.54	2.51	3.03	2.70	2.65	2.66	3.29	4.24	3.30	3.53	1.76	1.26	1.57	1.33
$t_-g_-o_-$ **(4C)**		5.07	3.30	3.34	3.36	4.10	2.41	2.68	2.51	4.03	2.54	2.45	2.52	5.35	6.99	4.11	6.63	3.04	2.15	2.09	2.18
$t_-o_+g_-$ **(4C)**		3.85	3.31	3.19	3.29	3.12	2.53	2.42	2.51	2.97	2.37	2.25	2.40	4.96	5.37	3.38	4.89	2.48	1.49	1.37	1.55
$o_+t_+g_-$ **(4C)**		3.80	3.20	3.15	3.20	3.19	2.56	2.62	2.54	3.01	2.45	2.32	2.39	5.26	5.93	3.88	5.33	2.49	1.60	1.72	1.63
$o_+g_-g_-$ **(5C)**		5.92				4.59				4.57				10.29				3.16			
$g_+o_-g_+$ **(5C)**		5.08	4.11	4.03	4.13	4.09	3.07	3.00	3.14	3.61	2.61	2.49	2.70	7.32	7.31	4.48	7.02	3.24	2.07	1.72	2.10
$o_+o_-g_-$ **(6C)**		5.44	5.51	5.41	5.47	4.32	4.37	4.35	4.42	3.82	3.38	3.55	3.43	7.39	8.91			3.50	4.51	4.27	4.52
$o_+g_-o_+$ **(6C)**		8.05	4.30	4.37	4.36	7.08	2.99	3.18	3.10	6.19	3.03	3.02	3.10	5.90	7.24	4.63	6.96	3.16	2.39	2.29	2.44
$g_+g_-g_+$ **(7C)**		12.81				12.27				9.97				16.66				10.89			
$o_+o_-o_+$ **(8C)**	10.6	*6.77*	*6.91*	*6.79*	*6.81*	*5.71*	*5.67*	*5.69*	*5.70*	*4.75*	*4.15*	*4.61*	*4.75*	10.95	10.51			6.02	6.95	6.83	6.95
mean dev			0.11	0.07	0.05		0.13	0.08	0.03		0.15	0.12	0.05		0.52	0.25	0.04		0.14	0.13	0.03

[a] Energies in kcal/mol. Absolute energy for the $t_+t_+t_+$ conformer is −2276.725 40 au at HF/3-21G(d) level, −2288.249 99 au at HF/6-31G(d)//HF/3-21G(d) level, and −2290.608 66 au at MP2(fc)/6-31G(d)//HF/3-21G(d) level. Stable conformer energies are shown in italics. [b] Energies in parentheses correspond to conformers for which one or several of the Si backbone dihedral angles are intermediate between the ideal values of two of the backbone conformers $t_\pm$, $g_\pm$, and $o_\pm$. [c] Lowest vibrational frequency in cm^{-1} calculated at HF/3-21G(d) level and scaled by 0.9085, as reported optimal for HF/3-21G in ref 32.

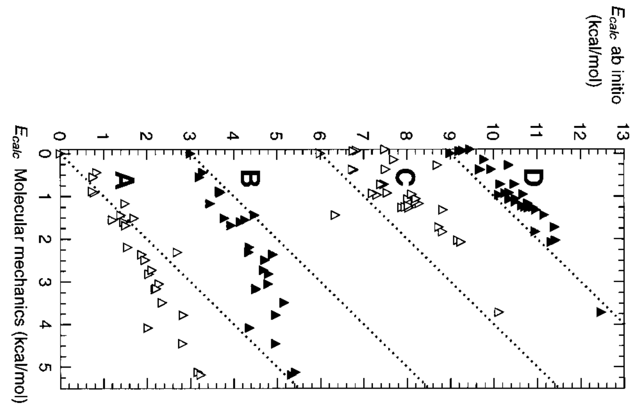

Figure 2. Ab initio energies of stable conformers plotted against molecular mechanics energies: (A) HF/6-31G(d) and (B) MP2/6-31G(d) against MM2; (C) HF/6-31G(d) and (D) MP2/6-31G(d), against MM3. Squared correlation coefficients R^2: (A) 0.86; (B) 0.80; (C) 0.58; (D) 0.90.

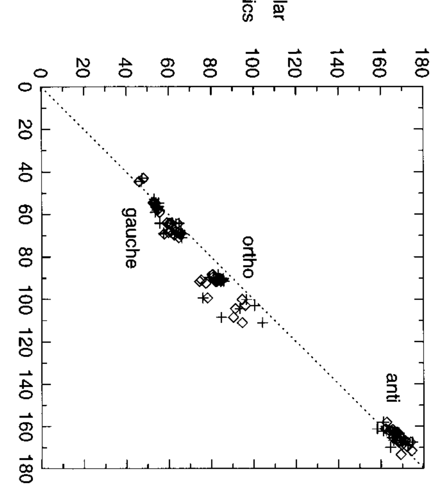

Figure 3. Absolute values of Si backbone dihedral angles α calculated with MM2 (+) or MM3 (◊) methods plotted against HF/3-21G(d) results.

We next review the stable conformers of n-Si_6Me_{14}. Subsequently, we use them to test the different increment sets.

Conformations of n-Si_6Me_{14}. Allowing each of the three backbone dihedral angles to acquire any of the values characteristic of t_+, t_-, g_+, g_-, o_+, and o_-, there are $6^3 = 216$ possible conformers. Since the terminal Si−Si bonds are related by symmetry, only 126 of these are distinct. They are arranged in 63 enantiomeric pairs. Since a complete two-dimensional search[16] for additional favored backbone dihedral angles did not reveal any in n-Si_5Me_{12}, we shall assume that in n-Si_6Me_{14}, too, this is the maximum number of conformers possible, with a single exception noted below. If some of the combinations do not correspond to potential energy minima, as was the case in n-Si_5Me_{12}, the actual number will be smaller. For longer oligosilanes the number of conformers increases rapidly, and already for n-Si_7Me_{16} we cannot presently optimize the geometry of all of them within reasonable time by conventional ab initio computational techniques, and even the use of the presumably

TABLE 4: Optimized Si Backbone Dihedral Angles in *n*-Si_6Me_{14} Conformers (deg)

conformer	HF/3-21G(d)	MM2[a]	MM3[a]
$t_+t_+t_+$ (**1A**)	163.3, 163.5, 163.3	167.3, 166.3, 167.3	167.6, 166.6, 167.6
$t_+t_+g_+$ (**2A**)	163.4, 162.3, 54.7	168.3, 161.6, 54.2	167.9, 163.9, 53.0
$t_+g_+t_+$ (**2A**)	162.2, 56.3, 162.2	162.5, 55.2, 163.9	165.0, 53.9, 165.0
$t_+t_+o_-$ (**2A**)	162.9, 166.8, −91.5	167.3, 169.3, −85.9	167.8, 168.4, −82.8
$t_+o_-t_+$ (**2A**)	166.0, −90.2, 166.0	170.7, −85.8, 170.7	169.6, −84.1, 169.6
$t_+g_+g_+$ (**3A**)	158.2, 57.9, 57.6	161.1, 54.3, 54.9	162.6, 54.9, 55.0
$g_+t_+g_+$ (**3A**)	54.7, 161.4, 54.7	55.2, 158.3, 55.2	53.6, 162.1, 53.6
$t_+o_-o_-$ (**3A**)	166.7, −88.4, −90.2	169.0, −82.9, −83.2	168.6, −81.5, −80.4
$o_+t_-o_+$ (**3A**)	91.0, −168.8, 91.0	85.5, −172.7, 85.5	83.2, −169.8, 83.2
$t_+g_+o_-$ (**4A**)	165.7, 68.2, −104.4	166.3, 63.6, −93.6	167.9, 60.8, −91.4
$t_+o_-g_+$ (**4A**)	167.6, −103.0, 64.2	174.8, −100.5, 64.9	173.9, −96.0, 61.1
$o_+t_-g_-$ (**4A**)	91.3, −165.5, −54.9	85.0, −165.1, −54.0	82.8, −165.6, −53.0
$o_+g_-g_-$ (**5A**)	111.1, −71.0, −69.2	104.2, −66.2, −65.6	94.6, −64.7, −57.8
$g_+o_-g_+$ (**5A**)		(72.8, −119.4, 72.9)	69.2, −113.0, 69.2
$o_+o_+g_-$ (**6A**)	90.5, 100.1, −64.0	84.9, 96.6, −61.6	83.7, 94.5, −59.1
$o_+g_-o_+$ (**6A**)	109.8, −62.8, 84.2	121.5, −67.3, 121.5	106.8, −65.8, 82.7
$g_+g_+g_+$ (**7A**)	54.4, 59.0, 54.4	53.1, 53.7, 53.1	52.6, 55.7, 52.6
$o_+o_+o_+$ (**8A**)	89.7, 86.8, 89.7	79.3, 76.1, 79.3	80.6, 78.2, 80.6
$t_+t_+g_-$ (**2B**)	162.9, 169.8, −67.9		166.1, 172.2, −63.4
$t_+t_-g_-$ (**2B**)			174.6, −169.5, −52.7
$t_+t_+o_+$ (**2B**)	161.6, 173.5, 92.4	(168.2, −179.1, 86.3)	165.5, 169.4, 77.4
$t_+t_-o_+$ (**2B**)		175.3, −172.1, 85.5	170.0, −169.0, 81.7
$t_+o_+t_-$ (**2B**)			173.2, 80.3, −168.9
$t_+g_-g_-$ (**3B**)	166.8, −69.1, −44.5	165.9, −66.5, −47.3	171.3, −65.0, −45.9
$o_+t_+o_-$ (**3B**)		(85.9, 179.8, −86.1)	78.6, 172.3, −85.5
$t_+o_+o_+$ (**3B**)		173.4, 79.7, 81.9	172.7, 76.1, 79.7
$g_+t_+g_-$ (**3B**)		(55.9, 179.8, −51.4)	51.9, 170.4, −62.2
$t_+g_+o_+$ (**4B**)	148.6, 67.3, 90.0	(163.9, 73.4, 81.2)	(162.6, 70.0, 79.6)
$t_+g_-o_+$ (**4B**)	175.0, −59.9, 92.2		
$t_+o_-g_-$ (**4B**)	167.8, −90.9, −68.5	(170.1, −79.1, −73.1)	168.3, −75.3, −59.8
$t_+o_+g_-$ (**4B**)		165.1, 89.6, −59.4	166.7, 86.0, −57.4
$o_+t_+g_+$ (**4B**)	90.9, 170.1, 52.8	81.2, 164.4, 53.2	
$o_+t_-g_+$ (**4B**)	91.4, −171.7, 68.9		84.7, −174.4, 61.9
$o_+g_+g_+$ (**5B**)	91.7, 64.4, 43.0	84.4, 63.4, 47.4	82.1, 64.3, 48.1
$g_+o_+g_-$ (**5B**)	64.2, 108.5, −68.9	55.9, 84.8, −57.6	60.2, −90.4, −65.8
$o_+o_+g_+$ (**6B**)	88.4, 91.6, 69.7		80.7, 74.5, 62.6
$o_+o_-o_+$ (**8C**)	104.6, −81.0, 104.6		

[a] Values in parentheses correspond to conformers for which one or several of the Si backbone dihedral angles are intermediate between the ideal values of two of the backbone conformers $t_\pm$, $g_\pm$, and $o_\pm$.

less reliable molecular mechanics methods becomes tedious. Below, we show that the simpler alternative system for estimating conformer energies of longer *n*-Si_nMe_{2n+2} chains, based on additive increments, will be adequate for those conformers that are of low energy.

All of the conformational minima are very shallow. The softest mode always corresponds to hindered rotation about one or more of the dihedral angles. We note that in the well-documented cases of the conformers of *n*-Si_4Me_{10}[5] and *n*-Si_4Cl_{10}[21], which are clearly distinct and separately spectroscopically observable, the softest mode frequencies are ∼30 and ∼10 cm^{-1}, respectively. Arbitrarily, we assume that 15 cm^{-1} is the lowest HF frequency that a dependably computed and truly stable conformer can have, and consider those with a normal mode of a lower frequency to be of questionable significance, as they may disappear at a higher level of theory. In practical terms, there is another reason for a conformer to be of minor importance, and that is its energy. Again arbitrarily, we concentrate on conformers that lie less than 2 kcal/mol above the $t_+t_+t_+$, $t_-t_-t_-$ pair. When compared to the $t_+t_+t_+$, $t_-t_-t_-$ conformer pair, the population of a conformer that has a relative energy 2.0 kcal/mol is ∼1% at room temperature.

We start a systematic examination of *n*-Si_6Me_{14} conformers by sorting them into 24 groups (Table 1) according to the types of bond conformations ($t_\pm$, $g_\pm$, $o_\pm$) present in the Si backbone and the nature of the interactions[16] between adjacent bonds (Figure 1). Conformations in category A have two favorable bond interactions, those in category B have one favorable interaction, and those in category C have none.

As seen in Figure 2, MM2 conformer energies agree slightly better with the corresponding HF/6-31G(d) energies than with the MP2/6-31G(d) energies. The opposite holds for the MM3 energies where the correlation with MP2 is much better than with HF energies. However, the MP2 energy differences are in general somewhat higher than the MM3 energy differences. The dihedral angles calculated by the two MM methods agree about equally well with the HF/3-21G(d) angles, with the ortho angle about 10° too small (Figure 3). The small differences in dihedral angles between the MM methods and HF/3-21G(d) seen for anti and gauche bond conformations may be related to the fact that MM values are fitted to observables averaged over vibrational motion, whereas the ab initio computations give the equilibrium value.

As expected,[16] conformers in category A are more likely to correspond to actual potential surface minima than those in category B, even though exceptions exist (Table 2). The conformers in category C are always less likely to be stable than those in categories A and B. At HF/3-21G(d) level of calculation, only one stable pair of enantiomeric conformers of category C was found, compared with 17 out of 18 in category A, and 13 out of 27 in category B. The number of stable conformer pairs in category B is somewhat larger at the MM3 level, and there is also some difference between the predictions produced by the various methods as to which structures are

TABLE 5: Additive Increment Sets {$E^0(\alpha)$, $E^0(\alpha,\beta)$}, {$E'(\alpha)$, $E'(\alpha,\beta)$}), and {$E''(\alpha)$, $E''(\alpha,\beta)$, $E''(\alpha,\beta,\gamma)$} (kcal/mol)

increment type	HF/3-21G(d)			HF/6-31G(d)//HF/3-21G(d)			MP2(fc)/6-31G(d)//HF/3-21G(d)			MM2			MM3		
	E^0	E'	E''	E^0	E'	E''	E^0	E'	E''	E^0	E'	E''	E^0	E'	E''
t_+	0.00	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000
g_+	0.70	0.645	0.678	0.69	0.520	0.658	0.15	0.109	0.168	0.88	0.863	0.842	0.03	−0.020	−0.012
o_+	0.89	0.987	0.905	0.61	0.699	0.623	0.57	0.644	0.560	0.81	1.015	0.775	0.35	0.550	0.328
t_+t_+	0.00	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000
t_+g_+	0.01	0.118	0.097	0.03	0.200	0.104	0.04	0.130	0.081	−0.25	−0.193	−0.193	−0.07	−0.021	−0.016
t_+o_-	0.08	0.010	0.081	0.11	0.035	0.097	0.09	−0.013	0.062	0.04	−0.101	0.053	0.04	−0.126	0.030
o_+g_-	0.91	1.018	0.905	0.69	0.997	0.730	0.71	0.839	0.604	1.29	1.450	1.472	0.82	0.932	0.876
o_+o_+	0.22	0.092	0.230	0.22	0.100	0.222	0.15	0.050	0.197	0.48	0.196	0.540	0.23	−0.108	0.239
g_+g_+	0.50	0.597	0.525	0.21	0.507	0.280	0.43	0.481	0.388	−0.04	0.087	0.036	0.13	0.217	0.150
t_+t_-	0.73	0.699	0.705	0.70	0.692	0.691	0.85	0.849	0.853	1.08	0.548	0.848	0.66	0.457	0.564
t_+g_-	0.80	0.835	0.847	0.57	0.827	0.625	0.95	0.884	0.893	2.93	1.369	2.727	0.94	0.956	0.973
t_+o_+	0.81	0.684	0.771	0.69	0.570	0.632	0.78	0.679	0.769	1.31	0.636	0.990	0.28	0.235	0.337
o_+g_+	0.91	0.877	0.935	0.54	0.633	0.599	0.87	0.814	0.904	2.37	0.868	2.283	0.83	0.607	0.896
o_+o_-	2.12	1.916	2.049	1.92	1.798	1.916	1.22	1.339	1.237	4.04			2.95	2.588	2.981
$t_+g_+o_-$			0.165			0.165			0.377			0.154			
$o_+t_-g_-$												0.203			
$o_+g_-g_-$			0.379			0.221			0.532			1.153			0.700
$o_+g_-o_+$			0.542			0.756			0.974			2.444			1.324
$g_+g_+g_+$						0.166						−0.288			
$t_+t_-o_+$												−0.236			−0.202
$t_+t_+o_+$															0.265
$t_+g_-g_-$												−1.287			
$t_+o_+o_+$												−0.350			
$o_+t_+o_-$															0.237
$t_+g_-o_+$						0.754									
$t_+o_+g_-$												−0.459			
$o_+g_+g_+$									−0.218			−0.998			
$g_+o_+g_-$												−1.034			
$o_+g_+o_-$												−1.204			−0.236
$o_+o_-o_+$									0.596						
t_+at_-			0.615			0.602			0.740			0.800			0.430
o_+ao_-			0.801			0.634			0.775			0.860			0.594

[a] Values in parentheses correspond to conformers for which one or several of the Si backbone dihedral angles are intermediate between the ideal values of two of the backbone conformers $t_\pm$, $g_\pm$, and $o_\pm$.

TABLE 6: Energies E_{calc} and E_{incr} for n-Si_4Me_{10} and n-Si_5Me_{12} (kcal/mol)

conformer		HF/3-21G(d)			HF/6-31G(d)//HF/3-21G(d)			MP2(fc)/6-31G(d)//HF/3-21G(d)			MM2			MM3		
		E_{calc}	E'_{incr}	E''_{incr}	E_{calc}	E'_{incr}	E''_{incr}	E_{calc}	E'_{incr}	E''_{incr}	E_{calc}	E'_{incr}	E''_{incr}	E_{calc}	E'_{incr}	E''_{incr}
n-Si_4Me_{10}	t_+	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	o_+	0.89	0.99	0.90	0.61	0.70	0.62	0.57	0.64	0.56	0.81	1.01	0.78	0.35	0.55	0.33
	g_+	0.70	0.64	0.68	0.69	0.52	0.66	0.15	0.11	0.17	0.88	0.86	0.84	0.03	−0.02	−0.01
	ΔE^a		0.08	0.02		0.13	0.02		0.06	0.01		0.11	0.04		0.12	0.03
n-Si_5Me_{12}	t_+t_+	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	t_+g_+	0.71	0.76	0.78	0.72	0.72	0.76	0.19	0.24	0.25	0.63	0.67	0.65	−0.04	−0.04	−0.03
	t_+o_-	0.97	1.00	0.99	0.72	0.73	0.72	0.66	0.63	0.62	0.85	0.91	0.83	0.39	0.42	0.36
	o_+o_+	2.00	2.07	2.04	1.44	1.50	1.47	1.29	1.34	1.32	2.10	2.23	2.09	0.93	0.99	0.89
	o_+g_-	2.50	2.65	2.49	1.99	2.22	2.01	1.43	1.59	1.33	2.98	3.33	3.09	1.20	1.46	1.19
	g_+g_+	1.90	1.89	1.88	1.59	1.55	1.60	0.73	0.70	0.72	1.72	1.81	1.72	0.19	0.18	0.13
	t_+t_-	0.73	0.70	0.71	0.70	0.69	0.69	0.85	0.85	0.85				0.66	0.46	0.56
	t_+g_-	1.50	1.48	1.52	1.26	1.35	1.28	1.10	0.99	1.06				0.97	0.94	0.96
	t_+o_+	1.70	1.67	1.68	1.30	1.27	1.26	1.35	1.32	1.33				0.63	0.78	0.66
	o_+o_-	3.90	3.89	3.86	3.14	3.20	3.16	2.36	2.63	2.36				3.65	3.69	3.64
	o_+g_+	2.50	2.51	2.52	1.84	1.85	1.88	1.59	1.57	1.63				1.21	1.14	1.21
	ΔE^a		0.04	0.03		0.05	0.02		0.07	0.03		0.13	0.03		0.09	0.03

[a] Mean deviation between E_{calc} and E_{incr}.

stable. With MM2 we found a smaller number of stable conformers than with either HF/3-21G(d) and MM3, as was also the case for n-Si_5Me_{12}. At the MM2 level a number of structures optimized to geometries with dihedral angles intermediate between gauche and ortho, and in Tables 2 and 4 these entries are given in parentheses.

The Most Stable Conformer. As in n-Si_5Me_{12}, the conformer of lowest energy at all computational levels except MM3 is the all-transoid pair with two favorable bond interactions, $t_+t_+t_+$, $t_-t_-t_-$, but in the MP2/6-31G(d) approximation, $t_+t_+g_+$ is only 0.2 kcal/mol higher. At MM3 level the conformer of lowest energy is $g_+t_+g_+$, in keeping with the enhanced (and, we believe, excessive) importance of van der Waals interaction built into this level of approximation.

The Meso Conformer. Of the other all-transoid possibilities, at the HF/3-21G(d) level the $t_+t_-t_+$, $t_-t_+t_-$ pair optimizes to $t_+t_+t_+$, $t_-t_-t_-$, while $t_+t_+t_-$, $t_-t_-t_+$ optimizes to the meso structure t_+at_- with a plane of symmetry. At this level of calculation, this is a true minimum, 0.61 kcal/mol above $t_+t_+t_+$, $t_-t_-t_-$, but the lowest vibrational frequency is only 6 cm^{-1}. Thus, in reality, t_+at_- might well merely be a transition state for the interconversion of $t_+t_+t_+$ and $t_-t_-t_-$. The $t_+t_+t_-$ conformer is

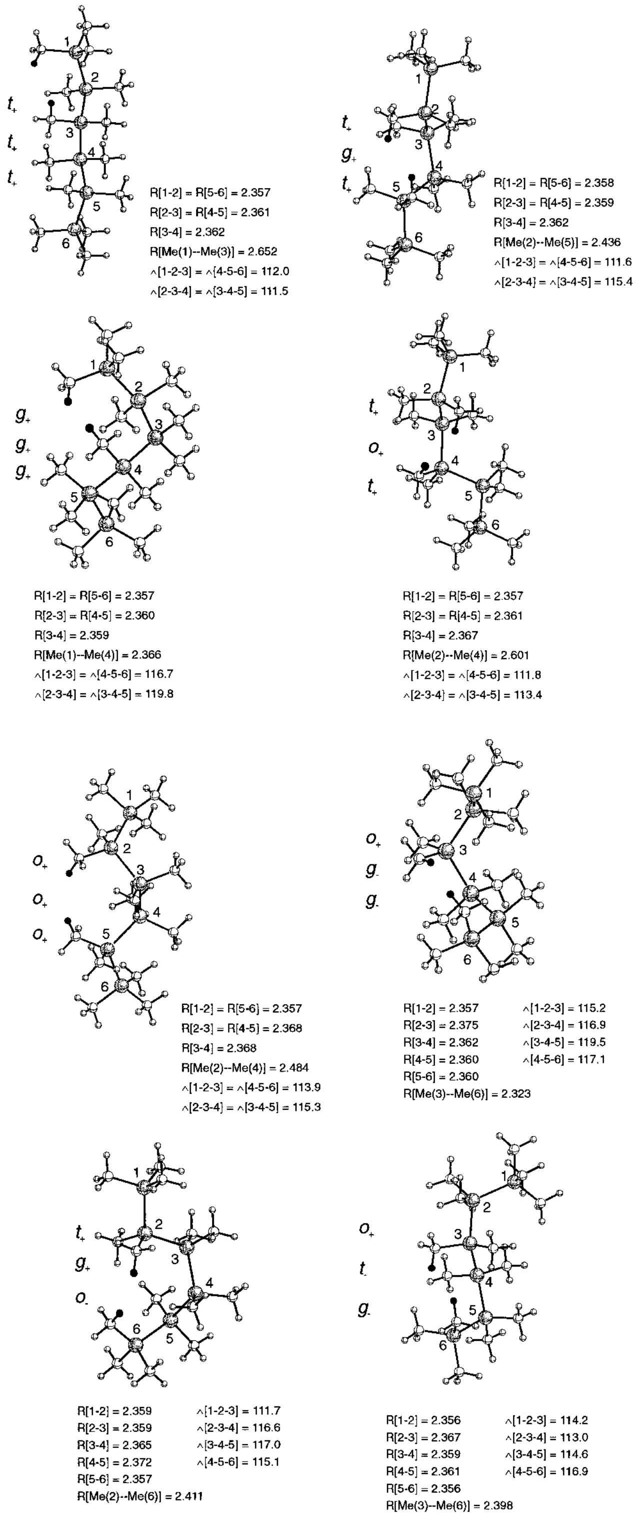

Figure 4. Optimized HF/3-21G(d) geometries for selected n-Si_6Me_{14} conformers. Si−Si bond lengths and closest Me−Me nonbonded distances are given in Å, and SiSiSi valence angles are given in deg. The H atoms that constitute the closest Me−Me distance are shown in black.

also unstable at the MM2 and MM3 levels, and it corresponds to a transition state at the MM3 level.

Either way, we believe that the t_+at_- conformation, which is not one of the 216 combinations of dihedral angles identified above, is likely to be important. It represents a low-energy "defect" in the all-transoid helical chain that reverses the helical sense and it may well play a role in the thermochromism of high molecular weight polysilanes. Note that of the other meso arrangements, o_+ao_- is stable but of rather high energy (2.60 kcal/mol at HF/3-21G(d) level), and the g_+ag_- arrangement corresponds to a transition state.

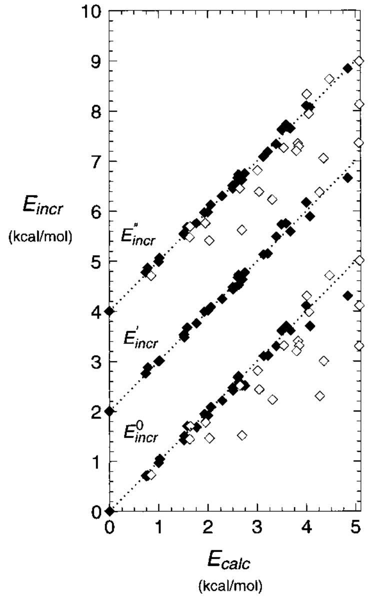

Figure 5. HF/3-21G(d) energies: E_{incr} and E_{calc} for stable conformers (◆) and unstable conformations (◇, for E^0_{incr} and E''_{incr} only) of n-Si_6Me_{14}. Squared correlation coefficients R^2: E^0_{incr}, 0.985; E'_{incr}, 0.993; E''_{incr}, 0.997 (stable conformers only). Dotted lines represent perfect agreement. The upper plots have been displaced by 2.0 and 4.0 kcal/mol.

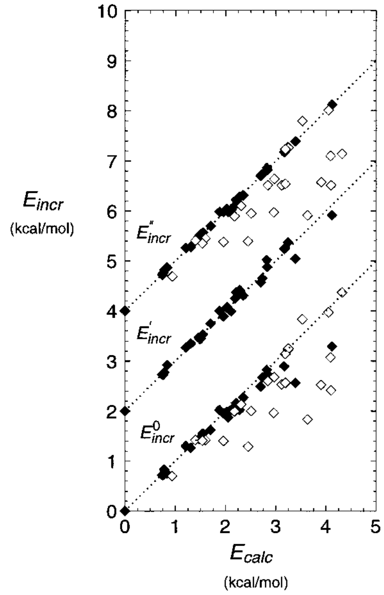

Figure 6. HF/6-31G(d)//HF/3-21G(d) energies: E_{incr} and E_{calc} for stable conformers (◆) and unstable conformations (◇, for E^0_{incr} and E''_{incr} only) of n-Si_6Me_{14}. Squared correlation coefficients R^2: E^0_{incr}, 0.858; E'_{incr}, 0.991; E''_{incr}, 0.999 (stable conformers only). Dotted lines represent perfect agreement. The upper plots have been displaced by 2.0 and 4.0 kcal/mol.

Other Conformers. According to the HF/3-21G(d) calculations, conformers of the next most stable group have one gauche or ortho twisted SiSi bond with no unfavorable interactions (group 2A). The spread among the 2A conformers is ~0.5 kcal/mol, with g more favorable than o (at the HF/6-31G(d)//HF/3-21G(d) level they are isoenergetic within 0.1 kcal/mol). The corresponding conformers of group 2B, with one unfavorable

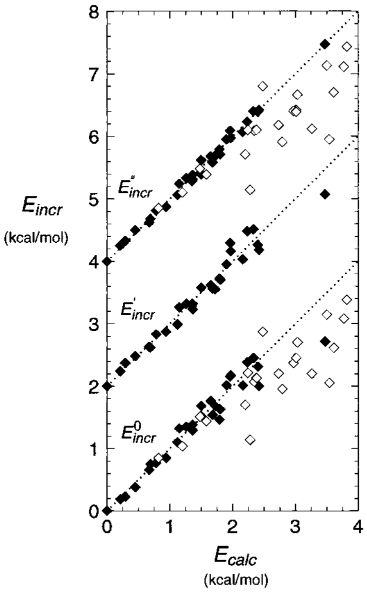

Figure 7. MP2(FC)/6-31G(d)//HF/3-21G(d) energies: E_{incr} and E_{calc} for stable conformers (◆) and unstable conformations (◇, for E^0_{incr} and E''_{incr} only) of n-Si$_6$Me$_{14}$. Squared correlation coefficients R^2: E^0_{incr}, 0.935; E'_{incr}, 0.968; E''_{incr}, 0.994 (stable conformers only). Dotted lines represent perfect agreement. The upper plots have been displaced by 2.0 and 4.0 kcal/mol.

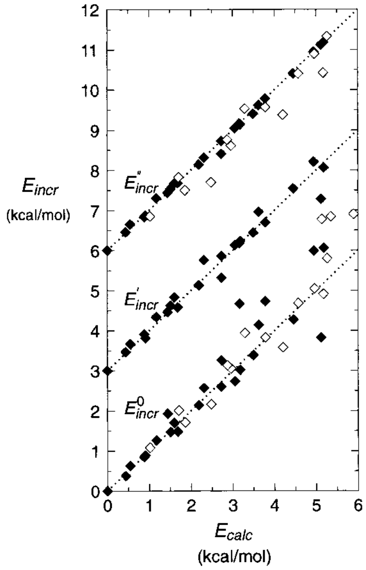

Figure 8. MM2 energies: E_{incr} and E_{calc} for stable conformers (◆) and unstable conformations (◇, for E^0_{incr} and E''_{incr} only) of n-Si$_6$Me$_{14}$. Squared correlation coefficients R^2: E^0_{incr}, 0.815; E'_{incr}, 0.944; E''_{incr}, 0.998 (stable conformers only). Dotted lines represent perfect agreement. The upper plots have been displaced by 3.0 and 6.0 kcal/mol.

bond interaction, are less stable than those in group 2A and in general equally or only slightly more stable than those of group 3A with two g or o twists.

Thereafter, several groups of conformers are of comparable energy. At the HF level, the ordering of the conformers that belong to group 4 does not agree with simple expectations. It is clear that the combinations o_+g_- or o_+g_+ are of comparable stability, since the energies of 4A and 4B conformers are nearly equal. At the MP2 level the 4A conformers are always more stable than the 4B conformers.

For the conformers in groups 3A, 3B, 4A, and 4B, it is always more favorable to have $g_\pm$ and $o_\pm$ twists separated by a $t_\pm$ bond conformation. Nonalternating arrangements of several gauche and ortho bond conformations are preferred; i.e., $o_+o_+g_-$ is more stable than $o_+g_-o_+$ (Table 2, groups 5A and 6A), reflecting the less stable o_+g_- and o_+g_+ combinations. Of the 13 stable enantiomeric conformer pairs in category B, five have t_+g_- and five have g_+o_+ interactions. However, all but two of the 13 conformers in category B are more than 2.0 kcal/mol above the $t_+t_+t_+$ conformer, and the lowest HF/3-21G(d) vibrational frequencies of the two exceptions are less than 10 cm^{-1} and it is questionable whether they are truly stable. Since the lowest vibrational frequency of the clear majority of stable conformers with one unfavorable interaction lies below 15 cm^{-1} (Table 2), it is unlikely that all of these structures will correspond to minima at higher computational levels. In contrast, 16 out of 17 conformers of category A with all favorable interactions (Figure 1) have their lowest vibrational frequency above 15 cm^{-1}, and are more likely to correspond to true minima. If one is interested only in minima whose lowest vibrational frequency exceeds 15 cm^{-1} and whose energy is at most 2 kcal/mol above that of the most stable conformer $t_+t_+t_+$, $t_-t_-t_-$ only conformations of category A need to be considered.

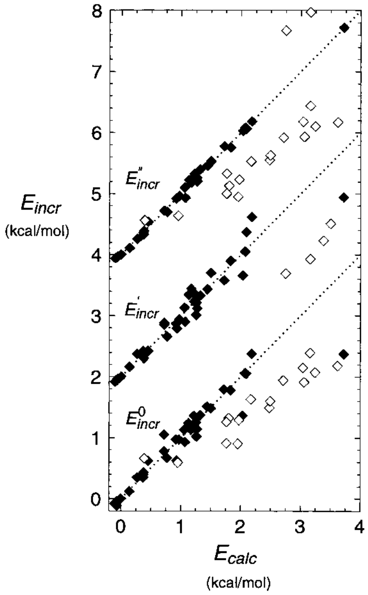

Figure 9. MM3 energies: E_{incr} and E_{calc} for stable conformers (◆) and unstable conformations (◇, for E^0_{incr} and E''_{incr} only) of n-Si$_6$Me$_{14}$. Squared correlation coefficients R^2: E^0_{incr}, 0.867; E'_{incr}, 0.923; E''_{incr}, 0.993 (stable conformers only). Dotted lines represent perfect agreement. The upper plots have been displaced by 2.0 and 4.0 kcal/mol.

The MM2 stability order is similar to those found at the two HF levels, especially to that obtained from HF/3-21G(d) calculations. However, the number of conformers is smaller at the MM2 level, and a comparison might not be fully justified. Some minor differences exist between the MM2 and HF stability orders, and the most obvious of these occurs in the 2B group, where two stable conformers exist at the HF/3-21G(d) level but only one at the MM2 level. Similar small differences were found between HF and MM2 in the previous study of n-Si$_5$Me$_{12}$. E.g., while the t_+g_-, t_-g_+ conformers of n-Si$_5$Me$_{12}$ and their enantiomers are stable at the HF/3-21G(d) level, they are not at the MM2 level of calculation.[16]

The MP2/6-31G(d) and MM3 methods give very similar results. They yield a different stability order than HF and MM2 since the conformers that contain $g_\pm$ dihedral angles are favored over those with $o_\pm$ dihedral angles, and are often nearly as stable as their $t_\pm$ counterparts. This is especially noticeable in the MM3 results where even the all-gauche conformer $g_+g_+g_+$ is of low energy (0.27 kcal/mol), quite contrary to what was found at

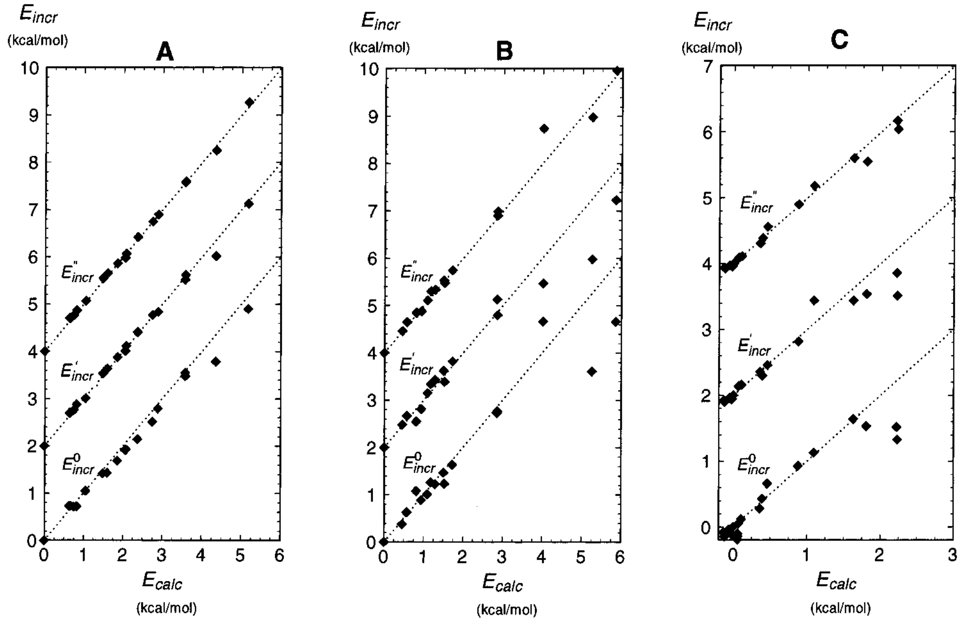

Figure 10. Energies E_{incr} and E_{calc} for selected stable n-Si_7Me_{16} and n-Si_8Me_{18} conformers at (A) HF/3-21G(d), (B) MM2, and (C) MM3 levels. Squared correlation coefficients R^2 at HF/3-21G(d) level (A) are E^0_{incr}, 0.988; E'_{incr}, 0.992; and E''_{incr}, 0.999. At MM2 level (B) they are E^0_{incr}, 0.926; E'_{incr}, 0.966; and E''_{incr}, 0.987, and at MM3 level (C) they are E^0_{incr}, 0.903; E'_{incr}, 0.943; and E''_{incr}, 0.990. Dotted lines represent perfect agreement. The upper plots have been displaced by 2.0 and 4.0 kcal/mol.

the HF/3-21G(d) level (3.13 kcal/mol). In the MM3 approximation the number of conformers below 3.0 kcal/mol is also larger than at any other level (Table 3), with the MP2 level a close second.

At all levels of calculation, the $g_+t_+g_+$ conformer is more stable than $t_+g_+g_+$. We therefore expect that among conformers of longer permethylated oligosilanes with a given number of gauche twists those that have these twists separated by transoid bond conformations will be most stable (e.g., $t_+g_+t_+g_+$ will probably be more stable than $t_+g_+g_+t_+$).

Comparison of Computational Methods. The difference between the two types of computational methods follows the trend already established for Si_4Me_{10}[5] and Si_5Me_{12}[16] and supports the interpretation given there. Whereas the HF approximation ignores the van der Waals attraction among the methyl substituents, and MM2 is parametrized to mimic HF,[27] the MP2 method includes at least some of this van der Waals attraction and therefore favors more compact structures (the parametrization of MM3 was explicitly designed to incorporate van der Waals interaction[28]).

In solution, the increased intramolecular van der Waals stabilization of the more compact structures will probably be compensated to some degree by a reduced intermolecular van der Waals interaction with solvent molecules, and they will probably lose their advantage. Our previous observation[16] that the MP2 (MM3) results seem to agree with gas-phase experimental results and the HF (MM2) with solution results probably applies to longer chains as well.

Conformer Structures. For n-Si_6Me_{14} the calculated spread in the Si backbone dihedral angles $\omega_1 - \omega_3$ is larger than in n-Si_5Me_{12} and n-Si_4Me_{10}. Among the stable n-Si_6Me_{14} conformers, ω calculated at the HF/3-21G(d) level for transoid bond conformations varies between 148.6° and 175.0° (Table 4), as compared to the n-Si_4Me_{10} value of 163.5°. For the gauche bond conformations, the range is 43.0°−71.0°, and for ortho, 81.0°−111.1°. Most of the variation is found among the less stable conformers. For conformers in the groups 1A−3A the Si backbone dihedral angles are within 5° of those in n-Si_4Me_{10}, suggesting only minor steric congestion. Angles in the range of 70°−80°, which constitute borderline cases between gauche and ortho conformations, and exceptionally small g_+ and large o_+ angles, are found in groups of type B and in groups 4A−6A.

The dihedral angles in the most stable 4A conformer, $o_+t_-g_-$, do not deviate significantly from the standard values, but in both other 4A conformers, $t_+g_+o_-$ and $t_+o_-g_+$, they are distorted at HF/3-21G(d) level by as much as 15° (Table 4). Similar deviations are seen in the stable conformers of group 4B. Above it was seen that structures with $o_\pm$ and $g_\pm$ twists next to each other lead to structures which are less stable than those which had such twists separated by one $t_\pm$. This relative instability relates to the distorted structure that the Si backbone has to adopt in these conformers.

The molecular mechanics methods give slightly different values for the optimized dihedral angles of the Si backbone but similar angle variation among conformers. For ortho dihedral angles, both MM2 and MM3 values are smaller than the HF/3-21G(d) values (Figure 3), while the gauche bond angles are slightly smaller and the transoid bond angles slightly larger. Since HF/6-31G(d) and MP2/6-31G(d) dihedral angles in n-Si_4Me_{10} are identical within 2°, the deviation for MM2 and MM3 is inherent to these empirical methods.

The SiSi bond lengths are in general slightly longer in $o_\pm$ twists than they are in $t_\pm$ and $g_\pm$ bond conformations (Figure 4). There also is a variation between conformers with $t_\pm$, $o_\pm$, and $g_\pm$ turns in SiSiSi valence angles with values for $t_\pm$ around 111°, for $o_\pm$ around 114°, and for $g_\pm$ around 117°.

***n*-Si_6Me_{14} Conformer Energies from Additive Increment Models**. A major objective of the present investigation is to test the use of additive increments $E(\alpha)$ and $E(\alpha,\beta)$ ($\alpha, \beta = t_\pm$, $g_\pm$, or $o_\pm$), representing bond-conformation and bond-interaction energies,[5] for conformer energies E_{incr} of longer oligosilanes by use of eq 1.

(i) Original Increment Sets $\{E^0(\alpha), E^0(\alpha,\beta)\}$. These increments were derived for several levels of theory from data obtained for n-Si_4Me_{10} and n-Si_5Me_{12}.[5] They reproduce well

the order of n-Si$_6$Me$_{14}$ conformer energies provided by the ab initio methods (Table 3). Some differences occur at the HF/6-31G(d) level of calculation, where some conformers with g$_\pm$ twists are erroneously predicted to be more stable than their o$_\pm$ counterparts.

The correlation between n-Si$_6$Me$_{14}$ conformer energies $E^0_{\rm incr}$ obtained from eq 1 using these published increment values and the $E_{\rm calc}$ energies calculated presently (cf. Table 2) is shown by plots labeled $E^0_{\rm incr}$ in Figures 5−9. For stable conformers the agreement is generally good, but the energies of some of the high-energy conformers deviate considerably. The mean deviations are in the range 0.11−0.52 kcal/mol, with the best agreement for HF/3-21G(d) and the worst for MM2. The agreement is better for conformers with energies below 3.0 kcal/mol (e.g., for the HF/3-21G(d) level the mean deviation then is 0.07 kcal/mol and for MM2 it is 0.16 kcal/mol). It is likely that the increment model is less suited for high-energy conformers because their dihedral angles deviate more strongly from the norm.

There also is a slightly better agreement between $E^0_{\rm incr}$ and $E_{\rm calc}$ for the ab initio methods than for the MM3 method. However, even for HF/3-21G(d) there are a few conformers for which $E^0_{\rm incr}$ and $E_{\rm calc}$ differ by as much as 0.54 kcal/mol. For the increments obtained from single-point calculations, HF/6-31G(d) and MP2/6-31G(d), the situation is slightly worse. Of the stable conformers in category A, those in groups 5A and 6A give particularly poor agreement.

For dihedral angle combinations that do not correspond to stable conformers the agreement between $E^0_{\rm incr}$ and $E_{\rm calc}$ is poor, with deviations as large as several kcal/mol, and for these, the increment model is useless. This is not surprising, since the increments were derived from n-Si$_4$Me$_{10}$ and n-Si$_5$Me$_{12}$, in which there are no interactions between methyl groups in positions 1 and 6, and the large steric repulsion between these groups in some conformations of n-Si$_6$Me$_{14}$ is therefore ignored. These repulsive effects are particularly significant in structures that contain one or two unfavorable bond interactions. As a result, in most cases the $E^0_{\rm incr}$ values underestimate the $E_{\rm calc}$ values (Figures 5−9).

The limitation of the additive increment method only to structures that correspond to stable conformers is not a serious problem for their intended future use, as long as we can recognize and eliminate the unstable and/or high-energy structures as discussed below. It appears more important to consider the deviations between $E^0_{\rm incr}$ and $E_{\rm calc}$ observed for a few of the stable conformers, since for these conformers the strain can be seen in geometry changes. For the t$_+$t$_+$t$_+$ conformer the average SiSi bond length is 2.360 Å at HF/3-21G(d) level, whereas in conformers in which there is a large deviation between $E^0_{\rm incr}$ and $E_{\rm calc}$ some SiSi bonds are stretched (Figure 4). For instance, in o$_+$g$_-$g$_-$ one SiSi bond is 2.375 Å long. On the other hand, the closest nonbonded distances between methyl groups in conformers in which there are large differences between $E^0_{\rm incr}$ and $E_{\rm calc}$ (e.g., t$_+$g$_+$o$_-$ and o$_+$g$_-$g$_-$) are similar to those found in g$_+$g$_+$g$_+$, for which a good agreement is found. A hint for the understanding of these contradictory observations is provided by the values of their Si backbone dihedral angles, which in these conformers almost always deviate significantly from the ideal values expected for t$_\pm$, g$_\pm$, and o$_\pm$ (Table 4). Thus, to decrease steric repulsion and keep methyl groups at attractive van der Waals distances the dihedral angles in the Si backbone are distorted from the norm. It seems as if steric effects disregarded when deriving $E^0(\alpha)$ and $E^0(\alpha,\beta)$ from n-Si$_4$Me$_{10}$ and n-Si$_5$Me$_{12}$ were responsible for deviations between $E^0_{\rm incr}$ and $E_{\rm calc}$. It is notable that the o$_+$g$_-$ segment appears in all of the conformers which show large deviations.

(ii) Improved Increment Sets $\{E'(\alpha), E'(\alpha,\beta)\}$. The now available computed energies of n-Si$_6$Me$_{14}$ conformers permit an improvement of the $E(\alpha)$ and $E(\alpha,\beta)$ increment values by a least-squares fit to computed conformer energies of all stable n-Si$_4$Me$_{10}$, n-Si$_5$Me$_{12}$, and n-Si$_6$Me$_{14}$ conformers (Table 2). The energies $E'_{\rm incr}$ derived from the resulting improved increments $E'(\alpha)$ and $E'(\alpha,\beta)$ agree better with the energies $E_{\rm calc}$ derived from the ab initio computations (plots $E'_{\rm incr}$ in Figures 5−9), and HF/3-21G(d) again yields a smaller mean deviation than methods based on single-point energies. Whereas there were some differences in the stability order for the 2B−3A−4A conformers at HF/3-21G(d) with the initial unadjusted increment set, they have now disappeared. The description of unstable structures is not improved (not shown in Figures 5−9, cf. Table 2).

No improvement is seen for the MM3 method. For this method, the $E^0_{\rm incr}$ and $E_{\rm calc}$ values for some conformers differ by as much as 1.3 kcal/mol, and an adjustment that removes this disagreement invariably produces other disagreements. Since molecular mechanics methods were found to exaggerate barrier heights,[16] in strongly distorted Si$_6$Me$_{14}$ conformers they probably overestimate the energy needed for the distortions of the Si backbone which occurs in some conformers. The situation is similar at the MM2 level, even though the mean deviation reduces from 0.52 to 0.25 kcal/mol when going from $E^0_{\rm incr}$ to $E'_{\rm incr}$.

(iii) Increment Sets with Nonadjacent Interactions $\{E''(\alpha), E''(\alpha,\beta), E''(\alpha,\beta,\gamma)\}$**.** The fact that the $\{E^0(\alpha), E^0(\alpha,\beta)\}$ increments derived from n-Si$_4$Me$_{10}$ and n-Si$_5$Me$_{12}$ results alone did not yield a perfect agreement between $E^0_{\rm incr}$ and $E_{\rm calc}$ for n-Si$_6$Me$_{14}$ reflects a lack of additivity. The least-squares treatment of a larger set of data ($E'_{\rm incr}$) does not provide much of a remedy, since it does not address this fundamental issue. This is perhaps best illustrated on results for n-Si$_4$Me$_{10}$, whose energies are described by a single increment. For example, for the o$_\pm$ conformer at the MM3 level, and for the g$_\pm$ conformer at HF/6-31G(d) level, the differences between $E'_{\rm incr}$ and $E_{\rm calc}$ are 0.20 and 0.17 kcal/mol, respectively. Clearly, an attempt to fit some of the grossly distorted high-energy conformers of Si$_6$Me$_{14}$ (groups 5A and 6A) can only be achieved at the expense of the agreement for the shorter oligosilanes. The situation is particularly sad for g$_\pm$ and o$_\pm$ of n-Si$_4$Me$_{10}$, since the conformers of Si$_6$Me$_{14}$ where large deviations between $E_{\rm calc}$ and $E'_{\rm incr}$ are found to contain o$_+$g$_-$ segments.

This problem could perhaps be solved by inclusion of a penalty function in the increment optimization, but a more promising way to handle it is to recognize the nonadditivity explicitly and to include increments $E(\alpha,\beta,\gamma)$ for the dihedral angle combinations that are responsible for particularly large deviations. We have done this only for those n-Si$_6$Me$_{14}$ conformers whose $E_{\rm calc}$ and $E^0_{\rm incr}$ values differed by more than 0.2 kcal/mol. This required the introduction of 3−6 new increments for the ab initio methods (Table 5), and of 6 for the MM3 method, respectively, and a least-squares optimization using eq 2 yielded augmented increment sets $\{E''(\alpha), E''(\alpha,\beta), E''(\alpha,\beta,\gamma)\}$ (Figures 5−9).

$$E_{\rm incr}(\alpha_1,\alpha_2,...,\alpha_{n-3}) - E({\rm t}_+,{\rm t}_+,...,{\rm t}_+) = \sum_{i=1}^{n-3} E(\alpha_i) + \sum_{i=1}^{n-4} E(\alpha_i,\alpha_{i+1}) + \sum_{i=1}^{n-5} E(\alpha_i,\alpha_{i+1},\alpha_{i+2}) \quad (2)$$

The correlation between E_{calc} and E''_{incr} is superior and mean deviations are below 0.05 kcal/mol for all four methods. However, for MM2 it requires the inclusion of 12 new $E''(\alpha,\beta,\gamma)$ increments to reduce the mean deviation to 0.04 kcal/mol, and this appears excessive. This increased lack of additivity in the MM2 results seems exaggerated. It could be related to the wide variation in the optimized dihedral angles (e.g., the $o_\pm$ twist in the $o_+g_-g_-$ conformer is ∼20° off the value in Si_4Me_{10}), which imposes demands on parameter values well outside the region for which they were optimized. These demands appears to be excessive in the case of MM2 and less so for MM3. We believe that the MM2 method is less reliable than the others when applied to oligosilanes.

To permit computation of relative energies of conformers with anti dihedral angles, we added two increments $E''(\alpha,\beta,\gamma)$ that were derived from the energies of the t_+at_- and o_+ao_- conformers of Si_6Me_{14}. Since the anti bond conformation only exists in these two combinations, $E''(a)$ does not need to be defined. The $E''(t_+at_-)$ increment fully describes the contribution of a t_+at_- segment to the energy of a permethylated oligosilane, and a sum of twice the $E''(o)$ plus the $E''(o_+ao_-)$ increments describes the contribution provided by an o_+ao_- segment.

Stabilities of *n*-Si_7Me_{16} and *n*-Si_8Me_{18} Conformers. The validity of the increment models can only be tested on longer oligosilanes. It is likely that the energies of even more grossly distorted high-energy conformers will again deviate from additivity, and to fit them without affecting the rest, one would need to include in eq 2 increments of the type $E(\alpha,\beta,\gamma,\delta)$, etc., ad infinitum. Clearly, to be useful the chain has to be truncated somewhere. A formal justification is the ever-increasing energy of the highly distorted conformers, which will be underestimated by E_{incr}. Once this is high enough for them to be of no practical interest, the chain can be truncated. It appears likely that the truncation point has now been reached, as E''_{incr} agrees with E_{calc} even for those conformers of *n*-Si_6Me_{14} whose energy is 4 kcal/mol above $E(t_+t_+t_+)$. We expect that only those conformers of Si_7Me_{16} and longer chains whose relative energies are even higher in relative energy will be subject to significant energy underestimate, and we have tested these notions on a few selected *n*-Si_7Me_{16} and *n*-Si_8Me_{18} conformers (Table 7).

HF/3-21G(d), MM2, and MM3 calculations were done for the following stable *n*-Si_7Me_{16} conformers: (i) the multitude of all-transoid conformers, (ii) the two conformers with favorable interactions that contain both t_+ conformations and one g_+ bond conformation, (iii) the four conformers with favorable bond interactions that have two g_+ and two t_+ bond conformations, (iv) conformers containing one o_- compared to one g_+ twist, and finally, (v) high-energy conformers with mixtures of $t_\pm$, $o_\pm$, and $g_\pm$ bond conformations, including some with unfavorable bond interactions (Figure 1), likely to show deviations from additivity. Five *n*-Si_8Me_{18} conformers were also investigated. These were selected so as to encompass the two most stable all-transoid conformers, two conformers with $g_\pm$ twists, and one high-energy conformer for which it may be difficult to calculate the conformer energy from increments.

For *n*-Si_7Me_{16} the existence of two all-transoid conformers has been proposed from experiments.[14] The most stable is assigned as $t_+t_+t_+t_+$, whereas the second was tentatively assigned as $t_+t_+t_-t_-$. At present it is not clear from calculations whether the latter has a symmetric structure ($t_+t_+t_-t_-$) or if it is better represented as $t_+t_+at_-$ since different levels of calculation give different results. For the time being, we shall assume the symmetric $t_+t_+t_-t_-$ structure. The deviation between E_{calc} and E^0_{incr} for the $t_+t_+t_-t_-$ conformer is large at the HF/3-21G(d) level and the stability order of $t_+t_+t_-t_-$ and $t_+t_+t_+g_+$ disagrees with that found from actual calculations (Table 7). The use of E'_{incr} leads to a lowering of the conformer energy of $t_+t_+t_-t_-$, and thus to a better stability order, and further improvement is obtained with E''_{incr}. The same is true for the ordering of $t_+t_+t_+t_-t_-$ and $t_+t_+t_+t_+g_+$ conformers of *n*-Si_8Me_{18}, where the correct order is only obtained with E'_{incr} and E''_{incr}.

At HF/3-21G(d) level the E^0_{incr} values are equal for the $t_+t_+t_+g_+$ and $t_+t_+g_+t_+$ conformers, but according to E_{calc} the $t_+t_+t_+g_+$ conformer is more stable by 0.07 kcal/mol. The E'_{incr} value clearly overcorrects this error, and the energy separation is only 0.03 kcal/mol too large when E''_{incr} is used. With the molecular mechanics methods, the correct ordering of MM2 conformer energies is found already with the original increment set. However, with MM3 the energy difference between $t_+t_+t_+g_+$ and $t_+t_+g_+t_+$ is merely 0.04 kcal/mol, and the ordering of these conformers cannot be correctly described with the increment method since with the $\{E''(\alpha), E''(\alpha,\beta), E''(\alpha,\beta,\gamma)\}$ set the two conformers become isoenergetic.

For Si_7Me_{16} and Si_8Me_{18} conformers that contain segments that are difficult to describe with increment methods the agreement at HF/3-21G(d) level is good when the $\{E''(\alpha), E''(\alpha,\beta), E''(\alpha,\beta,\gamma)\}$ set is used (within less than 0.09 kcal/mol for Si_7Me_{16} and 0.11 kcal/mol for Si_8Me_{18}). With this method, the mean deviation between E_{calc} and E_{incr} is also drastically reduced when the increment set is improved (Figure 10 and Table 7). Conformer energies derived from molecular mechanics based increments are not in equally good accordance with actual calculated energies. The deviation of E''_{incr} from E_{calc} is worst for MM2, but even for MM3 deviations by as much as 0.26 kcal/mol can be noted. Thus, usage of increment sets derived from molecular mechanics methods should not be encouraged. On the other hand, increment sets which are based on ab initio results are likely to give correct conformer energies for any permethylated oligosilane and polysilane with a precision of approximately 0.05 kcal/mol.

Conclusions

According to the ab initio methods used in this study, the all-transoid is the most stable conformer of *n*-Si_6Me_{14}. This is also the case at the MM2 level, whereas with MM3 several conformers which contain $g_\pm$ beside $t_\pm$ twists are of lower relative energy.

The purpose of the study was to verify that additive increment sets can be used to derive relative conformer energies of linear permethylated oligosilanes. Such increment sets were derived at three levels of sophistication. At the lowest level, increments were derived from relative energies of *n*-Si_4Me_{10} and *n*-Si_5Me_{12} conformers. For conformers which contain o_+g_- and o_+g_+ fragments this increment set leads to significant deviations between conformer energies derived from increments (E_{incr}) and those obtained from calculations (E_{calc}). Use of data from *n*-Si_6Me_{14} in the least-squares optimization of the increment sets gave only slightly better results. However, the inclusion of a small number (3−6) of increments $E(\alpha,\beta,\gamma)$ that describe next-nearest bond interactions for the problematic conformers leads to a dramatic improvement. With these increment sets conformer energies can be computed that agree with those calculated with mean deviations below 0.05 kcal/mol. A preliminary test against the energies of 20 Si_7Me_{16} and Si_8Me_{18} conformers that were not used in increment optimization shows an excellent agreement. The mean deviation with all methods is less than 0.07 kcal/mol, and with HF/3-21G(d) in particular it is 0.04 kcal/

mol. The situation is questionable for MM2 since 12 increments of the type $E(\alpha,\beta,\gamma)$ had to be included to obtain this level of agreement. This large degree of nonadditivity appears suspicious and we discourage the use of this method for oligosilanes.

It appears that the HF (and MM2) results better reflect the relative stabilities of the conformers in solution, whereas MP2 (and MM3) reflect the situation in the gas phase, but additional experimental data are desperately needed. Given that the increment sets are applicable also for long oligosilanes and polysilanes, the energies derived from the MP2-based increments should at present be the best available estimates of the stabilities of various conformations of such long chains in isolation. Energies obtained from HF-based increments probably are the best for solutions in nonpolar solvents.

The next objective in this series of investigations is to derive additive increment values that will accurately reproduce experimental relative free energies of all low-energy conformers of permethylated oligosilanes and polysilanes in isolation and in nonpolar solution. This requires calculations with a better basis set, a better treatment of electron correlation, inclusion of zero-point energies and rotational and vibrational entropies, and in the latter case, inclusion of solvation energies. It would have been hopeless to do this for all possible conformers of Si_4Me_{10}, Si_5Me_{12}, and Si_6Me_{14}, but with the guidance provided by the present study, it should be possible to perform the most demanding calculations on a rather limited set of conformers and still achieve the goal.

We recognize that the barriers that separate the conformational minima will ultimately be of interest as well. We have already examined the energy contour map of n-Si_5Me_{12} as a function of the two Si backbone dihedral angles at the MM2 and MM3 levels,[16] but much more remains to be done.

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Supporting Information Available: Tables listing the stability order of n-Si_6Me_{14} conformers, energies E_{calc} and E_{incr} of selected n-Si_7Me_{16} and n-Si_8Me_{18} conformers, calculated vibrational frequencies, and IR and Raman intensities for n-Si_6Me_{14} conformers; and schematic plots of the IR and Raman spectra of n-Si_6Me_{14} conformers. This material is available free of charge via the Internet at http://pubs.acs.org.

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