

Calculation of Relative Energies of Permethylated Oligosilane Conformers in Vapor and in Alkane Solution[†]

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The geometries of 35 conformers of $\text{Me}(\text{SiMe}_2)_n\text{Me}$ ($n = 4$, **1**; $n = 5$, **2**; $n = 6$, **3**; $n = 7$, **4**) were optimized at the MP2/VT-DZ level, and CCSD(T) single-point calculations were done at three MP2/VT-DZ conformer geometries of **1**. The relative ground-state energies of the conformers of **1–4** in the gas phase were obtained from the MP2/VT-DZ electronic energy, zero-point vibrational energy, and thermal corrections at 0, 77, and 298 K. Relative energies in an alkane solvent at 77 and 298 K were obtained by the addition of solvation energies, obtained from the SM5.42R model. The calculated energies of 26 of the conformers ($n = 4–6$) have been least-squares fitted to a set of 15 additive increments associated with each Si–Si bond conformation and each pair of adjacent bond conformations, with mean deviations of 0.06–0.20 kcal/mol. An even better fit for the energies of 24 conformers (mean deviations, 0.01–0.09 kcal/mol) has been obtained with a larger set of 19 increments, which also contained contributions from selected combinations of conformations of three adjacent bonds. The utility of the additive increments for the prediction of relative conformer energies in the gas phase and in solution has been tested on the remaining nine conformers ($n = 6, 7$). With the improved increment set, the average deviation from the SM5.42R//MP2 results for solvated conformers at 298 K was 0.18 kcal/mol, and the maximum error was 0.98 kcal/mol.

Introduction

The stable and readily available peralkylated linear oligosilanes and polysilanes, $\text{Si}_n\text{R}_{2n+2}$, are silicon analogues of alkanes and polyalkenes.¹ It is believed that many of the conformations of their silicon backbone have comparable energies, are separated by very small barriers, and are readily interconverted and essentially inseparable, even more so than the conformers of alkanes. The conformational properties reflect the intrinsic properties of the Si–Si bond as well as the length and bulk of lateral substituents. The composition of the equilibrium conformational mixture is sensitive both to the temperature and to the environment. Since the different conformations of a chain often have vastly different optical properties, especially in the near-UV region, solutions of oligosilanes^{2–6} and polysilanes^{1,7–9} and the neat solids¹⁰ commonly exhibit striking thermochromism, solvatochromism,¹¹ and similar phenomena. In principle, this permits a determination of the spectral properties of individual constituents of the conformational mixture, especially when combined with fluorescence and fluorescence excitation spectroscopy. We have been engaged in an experimental program directed toward this goal. However, even after the constituents of the conformational mixture have been individually spectrally characterized, the task of assigning their structures is not straightforward. Here, quantum theory can help in two ways, by predicting the relative conformer energies and by predicting conformer spectra. If reliable assignments can be made, then oligosilanes may well represent an ideal ground for the investigation of the conformational dependence of sigma

electron delocalization, a subject about which little is known from experiments or from theory.

Much computational work has been done to determine the relative energies of the conformers of decamethyltetrasilane **1**^{12–16} (Chart 1) and some longer permethylated silicon chains.^{13,15} It was found that the conformer energies can be expressed in terms of additive increments associated with the conformations of individual Si–Si bonds and pairs and triples of adjacent bonds, and such sets of energy increments have been compiled at several levels of theory.^{13,15} They are useful for the facile calculation of relative energies of permethylated silanes in the gas phase. Thermal energy corrections were previously applied in obtaining the HF/3-21G(d) relative energies of **1**^{13,16} and **2**¹³ but not **3**.¹⁵ None of the conformational computations explicitly included solvation effects even though almost all of the experimental work is done in solution, but this earlier work clearly identified the combinations of adjacent bond conformations and even the specific conformers that need to be included in a search for a reliable increment set.

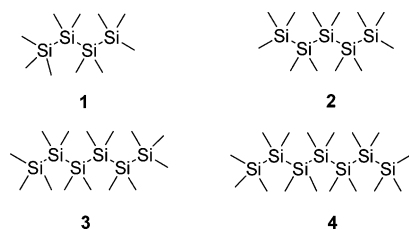
Permethylated oligosilanes were found to have up to six conformational minima for rotation around each internal Si–Si bond,^{17,18} as opposed to the three in linear alkanes. In $\text{Si}_4\text{Me}_{10}$ (**1**), they occur at Si–Si–Si–Si dihedral angles ω of approximately ± 55 (g_{\pm}), ± 90 (o_{\pm}), and $\pm 165^\circ$ (t_{\pm}), essentially independently of the level of calculation.^{19,20} The existence of the o_{\pm} conformer and the shift of the dihedral angle in the g_{\pm} conformer to values smaller than 60° are due to steric interactions between substituents in the 1 and 4 positions of the silicon backbone, and they were first computationally predicted²¹ and then observed^{22,23} in perfluoroalkanes. The splitting of the anti (a , 180°) minimum into t_{\pm} minima is due to steric interactions between substituents located in backbone positions 1 and 3.²⁴ The size of the substituent, relative to the bond lengths of the

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CHART 1: Structure of Me(SiMe₂)_nMe, *n* = 4 (1**), *n* = 5 (**2**), *n* = 6 (**3**), *n* = 7 (**4**), Me = CH₃****TABLE 1: Nomenclature for Dihedral Angle Conformations in Linear Chains²⁰**

conformation	ω
anti, a	$\pm 176\text{--}180^\circ$
transoid, t_\pm	$\pm 160\text{--}175^\circ$
deviant, d_\pm	$\pm 140\text{--}159^\circ$
eclipsed, e_\pm	$\pm 110\text{--}130^\circ$
ortho, o_\pm	$\pm 75\text{--}105^\circ$
gauche, g_\pm	$\pm 50\text{--}70^\circ$
cisoid, c_\pm	$\pm 25\text{--}49^\circ$
syn, s_\pm	$0\text{--}\pm 20^\circ$

backbone chain, that is necessary for the occurrence of the six minima was identified in a study of linear saturated A₄X₁₀ chains (A = C, Si; X = H, F, Cl, Br, CH₃, SiH₃).²⁴ In certain conformers of oligosilanes carrying larger substituents, some of these minima are shifted, commonly from ω values of 55° to approximately 40° and from 165° to approximately 155° .^{25,26} The nomenclature proposed²⁰ for chain conformations is summarized in Table 1.

For linear permethylated oligosilanes, Me(SiMe₂)_nMe, the number of possible conformers increases rapidly with *n* as the six favored dihedral angles, t_+ , t_- , o_+ , o_- , g_+ , and g_- , can combine in any order. For instance, in **3** there are 63 possible enantiomeric pairs.¹⁵ In the following, we consider only one member of an enantiomeric pair with the understanding that all properties not involving interactions with chiral light or other chiral objects are identical for the other member. In chains of more than four Si atoms, certain combinations of Si–Si–Si–Si backbone dihedral angles do not correspond to minima at some or all levels of calculation, reducing the number of stable conformers somewhat.^{13,15} This is related to the fact that certain combinations of adjacent backbone dihedral angles are generally favorable whereas others are unfavorable.^{13,15} Transoid dihedral angles having a positive sense of twist, t_+ , adjacent to transoid or gauche dihedral angles with the same sense of twist, t_+ or g_+ , or to an ortho dihedral angle having the opposite sense of twist, o_- , produce the low-energy conformers of **2**, t_+t_+ , t_+g_+ , and t_+o_- (the energy difference relative to the most stable conformer, ΔE , is less than 1 kcal/mol at the HF/3-21G(d) level of calculation¹⁵). Conformers of moderate relative energy, $\Delta E = 1\text{--}2$ kcal/mol, occur with o_+g_- , g_+g_+ , o_+o_+ , and t_+g_- combinations. Other combinations such as t_+o_+ and o_+g_+ are calculated to be much higher in energy, while the meso conformers t_+t_- , o_+o_- , and g_+g_- are not local minima on the *S*₀ potential energy surface (PES) at the HF/3-21G(d) level.^{13,15}

The softest vibrational mode in permethylated oligosilanes corresponds to rotation around a Si–Si bond, and the barriers to interconversion among conformers are calculated to be small.^{12,13,15} The barriers in **1** calculated at the HF/6-31G(d) level are 0.5 kcal/mol for the interconversion of the t_+ and t_- conformers, ~ 1.8 kcal/mol for the conversion of the t_+ conformer to o_+ , and less than 0.5 kcal/mol for the conversion of the o_+ conformer to g_+ .¹² A higher value, ~ 6 kcal/mol, was estimated for the barrier to conformational change in **1** from

variable-temperature NMR measurements in halogenated alkane solution²⁷ before it was realized that there are six rather than three conformers in the mixture. In the same study, the t_\pm conformer of **1** was found to be the most stable by 0.5 kcal/mol from variable-temperature Raman data. In longer chains, at the HF/6-31G(d) level of calculation, the barrier for interconversion between the extended conformers $2t_+t_+$ and $2t_-t_-$ is less than 1 kcal/mol, while the barrier between the twisted conformers $2g_+o_-$ and $2g_-o_+$ is 3.7 kcal/mol.¹³

Attempts to identify the three conformers of **1** experimentally using UV absorption spectroscopy on matrix-isolated photoselected samples allowed the separation of the spectra of the t_\pm conformer and the sum of the twisted (o_\pm and g_\pm) conformers.¹² Gas electron diffraction experiments on **1** confirmed the presence of the t_\pm and g_\pm conformers and found the existence of the o_\pm conformer probable.¹⁴ Raman studies²⁸ identified all three conformer pairs in matrix-isolated samples of *n*-Si₄Cl₁₀. The Cl substituent is similar in size to a methyl group, and the same six minima were calculated for *n*-Si₄Cl₁₀ at several levels of theory. The Raman spectra of the g_\pm and o_\pm conformers of **1** itself are calculated to resemble each other too much to permit a clear differentiation. Multiple instances of o_\pm conformations have been observed in permethylated cyclosilanes²⁹ and permethylated dendritic silanes.^{30,31}

Presently, we have attempted to find the relative energies of oligosilane conformers including corrections for zero-point vibrational energy (ZPVE), enthalpy, entropy, and solvation free energy, using computational methods that provide the best treatment currently possible for medium-sized molecular systems that include second-row atoms. The combined results provide the total relative free energy for conformers of **1–4** at three temperatures in the gas phase and two temperatures in solution phase.

For the purpose of simplifying the discussion when it is not necessary to refer to a specific conformer, *a* and t_\pm are defined as extended conformations, while o_\pm , and g_\pm are twisted conformations. Among twisted conformers, only those with one or at most two bonds in an o_\pm or g_\pm conformation, and the rest in t_\pm , have a reasonably low energy and are likely to be observed experimentally.

Computational Methods

Geometry optimizations were performed with Gaussian 98, revisions A.6, A.7, or A.9, or Gaussian 03, revisions C.02 or D.01. HONDO/S version 3.4.1³² was used for calculation of the solvation energies of rigid gas-phase geometries and in attempts to optimize the geometries of conformers of **1** in solution. Least-squares fitting of the energy and conformation matrices was performed with Mathematica 5.0.0.0³³ running under Windows.

Geometries were fully optimized with the MP2 method using a mixed basis set of VTZ quality on Si with polarization functions on Si and C (Si, 6-311G(d); C, 6-31G(d); H, 31G). This basis set, VTDZ, is the largest at which full optimization of conformers of **4** could be performed in a reasonable time with the available computational resources. Comparison of the basis set effect on the geometry and relative energy of the three conformers of **1**, resulting from full optimization at the MP2 level using the six basis sets listed in Table S1 of the Supporting Information, shows a maximum difference of 0.011 Å in Si–Si bond lengths, 1.5° in Si–Si–Si–Si dihedral angles, and 0.184 kcal/mol in relative energy. The optimization procedure was begun at the HF/3-21G(d) level and was continued at the MP2/

6-31G(d) level before concluding at the MP2/VT-DZ level. Symmetry was used when present. The estimated change in energy for a further convergence step was always less than -1.2×10^{-8} hartree for optimization at the MP2/VT-DZ level for all conformers except 2_{t+t-} .

Multiple attempts to locate a minimum corresponding to the t_{+t-} conformer of **2** were unsuccessful, as the geometry always optimized to t_{+t+} . The attempts included a search at the MP2/6-31G(d) level varying both Si–Si–Si–Si dihedral angles and an optimization with the Si–Si–Si–Si dihedral angles constrained, followed by full relaxation of the resulting geometry with the constraints removed. However, as the t_{+t-} conformational arrangement is believed to occur in longer Si chains, a scan of the PES at the MP2/6-31G(d) level was performed, and a saddle point on the surface corresponding to a t_{+t-} geometry was located.³⁴ For a further convergence step the predicted change in energy was -2.2×10^{-8} hartree. This geometry was used in an MP2/VT-DZ single-point calculation to obtain the electronic energy and in the calculations of solvation energy.

Single-point coupled cluster calculations using single, double, and triple (perturbative) excitations, CCSD(T)/VT-DZ, were performed at the MP2/VT-DZ geometries of the three conformers of **1**, **t**, **g**, and **o**.

Vibrational frequency calculations for the three conformers of **1** were performed at the MP2/6-31G(d), HF/6-31G(d), and HF/3-21G(d) levels of calculation in order to compare the relative zero-point vibrational energies ($\Delta ZPVE$ s). As the three levels gave nearly identical $\Delta ZPVE$ values and results were needed for a large number of conformer frequency calculations, only scaled HF/3-21G(d) vibrational frequencies were used subsequently. The term thermal correction refers to application of the zero-point energy at 0 K or enthalpy and entropy corrections at 77 or 298 K as the enthalpy correction at temperatures above 0 K included the ZPVE. The HF/3-21G(d) thermal corrections to entropy and enthalpy at temperatures of 298 and 77 K and the ZPVE were obtained by use of the freqchk utility in Gaussian 98. The scaling factors recommended by Scott and Radom for the HF/3-21G level were applied: ZPVE, 0.9207; enthalpy corrections, 0.9444; entropy corrections, 0.9666.³⁵ The t_{+t-} conformation was a saddle point at the HF/3-21G(d) level used to calculate the ZPVE and the thermal corrections.

Two types of calculations were performed on solvated oligosilanes with the continuum self-consistent reaction field (SCRF) method,³² using the solvation model SM5.42R³⁶ in the HONDO/S program³² at the HF/6-31G(d) level: (i) determination of ΔG_s^{298} (298 K) and ΔG_s^{77} (77 K) at a rigid MP2/VT-DZ gas-phase optimized geometry and (ii) geometry optimization of solvated conformers of **1** at 298 K. To obtain the relative energies of solvated oligosilane conformers a correction for the energy of solvation, ΔG_s , was added to the gas-phase relative energy.

Attempts to optimize the cyclopentane solvated geometries of the t_{+} , g_{+} , and o_{+} conformers of **1** using SM5.42 with a HF/6-31G(d) basis set failed to converge after 900 cycles. The final geometries differed from the starting MP2/VT-DZ-optimized geometries in ways that have been noted previously as typical of the use of the HF/6-31G(d) basis set on silanes.^{15,43} The final Si–Si bond lengths were 2.38–2.40 Å, an increase of 0.05–0.08 Å, and $\angle \text{Si–Si–Si}$ values were 1–2° larger while ω varied less than 1°. It is known that reoptimizing geometries in the presence of solvent generally gives a difference that is smaller than the average uncertainty in the model.³⁶ Subsequently, only the rigid-geometry solvation energies were used.

TABLE 2: Solvent Descriptors for Cyclopentane

	298 K ^a	77 K
ϵ	1.9608	2.2 ^b
n_D^{20}	1.4036	1.5318 ^a
γ	31.49	72.39 ^c
α	0.0	0.0
β	0.0	0.0

^a Reference 37. ^b Estimated to be 2.2 from $\Delta\epsilon/\Delta T$ of *n*-pentane.³⁸
^c Reference 40.

Cyclopentane solvent parameters at 298 K were obtained from the Minnesota Solvent Descriptor Database.³⁷ The solvent descriptors were the dielectric constant, ϵ , the index of refraction at optical frequencies, n_D^{20} , the macroscopic surface tension, γ , and Abraham's hydrogen bond acidity, α , and basicity, β (Table 2). The parameters for cyclopentane at 77 K (Table 2) were obtained from $\Delta\epsilon/\Delta T$, which was estimated to be 2.2 from the $\Delta\epsilon/\Delta T$ value of *n*-pentane,³⁸ and $\Delta n/\Delta T$ (and compared with the values for cyclohexane and *n*-pentane),³⁹ while γ was estimated from the slope of the line $\Delta\gamma/\Delta T$.⁴⁰

The values of additive energy increments were determined by least-squares optimization of a set of conformer $\Delta\Delta G_{\text{calc}}$ values against the number and type of conformations (i.e., **t**, **g**, or **o**) and interactions between adjacent conformations (i.e., the interaction of t_{+} and g_{+} in the $t_{+}g_{+}$ conformer) for each conformer in the set. The fitting was done on an overdetermined set of equations using the PseudoInverse function in Mathematica.³³

Results

The choice of conformers of **1–3** to optimize was based on experience gathered in previous work^{13,15} on the relative stability of gas-phase conformers of **1–3** and on the necessity of including all stable conformers and all possible reasonably low-energy combinations of bond conformations, preferably present in multiple conformers. The three stable conformers of **1**, the seven conformers of **2** that correspond to local minima at the MP2/6-31G(d) level of calculation, and the 2_{t+t-} conformer were included. The conformers of **3** used in the derivation of the additive increments consist of the seven lowest-energy stable conformers found earlier at the HF/3-21G(d) level¹⁵ plus the all- g_{+} and all- o_{+} conformers. In addition, four conformers of **3** that were previously found to contain important noncontiguous interactions,¹⁵ $t_{+}g_{+}o_{-}$, $o_{+}g_{-}o_{+}$, $o_{+}g_{-}g_{-}$, and $o_{+}g_{+}g_{+}$, were included. The meso conformers $t_{+}at_{-}$ and $o_{+}ao_{-}$ were included to allow the determination of the increments for **a**, **at**, and **ao** needed for conformers containing the unusual anti conformation. The existence of the anti conformation in longer chains is of possible importance, as it would provide a low-energy path for a reversal of helicity.^{13,15} To test the derived increment sets on conformers not used in the derivation, nine additional conformers, three of **3** and six of **4**, were also optimized.

The relative MP2/VT-DZ//MP2/VT-DZ electronic energies, ΔE_0 , of the 35 conformers of **1–4** are listed in Table 3 ordered by ΔE_0 , along with the HF/6-31G(d)//MP2/VT-DZ relative free energy of solvation, $\Delta\Delta G_s$ at 298 and 77 K, and the scaled HF/3-21G(d)//HF/3-21G(d) relative zero-point vibrational energy, $\Delta ZPVE$. Energies are listed relative to the energy of the all- t_{+} conformer of each compound. For the three conformers of **1**, CCSD(T)/VT-DZ//MP2/VT-DZ values are included for comparison. Important conformer geometry parameters are presented in Table S2 of the Supporting Information, again ordered by increasing ΔE_0 values.

The all- t_{+} conformer has been previously found to be the lowest-energy conformer in permethylated oligosilanes with ab

TABLE 3: Relative MP2/VTDZ//MP2/VTDZ Electronic Energy ΔE , HF/6-31G(d)//MP2/VTDZ Solvation Energy $\Delta\Delta G_s$, and Scaled HF/3-21G(d)//HF/3-21G(d) Zero-Point Vibrational Energy $\Delta ZPVE$ for Conformers of 1–4 (kcal/mol)

conformer	ΔE_0 , MP2/VTDZ	$\Delta\Delta G_s$ 298 K (liq)	$\Delta\Delta G_s$ 77 K (liq)	$\Delta ZPVE$
Si₄Me₁₀ (1)				
t ₊	0, −1553.6445773 ^a (0, −1553.8890969 ^a) ^b	0 (−9.963) ^c	0 (−6.110) ^c	0 (230.15449) ^d
g ₊	0.215 (0.207) ^b	−0.045	−0.052	0.044
o ₊	0.535 (0.505) ^b	−0.038	−0.041	0.071
Si₅Me₁₂ (2)				
t ₊ t ₊	0 (−1922.1818567) ^a	0 (−12.221) ^c	0 (−7.603) ^c	0 (277.30007) ^d
t ₊ g ₊	0.256	−0.030	−0.034	0.096
t ₊ o _−	0.596	−0.031	−0.034	0.092
g ₊ g ₊	0.640	−0.024	−0.035	0.150
t ₊ g _−	0.926	−0.021	−0.029	0.094
o ₊ o ₊	1.191	−0.041	−0.042	0.191
o ₊ g _−	1.265	−0.068	−0.056	0.174
t ₊ t _− ^e	0.964	−0.032	−0.030	0.037
Si₆Me₁₄ (3)				
t ₊ t ₊ t ₊	0 (−2288.3532114) ^a	0 (−14.462) ^c	0 (−9.078) ^c	0 (323.91724) ^d
t ₊ t ₊ g ₊	0.298	−0.044	−0.052	0.093
t ₊ g ₊ t ₊	0.354	−0.007	−0.008	0.104
g ₊ t ₊ g ₊	0.562	−0.083	−0.093	0.184
t ₊ t ₊ o _−	0.610	−0.044	−0.048	0.097
t ₊ o _− t ₊	0.623	−0.027	−0.029	0.096
t ₊ g ₊ g ₊ ^f	0.688	−0.011	−0.021	0.149
t ₊ at _−	0.706	+0.028	−0.028	0.053
o ₊ t _− o ₊ ^f	0.942	−0.091	−0.089	0.196
o ₊ t _− g _−	0.959	−0.066	−0.074	0.188
g ₊ g ₊ g ₊	1.213	−0.034	−0.047	0.201
t ₊ o _− o _− ^f	1.236	−0.208	−0.234	0.198
t ₊ g ₊ o _−	1.593	−0.043	−0.058	0.205
o ₊ g ₊ g ₊	1.734	−0.035	−0.047	0.238
o ₊ ao _−	1.815	−0.091	−0.093	0.265
o ₊ o ₊ o ₊	2.003	−0.071	−0.072	0.289
o ₊ g _− g _−	2.058	−0.066	−0.083	0.283
o ₊ g _− o ₊	3.279	−0.040	−0.081	0.470
Si₇Me₁₆ (4)^f				
t ₊ t ₊ t ₊ t ₊	0 (−2659.2566935) ^a	0 (−16.730) ^c	0 (−10.583) ^c	0 (370.53499) ^d
t ₊ g ₊ g ₊ t ₊	0.751	−0.039	−0.039	0.144
o ₊ t _− t _− o ₊	1.198	+0.037	+0.030	0.197
t ₊ o _− o _− t ₊	1.310	−0.039	−0.039	0.210
g ₊ o _− o _− g ₊	1.926	−0.040	−0.065	0.503
o ₊ g _− g _− o ₊	3.442	−0.028	−0.060	0.211

^a Total electronic energy in hartree. ^b CCSD(T)/VTDZ//MP2/VTDZ electronic energy. ^c The calculated ΔG_s (kcal/mol) for the reference conformer is given in parentheses. ^d The calculated and scaled ZPVE (kcal/mol) for the reference conformer are given in parentheses. ^e MP2/6-31G(d) stationary point geometry. ^f Conformers used only for testing increments.

initio^{12,13,15,16} and some molecular mechanics^{12,13,15} methods. The total conformer energy for five temperature/phase conditions was obtained as follows: (i) 0 K gas phase, E_{gcalc}^0 , from the sum of the electronic energy, E_0 , and the ZPVE, (ii) 77 K gas phase, $\Delta G_{\text{gcalc}}^{77}$, from the sum of the electronic energy, E_0 , and 77 K thermal corrections for enthalpy, H^{77} , and entropy, TS^{77} , (iii) 298 K gas phase, $\Delta G_{\text{gcalc}}^{298}$, from the sum of the electronic energy, E_0 , and 298 K thermal corrections for enthalpy, H^{298} , and entropy, TS^{298} , (iv) 77 K solution phase, $\Delta G_{\text{gcalc}}^{77}$, from the sum of E_0 , H^{77} , TS^{77} , and the solvation free energy at 77 K, ΔG_s^{77} , and (v) 298 K solution phase, $\Delta G_{\text{gcalc}}^{298}$, from the sum of E_0 , H^{298} , TS^{298} , and the solvation free energy at 298 K, ΔG_s^{298} . Equations 1–5 were used to calculate the relative energy at 0 K, $\Delta E_{\text{gcalc}}^0$, and the relative free energy, $\Delta\Delta G_{\text{gcalc}}$. The resulting values for conformers of 1–4 are listed in Table 4 (kcal/mol).

$$\Delta E_{\text{gcalc}}^0 = \Delta E_0 + \Delta ZPVE \quad (1)$$

$$\Delta\Delta G_{\text{gcalc}}^{77} = \Delta E_0 + \Delta H^{77} + T\Delta S^{77} \quad (2)$$

$$\Delta\Delta G_{\text{gcalc}}^{298} = \Delta E_0 + \Delta H^{298} + T\Delta S^{298} \quad (3)$$

$$\Delta\Delta G_{\text{gcalc}}^{77} = \Delta E_0 + \Delta H^{77} + T\Delta S^{77} + \Delta G_s^{77} \quad (4)$$

$$\Delta\Delta G_{\text{gcalc}}^{298} = \Delta E_0 + \Delta H^{298} + T\Delta S^{298} + \Delta G_s^{298} \quad (5)$$

Two levels of fitting the G_{calc} values of the gas-phase results at 0, 77, and 298 K and the solution-phase results at 77 and 298 K provided 10 sets of additive increments. Five sets of 15 increments were derived from the relative total free energy of each conformer, $\Delta\Delta G_{\text{calc}}$ (Table 4), for 26 conformers of 1–3 (Tables 3 and S1 of the Supporting Information) and are presented in Table 5 as the sum of the appropriate gas-phase MP2/VTDZ//MP2/VTDZ energies, HF/3-21G(d)//HF/3-21G(d) thermal corrections,⁴¹ and HF/6-31G(d)//MP2/VTDZ solvation energies in cyclopentane. Each increment provides the relative total free energy, $\Delta\Delta G_{\text{incr}}$, of either one Si–Si–Si dihedral angle, $G(\alpha)$, or the interaction between two contiguous Si–Si–Si–Si dihedral angles, $G(\alpha,\beta)$, yielding the increment set $\{G'(\alpha), G'(\alpha,\beta)\}$ (eq 6, Table 5). Inclusion of the interaction between noncontiguous dihedral angles, $G(\alpha,\beta,\gamma)$, which first appear in hexasilane, yields the improved increment sets $\{G''(\alpha), G''(\alpha,\beta), G''(\alpha,\beta,\gamma)\}$ (eq 7). The t₊at_− and o₊ao_− conformers

TABLE 4: MP2/VTDZ//MP2/VTDZ Relative Energy at 0 K, $\Delta E^0_{\text{gcalc}}$, and the Relative Gas-Phase Free Energy, $\Delta\Delta G_{\text{gcalc}}$, and Solution Phase Free Energy, $\Delta\Delta G_{\text{scalc}}$, at 298 and 77 K for Conformers of 1–4 (kcal/mol)

conformer	ΔE^0	$\Delta\Delta G_{\text{g}}^{77}$	$\Delta\Delta G_{\text{g}}^{298}$	$\Delta\Delta G_{\text{s}}^{77}$	$\Delta\Delta G_{\text{s}}^{298}$
Si₄Me₁₀ (1)					
t ₊	0	0	0	0	0
g ₊	0.259	0.317	0.550	0.265	0.505
o ₊	0.606	0.599	0.666	0.558	0.628
Si₅Me₁₂ (2)					
t ₊ t ₊	0	0	0	0	0
t ₊ g ₊	0.351	0.318	0.380	0.284	0.350
t ₊ o ₊	0.689	0.596	0.520	0.562	0.489
g ₊ g ₊	0.790	0.907	1.482	0.872	1.458
t ₊ g ₊	1.020	0.929	0.861	0.900	0.840
o ₊ o ₊	1.382	1.451	1.971	1.409	1.930
o ₊ g ₊	1.439	1.383	1.439	1.327	1.371
t ₊ t ₊	1.001	1.003	1.780	0.973	1.748
Si₆Me₁₄ (3)					
t ₊ t ₊ t ₊	0	0	0	0	0
t ₊ t ₊ g ₊	0.390	0.363	0.378	0.311	0.334
t ₊ g ₊ t ₊	0.458	0.538	0.870	0.530	0.863
g ₊ t ₊ g ₊	0.745	0.904	1.547	0.811	1.464
t ₊ t ₊ o ₊	0.708	0.630	0.545	0.582	0.501
t ₊ o ₊ t ₊	0.719	0.753	0.995	0.724	0.968
t ₊ g ₊ g ₊	0.837	0.860	1.102	0.839	1.091
t ₊ at ₊	0.759	0.451	−0.474	0.423	−0.502
o ₊ t ₊ o ₊	1.138	1.211	1.706	1.122	1.615
o ₊ t ₊ g ₊	1.147	1.145	1.366	1.071	1.300
g ₊ g ₊ g ₊	1.414	1.601	2.342	1.554	2.314
t ₊ o ₊ o ₊	1.433	1.404	1.586	1.170	1.378
t ₊ g ₊ o ₊	1.798	1.724	1.684	1.666	1.641
o ₊ g ₊ g ₊	1.972	1.905	1.967	1.858	1.923
o ₊ ao ₊	2.080	1.888	1.634	1.795	1.543
o ₊ o ₊ o ₊	2.292	2.393	3.050	2.321	2.979
o ₊ g ₊ g ₊	2.341	2.262	2.306	2.179	2.240
o ₊ g ₊ o ₊	3.747	3.832	4.493	3.751	4.453
Si₇Me₁₆ (4)					
t ₊ t ₊ t ₊ t ₊	0	0	0	0	0
t ₊ g ₊ g ₊ t ₊	0.896	1.031	1.578	1.061	1.600
o ₊ t ₊ t ₊ o ₊	1.396	1.352	1.927	1.313	1.460
t ₊ o ₊ o ₊ t ₊	1.520	1.601	2.715	1.562	2.048
g ₊ o ₊ o ₊ g ₊	2.428	2.583	3.514	2.518	3.438
o ₊ g ₊ g ₊ o ₊	3.653	4.105	4.243	4.045	4.195

were removed from the set of conformers whose corrected relative energies were used to determine the $\{G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma)\}$ sets. Instead, seven high-energy conformer interactions first appearing in **3** were included in the fitting of the $\{G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma)\}$ sets: t₊g₊o₊, o₊t₊g₊, o₊o₊o₊, o₊g₊o₊, o₊g₊g₊, o₊g₊g₊, and g₊g₊g₊. Five of these improved sets, each containing 19 increments, were derived from the same energy data for 24 conformers of **1–3** (Tables 3 and S1 of the Supporting Information) and are presented in Table 6.

Application of these additive increments is meant to provide an approximation to the free energy of any given conformer of any linear permethylated oligosilane or polysilane relative to the all-t₊ conformer of the same length under the specified conditions of phase and temperature, provided that the conformation does not loop back on itself (is sufficiently self-avoiding).

$$G_{\text{incr}}(\alpha_1, \alpha_2, \dots, \alpha_{n-3}) - G(t_+, t_+, \dots, t_+) = \sum_{i=1}^{n-3} G(\alpha_i) + \sum_{i=1}^{n-4} G(\alpha_i, \alpha_{i+1}) \quad (6)$$

TABLE 5: Additive Increment Sets $\{G'(\alpha), G'(\alpha, \beta)\}$ and Their Mean Deviation for the Gas Phase, G_{ginc} , at 0, 77, and 298 K, and Cyclopentane Solution Phase, G_{sinc} , at 77 and 298 K (kcal/mol)

increment type	gas phase			cyclopentane solution	
	G_{ginc} 0 K	G_{ginc} 77 K	G_{ginc} 298 K	G_{sinc} 77 K	G_{sinc} 298 K
$G'(\alpha)$					
t ₊	0	0	0	0	0
g ₊	0.251	0.296	0.474	0.235	0.469
o ₊	0.689	0.648	0.645	0.601	0.610
a	0.378	0.315	0.070	0.292	0.095
$G'(\alpha, \beta)$					
t ₊ t ₊	0	0	0	0	0
t ₊ o ₊	0.021	0.048	0.216	0.061	0.158
t ₊ g ₊	0.100	0.115	0.219	0.138	0.179
t ₊ g ₊	0.801	0.683	0.523	0.714	0.470
t ₊ t ₊	1.033	1.054	1.916	1.022	1.846
o ₊ o ₊	0.090	0.226	0.697	0.268	0.669
o ₊ g ₊	0.900	0.913	1.054	0.952	1.009
o ₊ g ₊	0.456	0.356	0.122	0.415	0.092
g ₊ g ₊	0.307	0.324	0.471	0.395	0.413
at	0.182	0.076	−0.163	0.077	−0.238
ao	0.153	0.146	0.246	0.162	0.174
mean dev.	0.126	0.132	0.270	0.140	0.248

TABLE 6: Additive Increment Sets $\{G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma)\}$ and Their Mean Deviation for the Gas Phase, G_{ginc} , at 0, 77, and 298 K, and Cyclopentane Solution Phase, G_{sinc} , at 77 and 298 K (kcal/mol)

increment type	gas phase			cyclopentane solution	
	G_{ginc} 0 K	G_{ginc} 77 K	G_{ginc} 298 K	G_{sinc} 77 K	G_{sinc} 298 K
$G''(\alpha)$					
t ₊	0	0	0	0	0
g ₊	0.279	0.321	0.516	0.250	0.454
o ₊	0.637	0.585	0.544	0.533	0.496
$G''(\alpha, \beta)$					
t ₊ t ₊	0	0	0	0	0
t ₊ o ₊	0.041	0.079	0.211	0.093	0.234
t ₊ g ₊	0.084	0.113	0.217	0.143	0.243
t ₊ g ₊	0.742	0.628	0.415	0.667	0.453
t ₊ t ₊	1.002	1.023	1.849	0.991	1.815
o ₊ o ₊	0.110	0.300	0.953	0.360	1.006
o ₊ g ₊	0.524	0.496	0.449	0.561	0.489
o ₊ g ₊	0.249	0.199	0.021	0.233	0.052
g ₊ g ₊	0.232	0.286	0.520	0.389	0.617
$G''(\alpha, \beta, \gamma)$					
t ₊ g ₊ o ₊	0.259	0.231	0.085	0.207	0.091
o ₊ t ₊ g ₊	0.092	0.069	−0.005	0.079	0.005
o ₊ o ₊ o ₊	0.148	0.059	−0.361	0.029	−0.389
o ₊ g ₊ o ₊	1.132	1.370	2.118	1.341	2.162
o ₊ g ₊ g ₊	0.281	0.215	−0.023	0.230	−0.009
o ₊ g ₊ g ₊	0.375	0.275	−0.112	0.223	−0.138
g ₊ g ₊ g ₊	0.098	0.089	−0.119	0.053	−0.151
mean dev.	0.038	0.065	0.200	0.077	0.182

$$G_{\text{incr}}(\alpha_1, \alpha_2, \dots, \alpha_{n-3}) - G(t_+, t_+, \dots, t_+) = \sum_{i=1}^{n-3} G(\alpha_i) + \sum_{i=1}^{n-4} G(\alpha_i, \alpha_{i+1}) + \sum_{i=1}^{n-5} G(\alpha_i, \alpha_{i+1}, \alpha_{i+2}) \quad (7)$$

The $\{G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma)\}$ increment sets were used to determine the relative energies of the 10 conformers of **3** and **4** listed in Table 7. The t₊t₊t₊ conformer of **3** and the t₊t₊t₊t₊ conformer of **4** are the reference conformers, for which all values are zero. The correlation between the relative total free energy of each conformer from ab initio calculation, $\Delta\Delta G_{\text{calc}}$, and that determined using the additive increment set $\{G'(\alpha), G'(\alpha, \beta)\}$, $\Delta\Delta G_{\text{ginc}}$, is shown in Figures S1 and S2 of

TABLE 7: Relative Energies of Selected Conformers of 3 and 4 from G_{calc} and from $\{G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma)\}$ Increments G_{ginc} at 0, 77, and 298 K and G_{ginc} at 77 and 298 K (kcal/mol)

conformer	G_{calc}			G_{calc}		$\Delta G_{\text{g}}(\alpha, \alpha\beta, \alpha\beta\gamma)$			$\Delta G_{\text{g}}(\alpha, \alpha\beta, \alpha\beta\gamma)$	
	0 K	77 K	298 K	77 K	298 K	0 K	77 K	298 K	77 K	298 K
Si₆Me₁₄ (3)										
t ₊ t ₊ t ₊	0	0	0	0	0	0	0	0	0	0
t ₊ g ₊ g ₊	0.837	0.860	1.102	0.839	1.091	0.875	1.039	1.768	1.030	1.768
o ₊ t ₋ o ₊	1.138	1.211	1.706	1.122	1.615	1.355	1.329	1.530	1.252	1.460
t ₊ o ₋ o ₋	1.433	1.404	1.586	1.170	1.378	1.424	1.550	2.262	1.520	2.231
Si₇Me₁₆ (4)										
t ₊ t ₊ t ₊ t ₊	0	0	0	0	0	0	0	0	0	0
t ₊ g ₊ g ₊ t ₊	0.895	1.030	1.563	1.060	1.600	0.958	1.154	1.986	1.175	2.011
o ₊ t ₋ t ₋ o ₊	1.395	1.351	1.499	1.312	1.460	1.356	1.328	1.510	1.232	1.460
t ₊ o ₋ o ₋ t ₊	1.520	1.601	2.715	1.562	2.048	1.465	1.628	2.483	2.465	1.613
g ₊ o ₋ o ₋ g ₊	2.428	2.583	3.514	2.518	3.438	2.577	3.104	4.474	3.882	3.048
o ₊ g ₋ g ₋ o ₊	3.653	4.105	4.243	4.045	4.195	3.123	2.926	3.069	2.602	2.881

the Supporting Information for the gas phase at 0, 77, and 298 K and in cyclopentane solution at 77 and 298 K, respectively. The results obtained by application of the $\{G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma)\}$ set of increments, $\Delta\Delta G_{\text{ginc}}$, are compared with the $\Delta\Delta G_{\text{calc}}$ results in Figures 1 and 2. In all figures the members of the set of nine conformers of **3** and **4** that were not included in the derivation but used to test the additive increments are indicated with filled symbols.

The mean deviations of the fit of the free energies obtained from the increment calculation to those obtained from the ab initio calculation for all conformers considered are listed at the bottom of Tables 5 and 6.

Discussion

We first discuss the geometries and relative energies of conformers of **1–4** in the gas phase and in solution and then consider the utility of the two additive increment systems, especially their ability to reproduce G_{calc} of the nine oligosilane conformers not used in derivation of the increment sets.

Gas-Phase MP2/VTZ Geometries. The MP2 method provides better agreement with experimental bond lengths of bonds involving second-row atoms than hybrid density functional theory (DFT) methods.⁴² It overestimates van der Waals attraction but is considered better than the currently standard DFT methods, which treat it poorly. It is most likely for this reason that incorrect dihedral angles were calculated for **1** using DFT (B3LYP/6-31G*).¹⁵ The combination of the MP2 method and a triple ζ basis set on silicon previously gave very good agreement with both experimental and MP4 results for the geometry and energy of disilane.⁴³ Piqueras et al. used Dunning's cc-pVTZ basis set on silicon for MP2 calculations of the structures of conformers of **1**,¹⁶ and the results agreed well with gas electron diffraction results.¹⁴ The MP2/cc-pVTZ method also reproduces the experimental enthalpy difference of 1-silabutane and ethylmethylsilane.⁴⁴

The MP2/VTZ conformer geometries of **1** (Table S2) differ very little from the MP2(fc)/cc-pVTZ geometries of Piqueras et al.¹⁶ The Si–Si–Si–Si dihedral angles, ω , are within 0.5°, the Si–Si–Si valence angles are 0.5–0.7° larger at the MP2/VTZ level, and the Si–Si bond lengths agree within 0.001 Å. The agreement of MP2/VTZ bond lengths with the gas electron diffraction values¹⁴ for **1** is within 0.003 Å for all Si–Si bonds except for the terminal bond of the o_± conformer, whose experimental bond length is 0.009 Å shorter than the 2.354 Å value calculated with either of the basis sets at the MP2 level.

At the MP2/VTZ level of calculation the conformers of **2** have ω and $\angle\text{Si–Si–Si}$ values within 3° and bond lengths

within 0.005 Å of those found in **1**, with three exceptions (Table S2). (i) The t₊g₋ conformer has an expanded gauche dihedral angle, ω , of -73.7° and an associated larger terminal $\angle\text{Si–Si–Si}$ value of 115.3° and a bond length of 2.365 Å. (ii) Both angles ω in the o₊g₋ conformer are increased, o₊ to 104.8° and g₋ to -65.2°, and the three $\angle\text{Si–Si–Si}$ angles and the internal bond length are larger than normally found at the MP2/VTZ level of calculation. Similar distortions of ω in t₊g₋ and o₊g₋ were previously observed at the HF/3-21G(d) level.¹³ (iii) The larger ω values of the t₊t₋ conformer, 166° and -170°, similar to those found at the HF/3-21G(d) level,¹³ may be similarly due to strong steric interactions, or perhaps the location of this saddle point between the minima of the t₊t₊ and t₋t₋ conformers dictates large dihedral angles.¹³

None of the three meso conformers of **2** are local minima on the PES at any of the four optimization methods previously used, HF/3-21G(d), MM3, MM2, and MM+,^{13,15} or those used in this work, MP2/6-31G(d) and MP2/VTZ. The t₊t₋ and o₊o₋ conformers were found to be saddle points at the HF/3-21G(d)¹³ and MP2/6-31G(d) levels. Geometries are not available for t₊o₊, o₊g₊, or g₊g₋ as these conformers of **2** are not potential energy minima at the MP2/6-31G(d) level.

As the Si chain is extended, conformers containing adjacent coiled conformations can encounter increased steric congestion. Thus the extensively coiled t₊g₊o₋, o₊g₊g₊, o₊g₋g₋, and o₊g₋o₊ conformers of **3** seek to reduce energetically unfavorable congestion through increased $\angle\text{Si–Si–Si}$ angles and Si–Si bond lengths and by twisting of ω from the standard values (Table S2 of the Supporting Information). In almost all these cases ω increases, although the terminal ω in 3o₊g₊g₊ decreases remarkably to 38.3°. The extent and direction of the alteration of ω in the four distorted conformers of **3**, listed above, are again similar to those seen in the same conformers at the HF/3-21G(d) level.¹⁵ Also for the t₊ conformations in the 4t₊g₊g₊t₊ conformer, ω is reduced by 7°. The completely coiled g₊o₋o₋g₊ and o₊g₋g₋o₊ conformers of **4** have g₊ conformations with ω values of 63.2° and 68.7°, respectively. The high-energy 4o₊g₋g₋o₊ conformer has o₊ conformations with ω equal to 106.7°.

Relative MP2/VTZ Electronic Energies. Relative electronic energies and relative free energies at three temperatures were previously calculated for the conformers of **1** at the MP2/cc-pVTZ level by Piqueras et al.¹⁶ The electronic energy order of the conformers of **1** is the same as that calculated previously using the HF/3-21G(d)¹⁵ and MP2/cc-pVTZ¹⁶ methods. The MP2/cc-pVTZ results are presented in Table 8 along with the current MP2/VTZ electronic and gas-phase energies and CCSD(T)/VTZ//MP2/VTZ electronic energies. The agree-

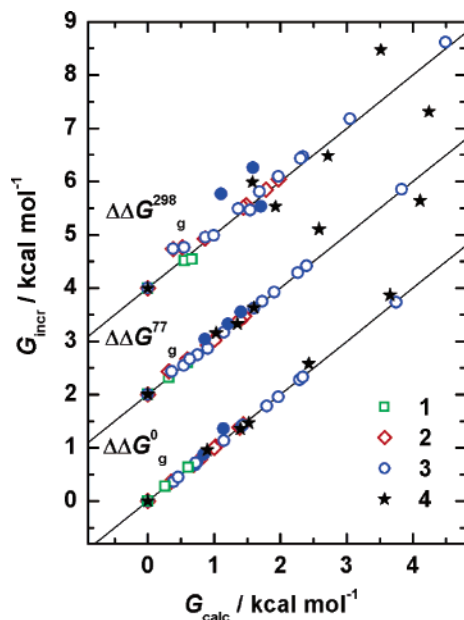


Figure 1. Energies $\Delta\Delta G_{\text{gincr}}$ and $\Delta\Delta G_{\text{gcalc}}$ using $\{G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma)\}$ increments for gas-phase conformers of **1** (green, \square), **2** (red, \diamond), **3** (blue, \circ), and **4** (black, \star). Filled symbols indicate conformers of the test set. Squared correlation coefficients R^2 : $\Delta\Delta G_{\text{gincr}}^0$, 0.996; $\Delta\Delta G_{\text{gincr}}^{77}$, 0.982; $\Delta\Delta G_{\text{gincr}}^{298}$, 0.924. Solid line represents perfect agreement. The upper plots have been displaced by 2.0 and 4.0 kcal/mol.

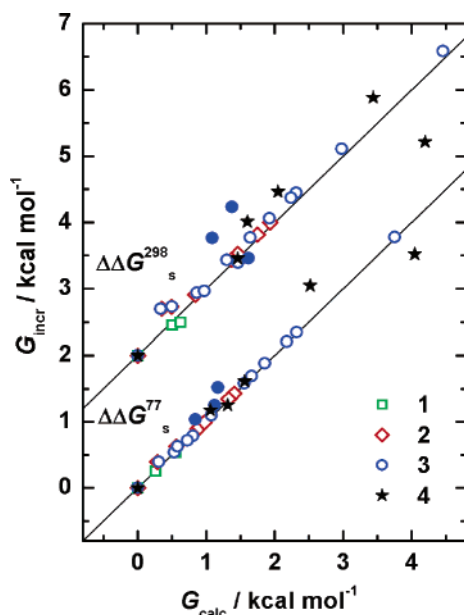


Figure 2. Energies $\Delta\Delta G_{\text{sincr}}$ and $\Delta\Delta G_{\text{scalc}}$ using $\{G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma)\}$ increments for solvated conformers of **1** (green, \square), **2** (red, \diamond), **3** (blue, \circ), and **4** (black, \star); filled symbols indicate conformers of the test set. Squared correlation coefficients R^2 : $\Delta\Delta G_{\text{sincr}}^{77}$, 0.976; $\Delta\Delta G_{\text{sincr}}^{298}$, 0.932. Solid line represents perfect agreement. The upper plot has been displaced by 2.0 kcal/mol.

ment is reasonable between the cc-pVTZ and VTDZ results, with a constant difference of 0.05 kcal/mol between the energies of the g_{\pm} conformer and 0.14 kcal/mol for the o_{\pm} conformer (Table 8). The agreement of ΔE_0 calculated with the MP2/VTDZ and the CCSD(T)/VTDZ methods at the same MP2/VTDZ geometry is excellent. For the g_{\pm} conformer, the values are the same to better than 0.01 kcal/mol, and for the o_{\pm} conformer, they differ by only 0.03 kcal/mol. This provides support for the use of the MP2/VTDZ approximation.

Zero-Point Vibrational Energy and Thermal Corrections.

The ZPVE and thermal corrections make important contributions to total conformer free energy at 0, 77, and 298 K. Several assumptions were made: All modes were calculated as harmonic vibrations in Gaussian 98, and although the oligosilanes have hindered internal rotation the corresponding low-frequency modes were not identified and treated separately.⁴¹ Thus the enthalpy and entropy corrections could have significant error, but we expect a large part of this error to cancel in the determination of relative enthalpy and entropy corrections. With regard to the following discussion it should be noted that the number of calculated conformers of **4** is limited and thus the span of energy corrections is not as representative as for **1–3**.

Application of the Δ ZPVE corrections calculated at the HF/3-21G(d) level and scaled³⁵ (Table 3) increases the range of the relative conformer energies by 0.07, 0.19, 0.47, and 0.50 kcal/mol for **1–4**, respectively, similarly as in previous work (~ 0.1 kcal/mol for **1** and **2**).¹³ The ZPVE is smaller for extended than for coiled conformers. Thus $t_{+}t_{+}$ and $t_{+}t_{-}$ have a smaller Δ ZPVE than $t_{+}o_{-}$, $t_{+}g_{-}$, and $t_{+}g_{+}$, and the differences are even larger for other twisted conformers of **2**.

The maximum increases in relative conformer energies due to enthalpy corrections at 298 K, ΔH , are ~ 0.02 , 0.10, 0.24, and 0.25 kcal/mol for **1–4**, respectively. The $t_{+}t_{-}$ conformer of **2** has been excepted as it has a calculated decrease of relative energy of 0.52 kcal/mol and, as noted above, is a saddle point on both the HF/3-21G(d) and the MP2/VTDZ PES's. At 77 K, also, the ΔH of the $2t_{+}t_{-}$ conformer decreases by 0.14 kcal/mol. Among the other conformers of **2**, a small decrease in the range of ΔH , to 0.07 kcal/mol, is observed at 77 K. The increase in relative conformer energy due to ΔH is greater at 77 K for **1**, **3**, and **4**, 0.06, 0.40, and 0.40 kcal/mol, respectively, than at 298 K. Conformers containing solely o_{\pm} and/or g_{\pm} bond conformations have the largest increase of ΔH , and conformers with a majority of t_{\pm} conformations have the smallest.

Entropy corrections substantially increase the energy difference among conformers. As with the enthalpy corrections, conformers rich in o_{\pm} and g_{\pm} bond conformations generally increase in relative energy when $T\Delta S$ is considered. The correction for vibrational entropy at 298 K introduces the largest change in the relative total free energy, $\Delta\Delta G$, among conformers, 0.32, 0.87, 2.24, and 1.34 kcal/mol for **1–4**, respectively. These amounts are comparable to the relative electronic energy differences, ΔE_0 . Several conformers of **2**, $t_{+}g_{-}$ and $t_{+}o_{-}$, and **3**, $t_{+}t_{+}o_{-}$, $t_{+}g_{+}o_{-}$, $o_{+}ao_{-}$, and $t_{+}at_{-}$, decrease in $\Delta\Delta G^{298}$ due to the $T\Delta S$ term. The largest decrease, -1.24 kcal/mol, is found for $3t_{+}at_{-}$ at 298 K. The change of the $\Delta\Delta G$ at 77 K due to $T\Delta S$ is also significant, 0.078, 0.23, 0.57, and 0.51 kcal/mol for **1–4**, respectively. At 77 K, the $T\Delta S$ correction is not negative for any conformers of **1**, **2**, or **4**, but two additional conformers of **3**, $o_{+}g_{+}g_{+}$ and $o_{+}g_{+}g_{-}$, have negative values for $T\Delta S$, for a total of six conformers. The value for $T\Delta S$ of $2t_{+}t_{-}$ at 298 K, $+1.34$ kcal/mol, is nearly twice as large as that of the conformer with the next largest $T\Delta S$ value, $+0.77$ kcal/mol for $2g_{+}g_{+}$, whereas at 77 K the $T\Delta S$ value of $2t_{+}t_{-}$ is within the range of values found for other conformers of **2**.

Albinsson et al.¹³ also found that vibrational entropies differed significantly and caused free energy differences among conformers of **1** and **2** at 298 K to differ by as much as 0.5–0.8 kcal/mol from potential energy differences at the HF/3-21G(d) level. In the present work, with the same method and basis set but scaling the contributions to the thermal correction separately, the maximum increases in the range of $\Delta\Delta G$ due to thermal corrections at 298 K are 0.33, 0.92, 2.40, and 1.59 kcal/mol,

TABLE 8: Calculated CCSD(T)/VTDZ//MP2/VTDZ Relative Electronic Energies and MP2/VTDZ and MP2/cc-pVTZ^a Relative Electronic and Gas-Phase Free Energies at 298 and 77 K of the Conformers of **1 (kcal/mol)**

conformer	MP2/VTDZ				CCSD(T)/VTDZ//MP2/VTDZ	MP2/cc-pVTZ ^a			
	ΔE_0	ΔE^0	ΔG_g^{77}	ΔG_g^{298}	ΔE_0	ΔE_0	ΔE^0	ΔG^{77}	ΔG^{298}
t	0	0	0	0	0	0	0	0	0
g	0.21	0.26	0.32	0.55	0.21	0.27	0.31	0.36	0.59
o	0.53	0.61	0.60	0.67	0.50	0.67	0.74	0.73	0.79

^a Reference 16.

and at 77 K, they are 0.10, 0.27, 0.81, and 0.66 kcal/mol, for **1–4**, respectively.

Solvation Energies. No prior calculations of the relative free energy of oligosilanes explicitly including solvation free energy are available, although solution-phase experimental studies are prevalent and few gas-phase results have been reported. Solute charge distribution and polarizability determine the electrostatic interaction of the solute with the solvent. Polarizability is particularly important because the solute and solvent respond self-consistently to each other's presence.⁴⁵ SCRF methods iteratively consider the electric field brought to bear on the solute by the solvent it has polarized and use this to predict a new solute electronic structure, which further alters the polarization of the solvent.⁴⁵

The choice of a continuum solvation method for calculating solvation energies was based on the availability of parameters for silicon. To quote a recent textbook,⁴⁶ "... molecular shaped cavities must be employed, the electrostatic polarization needs a description either in terms of atomic charges or quite high-order multipoles, and cavity and dispersion terms must be included." The continuum Solvation Model 5 (SM5) implemented in the HONDO/S program³² and used in this work meets the criteria listed above as it uses molecular-shaped cavities, represents the electrostatic potential with partial atomic charges,^{47,48} and treats cavity and dispersion terms through the solvent-accessible surface area.⁴⁹ As a universal solvation model, it provides parameters for water or any organic solvent.

The standard-state free energy of solvation, ΔG_s^0 , calculated using a rigid gas-phase geometry, consists of two contributions (eq 8)

$$\Delta G_s^0 = G_{\text{CDS}} + \Delta G_{\text{EP}} = G_{\text{CDS}} + G_{\text{P}} + \Delta E_{\text{E}} \quad (8)$$

The first of these, G_{CDS} , is from first solvent shell effects: cavitation, dispersion, and solvent structure. These are obtained by summing the product of the solvent-accessible surface area of each atom, the atomic surface tension, and a solvent descriptor. The second contribution, ΔG_{EP} , is the bulk electrostatic component of the solvent free energy. This consists of favorable solute–solvent interactions and associated solvent rearrangement costs, G_{P} , and the distortion energy of the solute electronic charge, ΔE_{E} .³⁶ For nonpolar solutes such as oligosilanes the atomic surface tension is the most important parameter in the SM5 model,⁵⁰ in which semiempirical atomic surface tensions are used to account for nonelectrostatic solvation effects.⁴⁵

The implicit semiempirical atomic surface tensions as well as the intrinsic Coulomb radii and geometrical factors used in the solvation model for Si were derived from a data set smaller than the data set used for the parameters of other atoms (C and H).⁵⁰ The mean unsigned error for the parametrization of silanes was 0.41 kcal/mol and was lower than that for the other types of silicon compounds examined.⁵⁰ The mean unsigned error in SM5.42R free energies of solvation using the HF/6-31G(d) basis set is 0.43 kcal/mol.⁵⁰ Since the free energy differences among

conformers of the same molecule are calculated using difference in solvation free energies, the errors should have a negligible effect. However, as the Coulomb radii integral in the SM5 model is valid only for a single temperature, 298 K, the single-point solvation energies calculated at 77 K are of unknown reliability.

Experimental measurements in an extensive study of permethylated oligosilanes, **1–4**, and $\text{Me}(\text{Si}_n\text{Me}_{2n})\text{Me}$, $n = 8, 10,^{3,6}$ were performed in a 3:7 (v/v) cyclopentane/isopentane mixture, so the best choice of a single solvent for the solvation calculations might have been isopentane; however as the necessary solvent parameters were not available, cyclopentane was chosen.

The relative solvation free energies, $\Delta\Delta G_s$, calculated for the MP2/VTDZ-optimized gas-phase geometries of **1–4** are listed in Table 3 for temperatures of 298 and 77 K, with the all-t₊ conformer of each compound taken as the reference. The calculated ΔG_s values are approximately −10.0, −12.3, −14.5, and −16.7 kcal/mol for **1–4**, respectively, at 298 K and −6.1, −7.6, −9.1, and −10.6 kcal/mol, respectively, at 77 K. In general, solvation stabilizes twisted conformers more than extended conformers. However, the maximum stabilization due to $\Delta\Delta G_s$ at 298 K (Table 3), <0.05, 0.07, 0.09, and 0.04 kcal/mol for **1–4**, respectively, is small compared to their destabilization due to the respective thermal corrections at 298 K, 0.33, 0.92, 2.40, and 1.59 kcal/mol. The relative solvent stabilization is calculated to increase upon going to 77 from 298 K for all conformers except 2o₊g_− and 2t₊t_−, whose stability drops by less than 0.01 kcal/mol. A single conformer, 4o₊t_−t_−o₊, is destabilized upon solvation by 0.03 kcal/mol at both 77 and 298 K. The increased stabilization due to solvation at 77 K relative to that at 298 K ranges from negligible to 0.041 kcal/mol for 3o₊g_−o₊, although the maximum stabilization among all conformers of a compound and thus the effect on the range of $\Delta\Delta G_s^{77}$ remain essentially the same.

We assumed previously that the increased intramolecular van der Waals stabilization of the more compact structures at the MP2 level would be compensated to some degree by a reduced intermolecular van der Waals interaction with solvent molecules and that they would lose their advantage.¹⁵ We therefore suggested that relative HF energies calculated for isolated conformers could mimic their relative energies in solution, since the HF method also disfavors compact structures by omitting their expected preferential intramolecular van der Waals stabilization relative to extended ones. Such differential favoring of extended structures was observed previously for some permethylated^{12,13,15} and ethylated^{25,26} oligosilanes upon going from HF/3-21G(d)//HF/3-21G(d) to MP2/6-31G(d)//HF/3-21G(d), and for **1** and **2** the HF/3-21G(d) relative free energies at 298 K are roughly twice the present $\Delta G_{\text{scal}}^{298}$ values.

The current results show that the underlying assumption is invalid, as the solvation stabilization $\Delta\Delta G_s$ is generally larger for twisted than for extended conformers. Examination of the additive contributions to ΔG_s^0 for the seven stable conformers of **2** at 298 K indicates that G_{P} , which quantifies the stabilizing interactions between solute and solvent and solvent rearrange-

ment costs, is the largest for the $2\text{o}+\text{g}-$ conformer and decreases in the order $2\text{g}+\text{g}+$, $2\text{t}+\text{g}+$, $2\text{t}+\text{o}-$, $2\text{t}+\text{g}-$, $2\text{t}+\text{t}+$, or essentially with the reduction in molecular compactness. However, the $2\text{o}+\text{o}+$ conformer has the smallest G_{P} value. Conversely, $2\text{o}+\text{o}+$ has the largest stabilization due to G_{CDS} , which quantifies first solvation-shell effects, with G_{CDS} values decreasing in the order $2\text{o}+\text{g}-$, $2\text{t}+\text{o}-$, $2\text{t}+\text{g}-$, $2\text{g}+\text{g}+$, $2\text{t}+\text{g}+$, and $2\text{t}+\text{t}+$. The spread of G_{P} is 0.058 kcal/mol, and that of G_{CDS} is 0.056 kcal/mol. Thus the inconsistent ordering of the conformers of **2**–**4** if a correlation between ΔG_{s}^0 and compactness is assumed can be explained as a delicate balance between G_{P} and G_{CDS} . The ΔE_{E} values, which quantify the cost of distorting the solute electronic charge distribution, have a spread of 0.02 kcal/mol. The conformers $2\text{o}+\text{g}-$, and then $2\text{g}+\text{g}+$, are destabilized the most, and $2\text{t}+\text{t}+$ are destabilized the least, with the other conformers having nearly the same value for ΔE_{E} . Thus, if one considers the G_{CDS} values as proportional to the dispersion interactions between the solute and solvent, then the assumption that coiled conformers have reduced intermolecular van der Waals interactions is generally wrong.

Order of Conformer Stability. At 0 K, the $\Delta E_{\text{gcalc}}^0$ values of **1** (Table 4) increase by less than ~ 0.1 kcal/mol compared to ΔE_0 (Table 3), and the conformer order remains the same. The order of the eight conformers of **2** does not change, except for the $\text{t}+\text{g}-$ and $\text{t}+\text{t}-$ conformers, which differ by 0.04 kcal/mol in ΔE_0 , with the former lower in energy, while the $\Delta E_{\text{gcalc}}^0$ value of the latter is 0.02 kcal/mol lower in energy. The highest-energy conformer of **2** is $\text{o}+\text{g}-$ at a $\Delta E_{\text{gcalc}}^0$ value of 1.44 kcal/mol. For conformers of **3**, the order of five of the 18 conformers changes. The large ΔZPVE of the $\text{g}+\text{t}+\text{g}+$ conformer, 0.18 kcal/mol, causes its $\Delta E_{\text{gcalc}}^0$ value to surpass that of the $\text{t}+\text{t}+\text{o}-$ and $\text{t}+\text{o}-\text{t}+$ conformers, while they remain nearly isoenergetic with one another. Similarly, a ΔZPVE value of 0.15 kcal/mol causes the $\Delta E_{\text{gcalc}}^0$ value of the $3\text{t}+\text{g}+\text{g}+$ conformer to exceed that of the $3\text{t}+\text{at}-$ conformer. The range of the relative energy increases by 0.47 kcal/mol from that of ΔE_0 , 3.28 kcal/mol, to 3.75 kcal/mol for $\Delta E_{\text{gcalc}}^0$, with the $\text{o}+\text{g}-\text{o}+$ conformer as the highest-energy conformer at both 0 and 77 K. The order of the six conformers of **4** does not change.

The 77 K gas-phase results show an increase in the range of $\Delta \Delta G_{\text{gcalc}}^{77}$ (Table 4) relative to ΔE_0 due to the temperature-dependent ΔH and $T\Delta S$ corrections, and the 298 K gas-phase results show similar trends. Half of the 35 conformers have a $\Delta \Delta G_{\text{gcalc}}^{77}$ lower in energy than $\Delta E_{\text{gcalc}}^0$. With the exception of the 1o_{\pm} conformer, which has a negligibly lower $\Delta \Delta G_{\text{gcalc}}^{77}$ value (0.008 kcal/mol), and the $4\text{o}+\text{t}-\text{t}-\text{o}+$ conformer, which has $\Delta \Delta G_{\text{gcalc}}^{77}$ lower by 0.044 kcal/mol, $\Delta \Delta G_{\text{gcalc}}^{77}$ increases for all the C_2 symmetric conformers, while $\Delta \Delta G_{\text{gcalc}}^{77}$ decreases or remains the same for conformers with lower symmetry (except for the $3\text{t}+\text{g}+\text{g}+$ conformer, which has $\Delta \Delta G_{\text{gcalc}}^{77}$ higher by 0.023 kcal/mol). With several exceptions, a similar trend occurs for the 298 K gas-phase results. The range of $\Delta \Delta G_{\text{gcalc}}^{77}$, 0.60, 1.45, 3.83, and 4.11 kcal/mol for **1**–**4**, respectively, hardly changes compared to the range of $\Delta E_{\text{gcalc}}^0$, while that of $\Delta \Delta G_{\text{gcalc}}^{298}$ (Table 4) increases to 0.67, 1.97, 4.49, and 4.24 kcal/mol, respectively.

The solvated conformer results exhibit a range for $\Delta G_{\text{gcalc}}^{77}$ of 0.56, 1.41, 3.75, and 4.05 kcal/mol at 77 K for **1**–**4**, respectively, and 0.63, 1.93, 4.45, and 4.20 kcal/mol, respectively, at 298 K (Table 4). For all conformers, the average energy difference between ΔE_0 and $\Delta E_{\text{gcalc}}^0$ is 0.16 kcal/mol. For the 77 K results the average energy difference between ΔE_0 and $\Delta G_{\text{gcalc}}^{77}$ is 0.18 kcal/mol and between ΔE_0 and $\Delta G_{\text{scale}}^{77}$ is 0.13 kcal/mol. At

298 K the average differences in relative energy are substantial, 0.42 kcal/mol between ΔE_0 and $\Delta G_{\text{gcalc}}^{298}$ and 0.35 kcal/mol between ΔE_0 and $\Delta G_{\text{scale}}^{298}$ (Table 4).

The $\Delta \Delta G_{\text{scale}}$ values of the three conformers of **1** can be compared with ΔG values determined from a van't Hoff plot of the relative intensities of two Raman bands that were assigned to the a and g_{\pm} conformers of **1**.²⁷ This assignment predated the identification of three conformational minima for **1**, and the single a conformer is now referred to as the two $\text{t}+$ and $\text{t}-$ conformers. The Raman intensity attributed to the " g_{\pm} " conformer presumably included the intensity of both the o_{\pm} and the g_{\pm} conformers, complicating the comparison between the experimental and the calculated free energies in solution. The 77 K $\Delta \Delta G_{\text{scale}}$ values for the $\text{t}+$, g_{\pm} , and o_{\pm} conformers are 0, 0.26, and 0.56 kcal/mol, respectively. The free energy for the " g_{\pm} " conformer relative to the a conformer at 77 K determined from the variable-temperature Raman experiments is 0.54 kcal/mol, which falls between the values calculated for the g_{\pm} and o_{\pm} conformers (Table 4).²⁷ At 298 K, the experimental results indicate that the g_{\pm} conformer is expected to have a similar population as the a conformer, due to the respective entropic contributions, whereas $\Delta \Delta G_{\text{scale}}$ indicates that the g_{\pm} and o_{\pm} conformers are 0.50 and 0.63 kcal/mol higher in free energy than the t_{\pm} conformer (Table 4).²⁷ At least some of the disagreement arises from the contribution of two twisted conformers, presumably with different relative free energies, to the Raman band assigned to a single g_{\pm} conformer.

In summary, comparison of the present MP2/VT-DZ energies for **1** and **2** with the earlier HF/3-21G(d)//HF/3-21G(d) results^{13,15} shows that the three conformers of **1** and also the four lowest-energy conformers of **2**, $\text{t}+\text{t}+$, $\text{t}+\text{g}+$, $\text{t}+\text{o}-$, and $\text{t}+\text{g}-$, remain in the same order for both methods, with and without corrections for ΔH and $T\Delta S$, but that the HF/3-21G(d) energy differences ΔE are larger. For the conformers of **1**, the results differ by 0.4–0.6 kcal/mol, and for the conformers of **2**, the results differ by at least 0.4 kcal/mol and by as much as 1.6 kcal/mol.

The relative energies presented in Table 4 are comprised of the sum of multiple contributions (eqs 1–5). The effect of these contributions, relative to the all- $\text{t}+$ reference conformer for each of **1**–**3**, can be generalized as follows: (i) ΔE_0 in itself separates conformers energetically by up to 3.3 kcal/mol for **3**, with extended conformers tending to be lower in energy than conformers with multiple twists (Table 3), (ii) ΔZPVE increases the energy difference by up to 0.47 kcal/mol for **3**, with twisted conformers having a higher ZPVE than extended conformers (Table 3), (iii) ΔH increases the relative energy of conformers by up to 0.24 kcal/mol for **3** at 298 K, and again twisted conformers tend to increase more in energy, (iv) $T\Delta S$ contributes to an increase in energy for most conformers, but many extended conformers are now stabilized, resulting in an increase in the range of relative energies of up to 2.4 kcal/mol at 298 K and 0.57 kcal/mol at 77 K, and (v) $\Delta \Delta G_{\text{s}}$ stabilizes all conformers by up to 0.09 kcal/mol at 298 K, with highly coiled conformers stabilized slightly more than extended and less coiled conformers (Table 3).

Since after ΔE_0 , $T\Delta S$ is responsible for the largest energy differentiation among conformers, the 298 K gas-phase and solution $\Delta \Delta G_{\text{calc}}^{298}$ values have the largest ranges, 4.49 and 4.45 kcal/mol, respectively. The $\Delta \Delta G_{\text{calc}}^{298}$ values of each conformer in the solution and the gas phase are very similar, differing by no more than 0.09 kcal/mol. The energy order of conformers at 298 K is the same for solution and the gas phase. The situation is similar at 77 K, with no change in conformer ordering and a

maximum difference of $\Delta\Delta G_{\text{calc}}^{77}$ for a single conformer of 0.09 kcal/mol between the two phases. The range of conformer $\Delta\Delta G_{\text{calc}}^{77}$ is smaller at 77 K, 3.8 kcal/mol. The energy order of conformers of **2** and **3** at 77 K changes from that at 298 K, while the order at 0 K (Table 4) and for ΔE_0 (Table 3) are each different.

Additive Increments. Previous work demonstrated that relative conformer energies can be fitted with a set of additive increments, which permit an easy estimation of relative energies of conformers for which no calculations are available. Simultaneous least-squares fitting provided increment sets that reproduced well the order of conformer relative energies,¹³ and when a few types of next-nearest-neighbor bond interactions for problematic conformers were included, the mean deviation between calculated relative energies and those obtained from an increment set was below 0.05 kcal/mol.¹⁵ The question remained whether such additivity continues to hold for free energies of solvated oligosilane conformers, since only then it would provide a useful facile route for estimation of conformer populations of all permethylated oligosilanes in alkane solutions, commonly used for spectroscopic studies.

The correlation between the conformer energies, G_{incr} , of **1–4** derived from the set of increments $\{(G'(\alpha), G'(\alpha, \beta))\}$ in Table 5, and computed energies G_{calc} (Table 4) is shown in Figure S1 of the Supporting Information for the gas phase and in Figure S2 of the Supporting Information for solution phase. Examination of Figures S1 and S2 indicates that the use of the increments G_{incr} provides relative energies that tend to agree reasonably well with the calculated G_{calc} although the agreement is worse for high-energy conformations. The size of the difference between G_{incr} and G_{calc} increases as the temperature increases. The average deviation among all conformers of **1–4** between the gas phase G_{incr} and G_{calc} is 0.13 kcal/mol at 0 K, 0.13 kcal/mol at 77 K, and 0.27 at 298 K. Similar average deviations are found for the solution phase: 0.14 kcal/mol at 77 K and 0.25 kcal/mol at 298 K. The difference between G_{incr} and G_{calc} for the **2**_{o+g-}, **3**_{o+g-o+}, **4**_{g+o-o-g+}, and **4**_{o+g-g-o+} conformers under all temperature and phase conditions is consistently larger than the differences found for the other conformers. Ottosson and Michl¹⁵ also found that conformers that contain o+g-segments have the largest deviation between energies from calculations and increments and observed that conformers containing this segment have large geometry distortions, particularly Si–Si–Si–Si dihedral angles, similar to those found at the MP2/VTDZ level (Table S2 of the Supporting Information). The distortions that result from unfavorable steric interactions and that increase the conformer energy are aggravated as an additional bond interaction is added, and attempts to fit the high-energy distorted structures with the same weight as nondistorted structures result in poor increment values for the set. If additional increments for conformers of **3** having problematic structures are included, then the fit might be expected to improve.

Indeed, the inclusion of nonadjacent interaction increments for three conformers of **3**, **t**_{g+o-}, **o**_{g-o+}, and **o**_{g-g-}, which contain o+g- interactions, and four conformers, **o**_{t-g-}, **o**_{o+o+}, **o**_{g+g+}, and **g**_{g+g+}, whose ΔE_0 is also above 1 kcal/mol (Table 3), significantly improves the agreement. For the resulting $\{(G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma))\}$ set of increments, the average deviation between the gas phase $\Delta\Delta G_{\text{incr}}$ and $\Delta\Delta G_{\text{calc}}$ is 0.04 kcal/mol at 0 K, 0.07 kcal/mol at 77 K, and 0.20 at 298 K, and essentially the same average deviations are found for the solution phase: 0.08 kcal/mol at 77 K and 0.18 kcal/mol at 298 K. The improved agreement between G_{incr} and G_{calc} found with the

$\{(G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma))\}$ set can be seen in Figures 1 and 2. A trial fitting in which the nonadjacent interaction of seven low-energy conformers of **3** instead of the seven high-energy conformers was used resulted in a higher mean deviation for the 0 K data. Clearly, consideration of high-energy nonadjacent interactions is important for the derivation of a useful $\{(G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma))\}$ set of increments, as found previously.¹⁵ These nonadjacent interactions serve mainly to provide a more reasonable partitioning of the energy for nonfavorable interactions. In using the $\{(G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma))\}$ increment set to determine $\Delta\Delta G_{\text{incr}}$ for the nine test conformers, an additive increment for $G(\alpha, \beta, \gamma)$ interactions was applicable only in the case of the **4**_{o+g-g-o+} conformer; however the agreement was improved for the lower-energy conformers relative to that resulting from use of the $\{(G'(\alpha), G'(\alpha, \beta))\}$ set. The agreement between $\Delta\Delta G_{\text{incr}}$ and $\Delta\Delta G_{\text{calc}}$ for the higher-energy conformers, **3**_{t+o-o-}, **4**_{g+o-o-g+}, and **4**_{o+g-g-o+}, suffered.

The purpose of the additive increment sets is to allow the determination of the relative energy and population of the conformers expected to be present in an experimental sample. As only relatively low-energy conformers will be of interest, the application of an increment set provides a simple route to determination of the conformers likely to be present. This is of particular importance for experiments in alkane solution, and it is somewhat unfortunate that solvation energies and other corrections are a little less amenable to description by additive increments than pure electronic energies.

Summary and Conclusions

The geometries of conformers of **2–4** were optimized at the highest level to date, MP2/VTDZ, and their relative electronic energies were determined at the MP2/VTDZ//MP2/VTDZ level. The conformers of **1** were treated at the same level, and single-point CCSD(T) calculations performed on the MP2/VTDZ-optimized geometries provided support for the adequacy of the MP2/VTDZ//MP2/VTDZ method. Calculated corrections for ZPVE enthalpy, entropy, and solvation free energy were applied to the electronic energy to provide relative free energies in the gas phase at 0, 77, and 298 K and in cyclopentane solution at 77 and 298 K. The spread of the relative free energies for the 35 conformers of **1–4** increased with temperature, primarily due to the entropy correction. The ZPVE, enthalpy, and entropy corrections generally destabilized twisted conformers more than extended conformers. Examination of the size of the ZPVE, enthalpy, and entropy contributions to the relative energy as a function of the number of twists or the type of twists failed to identify a reason that the energy of twisted conformers tends to increase more than extended conformers when the thermal corrections are applied. The enthalpy correction had a stronger correlation with the number of twists than the entropy correction.

The first numerical study of oligosilane solvation revealed that twisted conformers are generally stabilized more than extended conformers, contrary to prior expectations. The balance between the extent of stabilization due to solute–solvent interactions and associated solvent rearrangement costs and that due to first solvation-shell effects, particularly dispersion, determines the relative free energy of solvation of conformers.

Relative conformer energies can be well reproduced by using a simple additive increment set. The gas-phase increment sets at 0, 77, and 298 K and the solvated increment sets at 298 K provide a facile method of determining relative energy differences that include thermal corrections and, in the case of the 298 K solvated increments, solvation energies. The 77 K

solvated increment set should be considered with skepticism as the solvation energies were calculated using a Coulomb radii integral that is valid only at 298 K.⁵¹

A simpler and a more complicated set of additive energy increments were derived for each of the five temperature and phase combinations from the calculated conformer relative free energies. Summing the increments for each dihedral angle conformation and for interaction of adjacent conformations provides the relative free energy of a conformer with respect to the all-*t*₊ reference conformer. The simpler $\{(G'(\alpha), G'(\alpha, \beta))\}$ increment sets thus give only moderate agreement with the calculated free energy, with a mean square error of 0.152 kcal/mol for solution free energies at 298 K. The use of improved but still easily applied $\{(G''(\alpha), G''(\alpha, \beta), G''(\alpha, \beta, \gamma))\}$ sets of increments that also consider nonadjacent interactions significantly improves the agreement and permits an estimate of the solution free energies of permethylated oligosilane conformers with a mean square error of 0.098 kcal/mol.

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Supporting Information Available: Validation of the VTDZ basis set, selected geometrical parameters for all conformers of **1–4**, and the correlation between the conformer energies, G_{incr} , derived from the set of increments, $\{(G'(\alpha), G'(\alpha, \beta))\}$, and computed energies, G_{calc} for the gas phase and solution phase. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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