conformation, instead of the TG conformation used here. In that study there was a transition in the orientation of this group at 6 ps to the TG conformation; this conformation persisted for the remaining 36 ps of the simulation. In the present simulations, the hydroxymethyl group went from the starting TG conformation to either GT or GG early in the simulation; in one case ($\lambda = 0.7$ for β and α), this group oscillated three times from GT to GG and back again during the 10 ps of data collection. No transitions back to TG were observed in any of the simulations. During the total analysis time of 100 ps, the hydroxymethyl group spent approximately 15.5 ps in the GG form and 83 ps in the GT conformation, with very few transitions. This rotamer distribution, with no observed TG population, is in agreement with experimental data.[39-41] The source of this difference in exocyclic rotational behavior between the two MD simulations could be incomplete sampling of rare events,[42] differences between the SPC[38] and TIP3P[24] water models, and/or differences in the truncation method. In any case, the C6-O6H group is on the opposite side of the molecule from the anomeric group and so is unlikely to have a significant effect on the calculated free energy difference, which is of primary interest here.

Conclusions

Free energy simulations with an empirical force field show that a substantial interaction (3.03 ± 0.5 kcal/mol), mainly electrostatic, between the sugar and the solvent favors the β anomer of D-glucose, which predominates in aqueous solution at room temperature. There is a counterbalancing internal free energy of nearly the same magnitude, also mainly electrostatic, that favors the α form. Although the exact quantitative results of the simulations are expected to depend on the choice of potential function and parameters, the qualitative features of the analysis should be correct. The essential result is that the preference of D-glucose for the β anomer is primarily a solvation effect, as has been suggested from experimental studies.[3,43]

The results from the present study are not directly comparable to the intramolecular anomeric stabilization energy obtained in ab initio calculations, since the corresponding energy difference for the cyclohexane polyalcohols is not available. The simulation suggests that there is a significant intramolecular term favoring the α form. From the difference between the intramolecular contribution to the free energy in solution and the energy minimum in vacuum, it is clear that a dynamic average (in the presence of solvent) is required to obtain a meaningful result.

The anomeric preference found here does not result from any chemically distinct properties of the anomeric group, since it was treated the same as the other hydroxyl groups and had the same parameters whether axial or equatorial. Thus, the difference in solvation found in the present simulations arises from the structural and dynamic properties of the two glucose anomers rather than from a difference in hydrogen-bonding characteristics resulting from a configuration-dependent redistribution of charge.[11]

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Registry No. α-D-Glucopyranose, 492-62-6; β-D-glucopyranose, 492-61-5.

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(39) De Bruyn, A.; Anteunis, M. *Carbohydr. Res.* **1976**, *47*, 311.

(40) Nishida, Y.; Ohuri, H.; Meguro, H. *Tetrahedron Lett.* **1984**, *25*, 1575.

(41) Perkins, S. J.; Johnson, L. N.; Phillips, D. C.; Dwek, R. A. *Carbohydr. Res.* **1977**, *59*, 19.

(42) Post, C. B.; Dobson, C. M.; Karplus, M. K. *Proteins* **1989**, *5*, 337.

(43) Suggett, A. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1975; Vol. 4, pp 519-567.

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trans-Dimethyldisilyne ($Si_2(CH_3)_2$): An Achievable Synthetic Target

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Abstract: The trans, twist, and dimethyldisilavinylidene isomers of dimethyldisilyne have been studied at the configuration interaction level of theory, and the trans and dimethyldisilavinylidene are found to be minima. The relative energy of these two minima are evaluated with larger basis sets. Our final prediction of this energy difference is 12.0 kcal/mol with the *trans*-$H_3CSiSiCH_3$ being higher in energy. To aid in the prospective observation of the first potential silicon-silicon triple bond, the vibrational frequencies and infrared intensities are reported.

1. Introduction

In 1986 Sekiguchi, Zigler, and West[1] proposed dimethyldisilyne as an intermediate in the thermolysis of bis(7-silanorbornadiene) leading to the production of an anthracene adduct. In addition, they speculated that the anthracene product itself could decompose to yield dimethyldisilyne, citing mass spectral data yielding a peak with m/e 86 and having the correct isotopic ratios to implicate a composition of $C_2H_6Si_2^+$. Subsequent studies[2,3] provided evidence for the reaction of bis(7-silanorbornadiene) with disubstituted acetylene to yield 1,4-disilabarrelenes via a similar mechanism. These studies presented the first evidence for the possibility of a species containing a Si-Si triple bond. The parent

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(1) Sekiguchi, A.; Zigler, S. S.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4241.

(2) Sekiguchi, A.; Gillette, G. R.; West, R. *Organometallics* **1988**, *7*, 1226.

(3) Sekiguchi, A.; Zigler, S. S.; Haller, K. J.; West, R. *Recl. Trav. Chim. Pays-Bas* **1988**, 107, 197.

0002-7863/91/1513-1557$02.50/0

molecule Si_2H_2 has been the object of extensive theoretical studies,[4-17] and these have shown the linear triply bonded isomer to be a high-lying isomer with a Hessian index of two, i.e., two imaginary vibrational frequencies. The low-lying minima on the singlet potential energy surface have valence structures in dibridged (global minimum), disilavinylidene, and singly bridged conformations. A *trans*-disilyne structure is also found to be a minimum at correlated levels of theory.[4,13]

The significant question then is whether or not the observed dimethyldisilyne is really a triply bonded molecule. Does it assume a dibridged valence structure similar to Si_2H_2, or do the methyl substituents cause some other conformation to be more stable? We addressed this question in a previous theoretical study[18] including five valence isomers of dimethyldisilyne; linear, trans, twist, dibridged, and dimethyldisilavinylidene. At the SCF/DZ+d (self-consistent field method using a double-ζ basis set plus polarization functions on carbon and silicon) level of theory, we found only the twist and dimethyldisilavinylidene to be minima, with the dimethyldisilavinylidene being lower in energy by 14 kcal/mol. However, when electron correlation was included by obtaining the CISD (configuration interaction including all single and double excitations) energies at the SCF/DZ+d optimized geometries, the trans structure fell below the twist in energy. This fact and the very small imaginary frequency (29i cm^{-1}) of the trans stationary point leading to the twist structure suggest that the trans structure is in fact a minimum on the CISD/DZ+d potential energy surface and that the twist minimum is merely an artifact of the SCF method (for Si_2H_2 a twist minimum is found but disappears with an improved basis set[8,11-13]). In this paper, we expand our previous study by investigating the dimethyldisilavinylidene, trans, and twist structures of $Si_2(CH_3)_2$ at the CISD/DZ+d level of theory, including complete geometry optimizations and harmonic vibrational frequency analyses, to more reliably characterize the true minima.

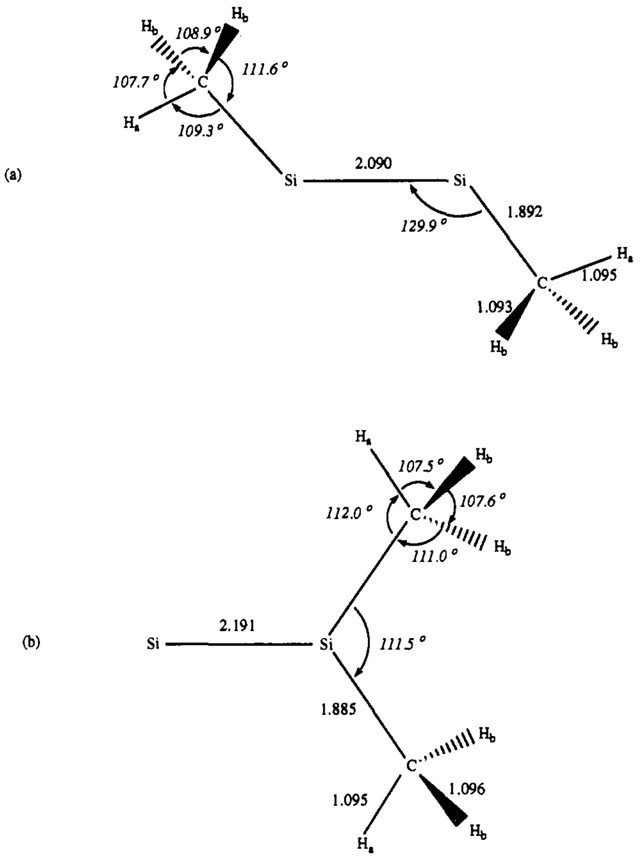

Figure 1. Optimized CISD/DZ+d geometries for the trans (a) and dimethyldisilavinylidene (b) structures of $Si_2(CH_3)_2$.

2. Theoretical Methods

Complete geometry optimizations using analytic CISD gradient techniques[19-21] were performed for the trans, twist, and dimethyldisilavinylidene isomers using a DZ+d basis set. Only the valence electrons have been explicitly correlated; the core-like orbitals (Si 1s, 2s, 2p, and C 1s) and their 12 virtual orbital counterparts were excluded from the CI. The CISD energies have been corrected to include the effects of unlinked quadruple excitations in an approximate manner by using Davidson's formula.[22] These Davidson corrected energies are denoted CISD+Q. The DZ+d basis set consisted of a standard Huzinaga-Dunning-Hay[23-25] double-ζ basis set of contracted Gaussian functions augmented by a set of six d-type polarization functions on the carbon and silicon atoms. The polarization function orbital exponents used were $\alpha_d(Si) = 0.50$ and $\alpha_d(C) = 0.75$. This DZ+d contraction scheme is designated

Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), H(4s/2s)

and contains 92 basis functions. Harmonic vibrational frequencies and quadratic force constants were evaluated for the trans and dimethyldisilavinylidene structure via finite displacement of analytic CI gradients. The number of configuration state functions included in the CI optimizations were 51 394 for the C_{2v} dimethyldisilavinylidene isomer, 51 294 for the C_{2h} trans isomer, and 98 910 for the C_2 twist isomer. For the vinylidene-type isomer, the number of configuration state functions included for the finite displacements were 98 914 for the A_2 modes, 99 106 for the B_1 modes, and 102 274 for the B_2 modes. The finite displacement gradients for the trans isomer included 98 910 configuration state functions for the B_g modes, 98 910 for the A_u modes, and 102 274 for the B_u modes.

To test the adequacy of the basis set, single point SCF and CISD energies were determined at the SCF/DZ+d and CISD/DZ+d optimized geometries, respectively, by using two larger basis sets, which we designate DZP and TZ2P. DZP is the same as DZ+d but appends a set of polarization p-type functions on the hydrogen atoms with $\alpha_p(H) = 0.75$. This basis set has 110 basis functions. The TZ2P basis set for carbon atoms is comprised of Dunning's[26] triple-ζ 5s3p contraction of Huzinaga's[23] 10s6p primitive set plus two sets of five d-type functions with $\alpha_d(C) = 1.5$ and 0.35. For silicon atoms we employed McClean and Chandler's[27] 6s5p contraction of Huzinaga's 12s9p primitive Gaussians supplemented by two sets of five d-type functions with $\alpha_d(Si) = 1.0, 0.25$. For hydrogen we used the above described DZP basis set. The contraction scheme for the TZ2P basis set is designated

Si(12s9p2d/6s5p2d), C(10s6p2d/5s3p2d), H(4s1p/2s1p)

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(4) Colegrove, B. T.; Schaefer, H. F. *J. Phys. Chem.* **1990**, *94*, 5593-5602.

(5) Koseki, S.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 118.

(6) Koseki, S.; Gordon, M. S. *J. Phys. Chem.* **1988**, *92*, 364.

(7) Kalcher, J.; Sax, A. F. *Chem. Phys. Lett.* **1987**, *133*, 135.

(8) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270.

(9) Clabo, D. A.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *84*, 1664.

(10) Baird, N. C. *Can. J. Chem.* **1985**, *63*, 71.

(11) Binkley, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 603.

(12) Kalcher, J.; Sax, A.; Olbrich, G. *Int. J. Quantum. Chem.* **1984**, *25*, 543.

(13) Lischka, H.; Köhler, H. *J. Am. Chem. Soc.* **1983**, *105*, 6646.

(14) Kawai, F.; Noro, T.; Murakami, A.; Ohno, K. *Chem. Phys. Lett.* **1982**, *92*, 479.

(15) Snyder, L. C.; Wasserman, Z. R.; Moskowitz, J. W. *Int. J. Quantum Chem.* **1982**, *21*, 565.

(16) Obara, S.; Kitaura, K.; Morokuma, K. *Theor. Chim. Acta (Berlin)* **1981**, *60*, 227.

(17) Wirsam, B. *Theor. Chim. Acta (Berlin)* **1972**, *25*, 169.

(18) Thies, B. S.; Grev, R. S.; Schaefer, H. F. *Chem. Phys. Lett.* **1987**, *140*, 355.

(19) Saxe, P.; Fox, D. F.; Schaefer, H. F.; Handy, N. C. *J. Chem. Phys.* **1982**, *77*, 5584.

(20) Osamura, Y.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1981**, *75*, 2919.

(21) Goddard, J. D.; Handy, N. C.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 1525.

(22) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum. Chem.* **1974**, *8*, 61.

(23) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(24) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(25) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 3, pp 1-27.

(26) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

(27) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

Table I. Geometrical Parameters for $Si_2(CH_3)_2$ Structures Optimized with the DZ+d Basis Set[a]

structure	description	SCF	CISD
trans	*r*(Si–Si)	2.083	2.090
	r(C–Si)	1.895	1.892
	r(C–H_a)	1.087	1.095
	r(C–H_b)	1.085	1.093
	θ(C–Si–Si)	132.2	129.9
	α(H_a–C–H_b)	107.8	107.7
	α(H_b–C–H_b)	109.0	108.9
	β(H_a–C–Si)	109.2	109.3
	β(H_b–C–Si)	111.6	111.6
dimethyldisilavinylidene	*r*(Si–Si)	2.191	2.191
	r(C–Si)	1.889	1.885
	r(C–H_a)	1.086	1.095
	r(C–H_b)	1.088	1.096
	θ(C–Si–C)	111.4	111.5
	α(H_a–C–H_b)	107.6	107.5
	α(H_b–C–H_b)	107.5	107.6
	β(H_a–C–Si)	112.2	112.0
	β(H_b–C–Si)	110.9	111.0

[a] Bond lengths are in angstroms and angles are in degrees.

and contains 140 basis functions. For the TZ2P basis set we have switched from six to five functions in the d set to reduce the number of basis functions to a more manageable level.

The electron configuration for the three structures are

$$\text{trans:}\quad (\text{core})6a_g^2 6b_u^2 7a_g^2 7b_u^2 2a_u^2 2b_g^2 8a_g^2 8b_u^2 9a_g^2 9b_u^2 3a_u^2$$

$$\text{twist:}\quad (\text{core})7a^2 7b^2 8a^2 8b^2 9a^2 9b^2 10a^2 10b^2 11a^2 11b^2 12a^2$$

dimethyldisilavinylidene:

$$(\text{core})8a_1^2 4b_2^2 9a_1^2 10a_1^2 3b_1^2 5b_2^2 1a_2^2 11a_1^2 6b_2^2 12a_1^2 4b_1^2$$

Canonical cotton coordinate systems were used with the Si–Si bond along the *x*-axis when there is a choice.

3, Results and Discussion

As anticipated from the previous SCF results, the CISD/DZ+d frequencies revealed the trans isomer to be a minimum. Also as expected, we were unable to locate a twist stationary point. Thus the SCF/DZ+d level imaginary frequency of the trans stationary point corresponding to twisting deformation is merely an artifact of the SCF method. The dimethyldisilavinylidene remains a minimum at the CISD/DZ+d level.

Figure 1 shows the optimized CISD/DZ+d geometrical parameters for the dimethyldisilavinylidene and trans structures. These are also reported in Table I, where the SCF/DZ+d values[18] are included for comparison. The dimethyldisilavinylidene structure is virtually the same with both methods. The only noticeable change is a slight lengthening (0.01 Å) of the C–H bonds and an even smaller (0.004 Å) contraction of the Si–C bond. The trans CISD/DZ+d geometry is also quite similar to the SCF/DZ+d geometry. In this case the Si–Si and C–H bonds are slightly lengthened by correlation effects, and the C–Si–Si angle is 2.3° smaller. Once again the Si–C bond is shortened, this time by 0.003 Å.

In view of the fact that CISD generally lengthens bonds, the contraction of the Si–C bonds for both structures and the lack of change of the Si–Si bond for dimethyldisilavinylidene seems a bit odd. These features are easily explained, however, by an examination of the composition of the CI wave function. The trans wave function has a leading coefficient (c_0) of 0.9190 corresponding to the ground-state electron configuration. Other significant contributions include $9b_u^2 \rightarrow 10a_g^2$ ($c_1 = -0.0856$), $3a_u^2 \rightarrow 3b_g^2$ ($c_2 = -0.0688$), and $3a_u9b_u \rightarrow 3b_g10a_g$ ($c_3 = 0.0677$ and $c_4 = -0.0500$) excitations. Since the $3a_u$ orbital is a Si–Si π orbital and the $3b_g$ is a Si–Si π^* orbital, the effect of promoting one or two electrons from the $3a_u$ to the $3b_g$ is to lengthen the Si–Si bond. However, the π orbital ($3a_u$) is mildly Si–C π^* antibonding, while the π^* orbital ($3b_g$) has no Si–C bonding character. Thus this transition also has the effect of shortening the Si–C bonds. Promoting one or both of the electrons in the $9b_u$ orbital to the $10a_g$ orbital counterbalances the Si–Si bond lengthening somewhat. Both of these orbitals have in-plane Si–Si π^* character, but the $10a_g$ orbital is also slightly Si–Si σ bonding. Thus the net effect of including these excited configurations in the trans wave function is to lengthen the Si–Si bond and shorten the Si–C bonds slightly. For dimethyldisilavinylidene the contribution of the SCF function to the CISD wave function is $c_0 = 0.9238$. The most important configuration after the SCF reference function ($c_1 = 0.0790$) is the $\pi \rightarrow \pi^*$ transition, $4b_1^2 \rightarrow 5b_1^2$. These orbitals are similar in composition to the trans π and π^* orbitals, and so this excitation causes a lengthening of the Si–Si bond and a contraction of the Si–C bond. The $6b_2^2 \rightarrow 7b_2^2$ ($c_2 = -0.0316$) transition, however, opposes lengthening of the Si–Si bond, as can be seen in Figure 2.

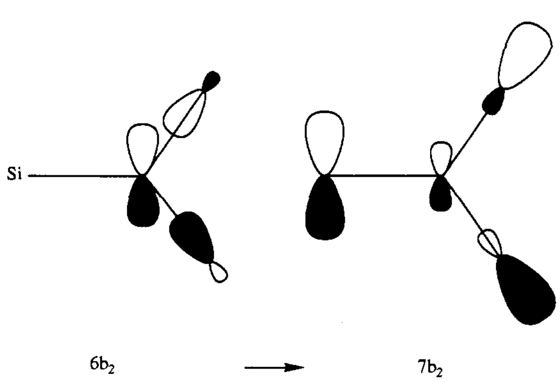

Figure 2. Schematic of the $6b_2$ and $7b_2$ orbitals for dimethyldisilavinylidene.

Compared to Si_2H_2 at a comparable level of theory[4] (CISD/DZP), the vinylidene-type structure is about the same (Si–Si bond length and R–Si–R angle are only slightly different), while the *trans*-dimethyldisilyne has a larger R–Si–Si angle ($\Delta\theta$ = 5.4°). More instructive perhaps is a comparison of the predicted Si–Si bond length of the dimethyldisilyne isomers with the known experimental Si–Si double bond lengths of substituted disilenes. The disilenes which have been synthesized all have large substituents groups (e.g., *tert*-butyl, mesityl, and 2,6-diethylphenyl), and they all have Si–Si bond distances of 2.14–2.15 Å.[28,29] Our prediction for the Si–Si bond length in dimethyldisilavinylidene, which formally has a double bond, is 2.191 Å, 0.04 Å longer than the experimentally known double bond values. On the other hand, our prediction for the Si–Si bond length in the trans isomer is 2.090 Å, 0.05 Å shorter than the experimental values for a Si–Si double bond. This confirms the expectation that the Si–Si bond in the trans structure is stronger than a double bond.

Table II lists the SCF/DZ+d and CISD/DZ+d harmonic vibrational frequencies and infrared intensities. On the whole, the CISD frequencies are lower than the SCF, with few exceptions (Si–Si stretch, C–Si–Si symmetric and antisymmetric bends for the trans structure). The C–Si–Si–C twist mode for the trans structure goes from 29i cm^{-1} at the SCF level to 105 cm^{-1} at the CISD level. This transition from a low imaginary frequency to a low real frequency when comparing SCF to CI results has previously been documented[4] for Si_2H_2 and seems to be a trend for the trans configuration of unsaturated silicon hydrides.[30]

The infrared spectra for the two isomers should be easily distinguishable, thus providing a tool for conformational identification should an infrared spectrum be obtained. The spectrum of the trans isomer displays one mode (the b_u C–Si antisymmetric stretch at 711 cm^{-1}; harmonic approximation, CISD/DZ+d level of theory) which is predicted to be much more intense in the IR than any other peak. Some of the other b_u modes should be

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(28) Masamune, S. In *Silicon Chemistry*; Corey, J. Y.; Corey, E. R., Gaspar, P. P., Eds.; Ellis Horwood Limited: West Sussex, England, 1988; pp 257–268.

(29) West, R.; Fink, M. J.; Michalczyk, M. J.; De Young, D. J.; Michl, J. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood Limited: West Sussex, England, 1985; pp 1–14.

(30) Colegrove, B. T.; Schaefer, H. F. *J. Chem. Phys.* **1990**, *93*, 7230.

(31) Nagase, S.; Kudo, T.; Ito, K. In *Applied Quantum Chemistry*; Smith, V. H., Schaefer, H. F., Morokuma, K., Eds.; D. Reidel Publishing Company: Dordrecht, Holland, 1986; pp 249–267.

Table II. Harmonic Vibrational Frequencies for $Si_2(CH_3)_2$ Structures Obtained by Using the DZ+d Basis Set

structure	symmetry	description	SCF freq	SCF int	CISD freq	CISD int
trans	A_g	C–H asym stretch	3285	0	3212	0
		C–H sym stretch	3206	0	3126	0
		methyl asym def	1595	0	1526	0
		methyl sym def	1434	0	1376	0
		methyl rock	878	0	847	0
		Si–C sym stretch	789	0	782	0
		Si–Si stretch	472	0	487	0
		C–Si–Si sym bend	222	0	224	0
	B_g	C–H asym stretch	3306	0	3231	0
		methyl asym def	1592	0	1518	0
		methyl rock	851	0	824	0
		methyl conrotatory rotation	40	0	18	0
	A_u	C–H asym stretch	3306	19	3231	8
		methyl asym def	1595	14	1520	15
		methyl rock	789	36	808	<1
		twist(C–Si–Si–C)	29i	11	105	6
		methyl disrotatory rotation	53	10	15	10
	B_u	C–H asym stretch	3285	19	3212	12
		C–H sym stretch	3205	46	3124	23
		methyl asym def	1591	37	1522	34
		methyl sym def	1432	4	1378	4
		methyl rock	853	34	824	20
		C–Si asym stretch	717	61	711	64
		C–Si–Si asym bend	76	17	96	10
dimethyldisilavinylidene	A_1	C–H asym stretch	3281	9	3208	5
		C–H sym stretch	3192	21	3112	11
		methyl asym def	1598	8	1531	8
		methyl sym def	1445	2	1386	3
		methyl rock	970	84	943	78
		C–Si sym stretch	730	15	721	6
		Si–Si stretch	506	3	499	7
		C–Si–Si sym bend	207	1	199	1
	A_2	C–H asym stretch	3256	0	3196	0
		methyl asym def	1581	0	1508	0
		methyl rock	790	0	766	0
		methyl conrotatory rotation	98	0	94	0
	B_1	C–H asym stretch	3266	28	3196	15
		methyl asym def	1592	18	1520	21
		methyl rock	852	1	828	2
		out-of-plane (Si–Si–C–C) bend	174	≪1	164	<1
		methyl disrotatory rotation	119	≪1	117	<1
	B_2	C–H asym stretch	3282	15	3208	8
		C–H sym stretch	3192	23	3111	15
		methyl asym def	1590	9	1522	11
		methyl sym def	1437	20	1380	23
		methyl rock	823	48	800	51
		Si–C asym stretch	755	15	746	8
		C–Si–Si asym bend	125	10	106	7

[a] Frequencies are in cm^{-1} and intensities are in km/mol.

Table III. The Total (E_{tot}) and Relative (E_{rel}) Energies of the Trans and Dimethyldisilavinylidene Isomers for the DZ+d, DZP, and TZ2P Basis Sets[a]

			DZ+d	DZP	TZ2P
trans	E_{tot}	SCF	−656.953 187	−656.963 026	−657.010 835
	(hartree)	CISD	−657.358 062	−657.402 368	−657.482 046
		CISD+Q	−657.421 043	−657.471 239	−657.559 079
dimethyldisilavinylidene	E_{tot}	SCF	−656.985 309	−656.995 110	−657.045 975
	(hartree)	CISD	−657.378 441	−657.423 313	−657.506 283
		CISD+Q	−657.436 121	−657.486 992	−657.578 506
	E_{rel}	SCF	20.2	20.1	22.1
	(kcal·mol^{-1})	CISD	12.8	13.1	15.2
		CISD+Q	9.5	9.9	12.2

[a] The DZ+d energies are for fully optimized structures, while the DZP and TZ2P results are single point energies at the DZ+d geometries. The SCF results from ref 18 are included for comparison with the present CISD results.

observable but much less intense, while the a_u modes have very small intensities and the a_g and b_g modes are forbidden. The infrared spectrum of the dimethyldisilavinylidene is more congested, having only the a_2 vibrations forbidden. The most intense peaks are two methyl rocking modes (an a_1 at 943 cm^{-1} and a b_2 at 800 cm^{-1}). Generally speaking, the harmonic vibrational frequencies predicted here at the CISD/DZ+d level of theory should be of the order of 8% above the true fundamentals.

Table III contains an energetic analysis of the two structures, including SCF, CISD, and CISD+Q results. Since the CISD/

DZ+d optimized geometries are so similar to the SCF/DZ+d geometries, the CISD/DZ+d and CISD+Q/DZ+d relative energies are very similar to the previously reported[18] single point CISD energies at the SCF optimized geometries. The relative energy difference increased with the larger TZ2P basis set; however, higher excitations should decrease the energy difference. Therefore we expect that our CISD+Q/TZ2P energy determination is close to the right answer. Our best ab initio prediction of the relative energies of the two minima is obtained by adding the CISD/DZ+d zero point energies to the TZ2P energies; this yields a relative energy of the trans relative to the dimethyldisilavinylidene of 12.0 kcal/mol.

4. Conclusions

We have predicted that the trans isomer of dimethyldisilyne is a minimum on the CISD/DZ+d potential energy surface and lies only 12.0 kcal/mol above the ground-state dimethyldisilavinylidene isomer. The trans isomer is most likely kinetically stable to isomerization to the dimethyldisilavinylidene structure, however, since the 1,2-methyl shift from one silicon atom to the other is expected to have a reasonably high activation energy. The transition state for this rearrangement should have one methyl group in a bridging position as it migrates between silicon atoms. We attempted to locate the transition state, but, as is often the case with transition state searches, we did not seem to be converging to a stationary point within a reasonable amount of time. This is not surprising as the symmetry of the transition state is necessarily C_1 since the methyl group must rotate, and there are 24 internal degrees of freedom. That such a bridging transition-state isomer should be significantly higher in energy that either the trans or dimethyldisilavinylidene isomers is supported by the instability of the dibridged isomer. In our previous paper,[18] we found the dibridged isomer to be 22.8 and 13.1 kcal/mol (CISD+Q energy and SCF optimized geometry, DZ+PP basis set), respectively, above the vinylidene and trans isomers. Thus it is quite possible that the barrier to rearrangement is large enough for *trans*-$Si_2(CH_3)_2$ to be an isolable species. Since the structures synthesized by West and co-workers[1-3] have a methyl group bonded to each silicon, the likely intermediate is the trans isomer of dimethyldisilyne. Obviously, the definitive synthesis of dimethyldisilyne would be a major accomplishment in organic chemistry.

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AM1 Calculations of Reaction Field Effects on the Tautomeric Equilibria of Nucleic Acid Pyrimidine and Purine Bases and Their 1-Methyl Analogues

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Abstract: Semiempirical AM1 quantum-chemical calculations of the principal tautomers of cytosine, thymine, uracil, 1-methylcytosine, 1-methylthymine, 1-methyluracil, adenine, and guanine were carried out for the isolated molecules, and for the same molecules in a polarizable dielectric medium with the relative permittivity of water, using the self-consistent reaction field method. In almost all cases, the same tautomer is predicted as most stable regardless of the method used and environment applied. However, the calculations imply significant quantitative differences in the relative stabilities of the tautomers in different media, which need to be taken account of in the nucleic acid base pairing/mispairing probability estimations based on quantum-chemical data.

Introduction

Tautomeric equilibria of the nucleic acid bases are of great importance and significance. Normal base pairing can only take place between the specific correctly positioned tautomers. However, abnormal pairing can occur between minor tautomers and such abnormal pairing can lead to mutations. Because of the importance of this concept, the tautomerism of the parent nucleic acid bases has been the subject of much investigation within the general framework of heterocyclic tautomerism as a whole: the early work has been summarized in ref 1 and later work, up until about 1975, in ref 2. Kwiatkowski and Pullman reviewed the detailed structures of biological pyrimidines in 1975,[3] as had Pullman and Pullman for the corresponding purines in 1971.[4]

To summarize, it has been conclusively shown that in almost all cases uracil (**13**), thymine (**19**), cytosine (**2**), adenine (**29**), and guanine (**37**) exist predominantly in the structures shown, whether it be in the crystalline state, in aqueous solution, in solutions of nonpolar solvents, or in the gas phase. Although, over the years, many claims to the contrary have appeared (i.e. that these compounds exist, in one phase or another, predominantly in one of the other possible tautomeric forms), all such claims have been disproved (see refs 1 and 2 for detailed rebuttals of several of them). In contrast to this clear picture of which are the dominant tautomeric forms, far less attention has been paid to the *quantitative* tautomeric equilibrium constants between these dominant forms and the next most important form or forms, despite the obvious importance of such quantitative data to considerations of spontaneous mutations. Thus little experimental data are available on the energy differences between the tautomeric forms.

By contrast, numerous investigations have taken place of the heats of formation of the various tautomers as calculated by both ab initio and semiempirical molecular orbital methods and several reviews on this topic have been published in recent years.[5-7] A

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(1) Katritzky, A. R.; Lagowski, J. M. *Adv. Heterocycl. Chem.* **1963**, *1*, 339.

(2) Elguero, J.; Marzin, C.; Katritzky, A. R.; Linda, P. The Tautomerism of Heterocycles. *Advances in Heterocyclic Chemistry*, Supple. 1, Academic Press: London, 1976.

(3) Kwiatkowski, J. S.; Pullman, B. *Adv. Heterocycl. Chem.* **1975**, *18*, 199.

(4) Pullman, B.; Pullman, A. *Adv. Heterocycl. Chem.* **1971**, *13*, 77.

(5) Kwiatkowski, J. S.; Zielinski, T. J.; Rein, R. *Adv. Quantum Chem.* **1986**, *18*, 85.

0002-7863/91/1513-1561$02.50/0