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A Theoretical Study of Trimethylsilyl Radical and Related Species

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Energies and structures for a series of silicon-centered radicals were calculated by ab initio methods. The lowest energy conformation of trimethylsilyl radical is found to be pyramidal. The angle formed by an Si–C bond and the plane formed by Si with the other two carbons is found to be 51.7°. The inversion barrier through the higher energy planar C_{3v} structure is calculated to be 13.3 kcal/mol. The planar C_{3h} structure lies still higher in energy. In the planar forms of the methyl-substituted radicals, the methyl groups are slightly distorted so that the CH bond more eclipsed with the SOMO is bent away from this MO. The results are compared to the *tert*-butyl radical and interpretations for the various conformations offered. Substituent effects on the degree of pyramidalization and on the barrier to inversion in silyl radicals are substantial. Substitution of three fluorines for hydrogens in $\cdot SiH_3$ raises the barrier from 5 to 68 kcal/mol. Successive substitution of methyl groups for hydrogens also increases the pyramidal-planar barrier.

Introduction

Silicon-centered free radicals play important roles in a number of organosilicon reactions ranging from peroxide-catalyzed hydrosilylation of olefins to a variety of transformations involving metals. Many of these reactions exhibit a preference for retention of configuration at silicon, as for example in the abstraction of Cl from CCl_4 by certain silyl radicals.[1] The experimental evidence is consistent with a considerable barrier to inversion and/or an inversion process that is slow relative to the abstraction process.[2]

AH_3 type molecules involving third-row elements are generally found to have greater inversion barriers than their second-row analogues.[3] Silyl radical is pyramidal,[4] while methyl radical is planar.[4c,d,5] However, the preferred geometry of both carbon and silicon radicals is dependent on substituents at the radical center. As electronegative groups such as F replace H in CH_3, the preferred structure becomes more pyramidal and the barrier to inversion increases.[6] Ab initio calculations[7] indicate the *tert*-butyl radical to be pyramidal, although a controversy still exists over interpretation of experimental data relating to whether *tert*-butyl radical is planar[8] or pyramidal.[9]

Inclusion of the radical center in a ring system can, of course, have a major effect on geometry and reactivity. We have explored experimentally a substantial amount of reaction chemistry of 1,2-dimethylsilacycloalkanes, including some radical reactions.[10] The predominant retention stereochemistry shown in these reactions, as well as some preliminary calculations,[11] indicates considerable barriers to inversion in the radicals. These cyclic systems with the possibility for geometric isomerism offer promise of affording compounds with an inversion barrier that would be in a suitable region for experimental measurement. Consequently, we have undertaken the present theoretical study in order to obtain information about trends of structural effects on the inversion barriers of silyl radicals.

In a recent report[12] the inversion barrier for the α-NpPhMeSi radical has been estimated. Absolute rate constants of the reaction of Et_3Si radicals with organic halides were obtained by using benzil as probe by laser flash photolysis. Experimental data[2b] concerning the optical purity of product obtained in reactions of α-NpPhMeSiH with CCl_4 at varying CCl_4 concentration were used in a Stern–Volmer type equation to yield k_{inv}, assuming that $Et_3Si\cdot$ and α-NpPhMeSi$\cdot$ react with CCl_4 at equal, nearly diffusion-controlled, rates. With the value for k_{inv} obtained and with the assumption of a normal preexponential factor for inversion at Si, the activation barrier for the inversion was calculated to be 5.6 kcal/mol.

There have been a number of theoretical studies [13] of $\cdot SiH_3$ at various levels of ab initio theory. Each predicts the $\cdot SiH_3$ radical to be pyramidal. In the present work ab initio unrestricted Hartree–Fock calculations were undertaken to study the energies and structures of the tri-

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Table I. Geometric Parameters and Energies for Five Conformations of Trimethylsilyl Radicals[a]

	pyramidal forms			planar forms	
	C_{3v} (I)	C_3 (II)	C_{3v} (III)	C_{3v} (IV)	C_{3h} (V)
energy, hartrees	−407.584 040 −405.593 913	−407.581 688	−407.579 058	−407.562 831 −405.572 299	−407.562 361 −405.571 867
ΔE, kcal/mol	0	1.48	3.13	13.31 13.56	13.60 13.83
γ, deg	51.7 51.9	51.5	49.9	≡ 0	≡ 0
$h/\hat{h}$, Å/Å	0.606/0.314 0.607/0.315	0.604/0.312	0.586/0.302	≡ 0/0	≡ 0/0
d(Si-C)	1.933 1.926	1.937	1.942	1.934 1.928	1.936 1.930
d(C-H_a)	1.088 1.088	1.086	1.085	1.084 1.084	1.085 1.085
d(C-H_b)	1.085 1.085	1.087	1.086	1.085 1.085	1.084 1.084
d(C-H_c)		1.085			
∠(C-Si-C)	110.65 110.57	110.74	111.31	≡ 120	≡ 120
∠(Si-C-H_a)	110.92 110.85	110.46	111.42	113.23 113.26	108.82 108.73
∠(Si-C-H_b)	110.83 110.76	110.61	110.71	109.50 109.45	111.74 111.72
∠(Si-C-H_c)		111.58			

[a] The first value listed is a 6-21G result; the second is 3-21G. Bond lengths are reported in angstroms and bond angles in degrees.

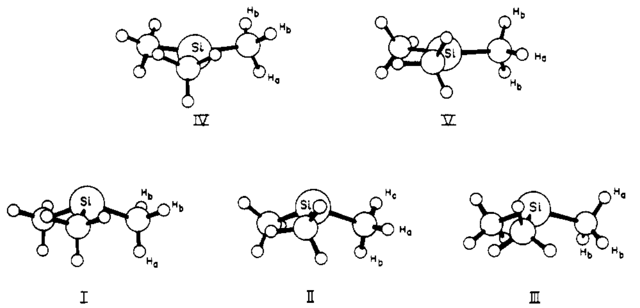

Figure 1. Geometries of five conformations of trimethylsilyl radicals.

methylsilyl radical (·$SiMe_3$) in five conformations. The gradient method was used to optimize the geometric parameters. The 3-21G and 6-21G split valence sets were used within the Gaussian 80 series of programs. In all the calculations S^2 = 0.75–0.77. Calculations at the same level of theory were carried out with ·CMe_3 in order to make direct comparisons. In addition, a range of substituent effects on geometries and inversion barriers has been explored in 3-21G calculations on ·SiH_2X (X = H, CH_3, F) and ·SiF_3.

Results

The most complex radical system studied in the present work is ·$SiMe_3$. The carbon analogue ·CMe_3 is a richly studied species, both experimentally and theoretically, and comparisons of the two group 4 analogues should be instructive. The ·$SiMe_3$ conformations of most importance in the discussion are shown in Figure 1. In the cases of three geometries, minimizations have been performed at both 3-21G and 6-21G levels, and the results differ insignificantly, both with respect to geometries and relative energies. The calculated energies and geometric parameters are shown in Table I. Both ·CMe_3 and ·$SiMe_3$ are predicted to be pyramidal. The degree of pyramidalization in various structures is a matter of interest, and several measures of that quantity have been used by various authors. One measure is the angle, variously called γ and θ_b,[7a,b] between a plane defined by the radical center and two attached atoms and the third bond to the radical center. A second measure, here designated h, is the perpendicular distance between the radical center and the plane defined by the three attached atoms. Since we are considering radicals of several types, with widely different bond lengths, we consider it more meaningful to define a new h, to be designated $\hat{h}$, in which the plane, rather than being defined by three atoms, is defined by three points 1.0 Å away from the radical center along the bonds to the attached atoms. The value of γ for ·$SiMe_3$ in its most stable geometry, I, is 51.7°, and $\hat{h}$ is 0.314 Å. The corresponding values for ·CMe_3 from a 4-31G basis set calculation are 22.1° and 0.129 Å.[7a,b]

In the pyramidal geometries of ·CMe_3 the H atom (H_a) anti to the orbital containing the single electron is less tightly bound than the H atoms gauche (H_b). The CH_a bond lengths are calculated to be slightly longer than CH_b in each case. In the planar structures of ·CMe_3, CH_a is longer than CH_b for the C_{3v} geometry and CH_b is longer than CH_a in the C_{3h} geometry. In ·$SiMe_3$ the two types of CH bonds are essentially identical in length and are nearer a common length in all five geometries (three pyramidal and two planar) than is the case for ·CMe_3. The foregoing is true also for ·SiH_2Me. In the pyramidal structure VIII the CH_a bond length is very slightly longer than the CH_b lengths (see Figure 2 and Table II).

The methyl groups are tilted in both planar $SiMe_3$ radicals so that there is no local C_3 axis through any methyl group. If all SiCH angles in ·$SiMe_3$ were equal, a right circular cone would be formed (assuming equal CH distances) with the hydrogens in the base and Si at the apex. However this cone is tilted in the planar structures; i.e., the angle $SiCH_a$ is greater than $SiCH_b$ in planar C_{3v} ·$SiMe_3$, and $SiCH_b$ is greater than $SiCH_a$ in C_{3h} ·$SiMe_3$. Also, the methyl group in planar bisected ·SiH_2Me (IX) shows the same kind of distortion.

The SiC bonds are somewhat longer than anticipated in all geometries for ·$SiMe_3$. When third-row atoms are bound to terminal heavy atoms, the 3-21G and 6-21G programs predict bond lengths that are greater than normal.[14] Normal Si–C bond lengths are in the range

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Table II. Geometries and Energies of SiH_2X Radicals[a]

	X = H		X = CH_3[b]		X = F	
	C_{3v} (VI)	D_{3h} (VII)	pyramidal C_s (VIII)	planar C_s (IX) (bisected)	C_s (X)	C_{2v} (XI)
energy, hartrees	−289.080 539	−289.072 490	−327.917 811	−327.906 509	−387.458 971	−387.437 697
ΔE, kcal/mol	0	5.05	0	6.30	0	13.35
γ, deg	48.9	≡ 0	49.3	≡ 0	53.3	≡ 0
$h/\hat{h}$, Å/Å	0.439/0.295	≡ 0/0	0.487/0.302	≡ 0/0	0.493/0.322	≡ 0/0
α, deg	107.17	≡ 90	104.66	≡ 90	108.93	≡ 90
β, deg			109.06	≡ 90	108.73	≡ 90
d(Si-X)	1.486	1.474	1.924	1.922	1.640	1.643
d(Si-H)			1.491	1.477	1.483	1.460
$\angle$(H-Si-X)	111.67	≡ 120	112.06	120.77	109.86	115.65
$\angle$(H-Si-H)			109.72	118.46	110.71	128.70
d(C-H_a)			1.086	1.083		
d(C-H_b)			1.084	1.084		
$\angle$(Si-C-H_a)			110.66	111.86		
$\angle$(Si-C-H_b)			110.50	109.76		

[a] Values are 3-21G optimized. Bond lengths are reported in angstroms and bond angles in degrees. [b] Of two pyramidal and two planar structures optimized, only the lower energy structure in each is reported here.

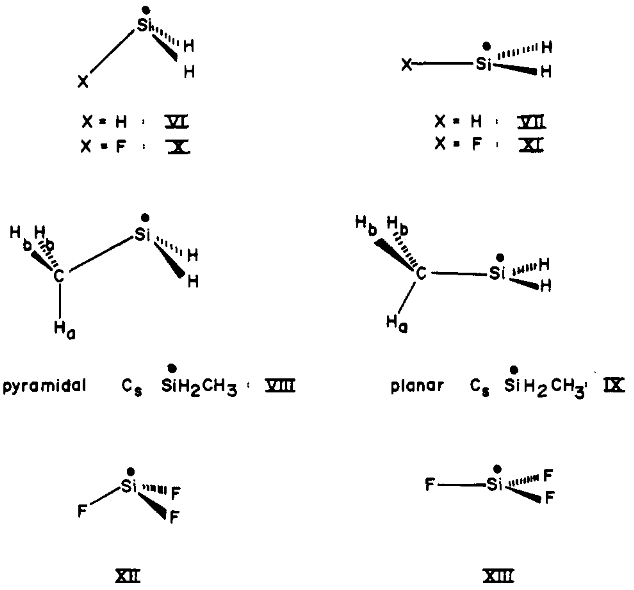

Figure 2. Geometries of monosubstituted $\dot{S}iH_2X$ and $\dot{S}iF_3$ radicals.

1.86–1.88 Å, but 3-21G and 6-21G give Si–C lengths of ca. 1.9 Å. A split valence set for third-row atoms has recently been supplemented by d type functions (3-21G*).[15] These were shown to give Si–C lengths more in agreement with known experimental measurements. All other parameters are very reasonable without inclusion of d functions, and the split valence sets are generally recognized as yielding reasonable energy differences between isomers.

Table III. Geometries and Energies for Two Conformations of Trifluorosilyl Radical

	C_{3v} (XII)	D_{3h} (XIII)
energy, hartrees	−584.242 775	−584.134 313
ΔE, kcal/mol	0	68.06
γ, deg	61.7	≡ 0
$h/\hat{h}$, Å/Å	0.612/0.380	≡ 0/0
α, deg	112.32	≡ 90
d(Si-F), Å	1.610	1.616
$\angle$(F-Si-F), deg	106.44	≡ 120

The calculations predict the inversion barrier for $\cdot SiMe_3$ to be 13.3 kcal/mol with the planar C_{3v} structure slightly lower in energy than the planar C_{3h} geometry. The stabilities of the planar geometries are reversed in $\cdot CMe_3$, and the planar-pyramidal barrier is only 1.23 kcal/mol.[7b] For calculations done on the series SiH_2X (X = H, Me, F), the results of which are shown in Table II, the pyramidal form in each is stabler than the planar and the barrier energy increases in the series $\cdot SiH_3 < \cdot SiH_2Me < \cdot SiH_2F$. The respective barrier energies are 5.1, 7.1, and 13.3 kcal/mol, as calculated by using the 3-21G split valence basis set. Substitution at the silyl radical center by three F atoms results in the largest barrier to planarity observed in these calculations, 68.1 kcal/mol. The calculated parameters for $\cdot SiF_3$ are shown in Table III. In carbon radicals the lower energy structure is planar in $\cdot CH_3$, while pyramidal $\cdot CF_3$ is calculated to be lower in energy than planar $\cdot CF_3$ by 27.4 kcal/mol.[5i]

Discussion

Preferred Geometries. The methyl groups of planar $\cdot SiMe_3$ are slightly distorted, as indicated above, and the methyl groups in carbon radicals are also found to be distorted. In the pyramidal ethyl,[16] propyl,[17] isopropyl,[18] and *tert*-butyl[7] radicals the β-CH bond(s) that is most eclipsed with the half-filled MO on the carbon radical center is longer than the β-CH bond(s) that is more perpendicular to the singly occupied MO (SOMO). In $\cdot CMe_3$ the "eclipsed" CH bonds range from 0.005 to 0.007 Å longer than the "perpendicular" bonds. in $\cdot SiMe_3$ where the SiC bonds are longer and the β-CH and SOMO interaction is expected to be smaller, the CH bonds are closer to each other in length; the difference between the two types of bonds ranging from 0.0007 to 0.0024 Å, but nevertheless consistently having the eclipsed bond longer.

In the lowest energy pyramidal form of $\cdot SiMe_3$, the SiCH bond angles are all nearly the same, but this is not the case in the planar forms. For methyl groups in planar $\cdot SiMe_3$ and also for methyl groups in planar forms of carbon radicals, the C–H bonds more nearly eclipsed with the singly occupied orbital experience a widening of the $\cdot$SiCH or $\cdot$CCH angle. For example, in planar C_{3v} $\cdot SiMe_3$, $SiCH_a$ and $SiCH_b$ are 113.2° and 109.5°, respectively; while in planar C_{3h} $\cdot SiMe_3$, $SiCH_a$ and $SiCH_b$ are 108.8° and 111.7°,

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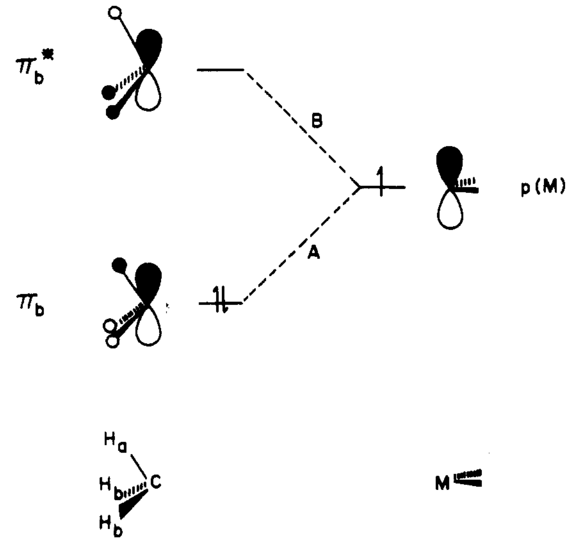


Figure 3. Interaction of π_b and π_b^* of the methyl group with the SOMO on the radical center M in bisected radicals. The interactions result in a tilt of CH_a away from the radical center.

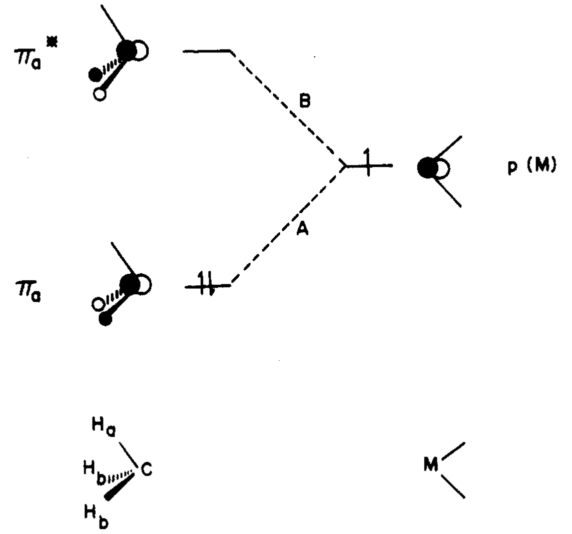
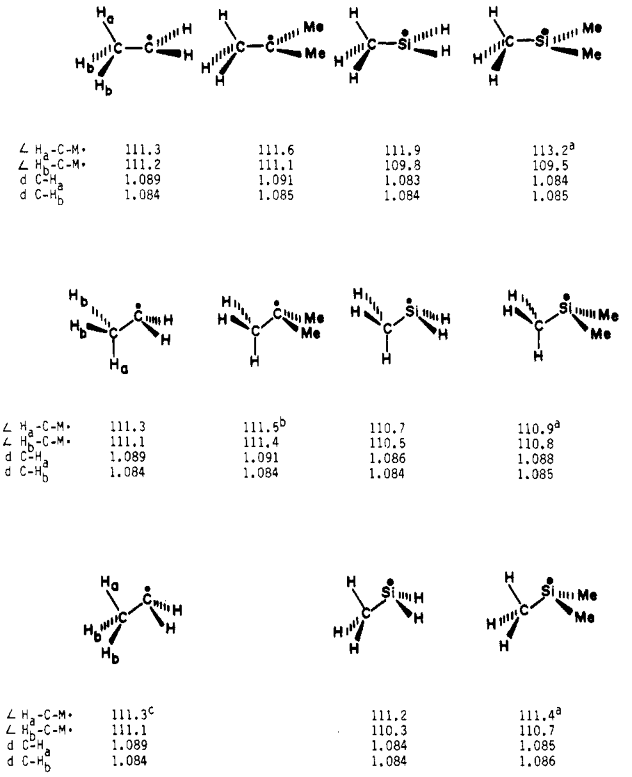


Figure 4. Interaction of π_a and π_a^* of the methyl group with the SOMO on the radical center M in eclipsed radicals. The interactions result in a tilt of CH_a toward the radical center.

respectively. Likewise in planar $\cdot SiH_2Me$, $SiCH_a$ is 111.9° and $SiCH_b$ is 109.8°.

The tilt of the methyl groups in the planar forms of carbon- and silicon-centered radicals in this report may be explained from a hyperconjugative standpoint by PMO theory[19,20] using reasoning similar to that which Pross et al.[19] have applied to $MeNH_2$ with planar N. Figure 3 shows the interactions of importance between π(Me) group orbitals and the p orbital on the radical centers in the bisected forms of the radicals. The three electrons are now distributed over two orbitals in interaction A, and the interaction is repulsive,[21] and more so above the plane than below. The major interaction will be between π_b^* and the SOMO (interaction B).[22] The overlap will be greatest below the C–M bond since the in-plane hydrogen is subtracted from the C(2p) orbital. This produces a tilt of the methyl group so that CH_a is bent away from M. Again, the $SiCH_a$ angle is larger than the $SiCH_b$ angle in planar C_{3v} $\cdot SiMe_3$.



∠ H_a-C-M·	111.3	111.6	111.9	113.2[a]
∠ H_b-C-M·	111.2	111.1	109.8	109.5
d C-H_a	1.089	1.091	1.083	1.084
d C-H_b	1.084	1.085	1.084	1.085

∠ H_a-C-M·	111.3	111.5[b]	110.7	110.9[a]
∠ H_b-C-M·	111.1	111.4	110.5	110.8
d C-H_a	1.089	1.091	1.086	1.088
d C-H_b	1.084	1.084	1.084	1.085

∠ H_a-C-M·	111.3[c]	111.2	111.4[a]
∠ H_b-C-M·	111.1	110.3	110.7
d C-H_a	1.089	1.084	1.085
d C-H_b	1.084	1.084	1.086

Figure 5. Methyl group parameters in some Si and C radical conformations. Values are 3-21G results except: [a]6-21G, [b]4-31G, [c]not fully optimized.

Turning now to the eclipsed radical forms, the major interaction will be the π_a^* methyl group orbital with the SOMO (Figure 4). This interaction, though stabilizing and attractive with respect to the methyl group itself, will result in a tilt of the CH_a bond toward M because of the repulsion in the region below the C–M bond due to the opposite phasing of the hydrogen orbitals and the SOMO. Thus in planar C_{3h} $SiMe_3$ the angle $SiCH_b$ is larger than $SiCH_a$. In the situations above simple VSEPR arguments may also be used to explain the tilt observed in the methyl groups. Here the SOMO repulses the methyl C–H bonds closest to it.

Concomitant with this angle bending, there should be a CH_a bond stretching in the bisected form because of increased electron density in the π_b^* methyl group orbital. This is evident in the ethyl radical where CH_a is 1.089 Å and CH_b is 1.084 Å. However in methylsilyl radical there is no difference between CH_a and CH_b bond lengths. If angle bending is easier than C–H bond stretching, then one might see the hyperconjugative effect on the H–C–M angle without seeing the effect on the H–C bond length, and this may be what is happening in the cases of the silyl radicals, where little or no differences are calculated for the C–H_a and C–H_b bond lengths. In the silyl radicals, HCSi angle bending would be expected to be easier to accomplish than the HCC bending of the alkyl radicals because of the generally smaller bending force constants for H–C–Si an-

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(22) A further indication that it is the B interactions that predominant in $\cdot SiH_2CH_3$ is that while the CH_3 group degeneracy of π_a^* with π_b^* is removed, there is very little splitting of the π_a and π_b degenerate level.

Table IV. Comparison of Pyramidalization of Silicon-Centered Radicals

	XII	X	I[a]	II[a]	III[a]	VIII[a]	VI
$\hat{h}$, Å	0.380	0.322	0.314	0.312	0.302	0.302	0.295
γ, deg	61.7	53.3	51.7	51.5	49.9	49.3	48.9
ΔE, kcal/mol	68.06	13.35	13.31	11.83	10.18	6.30	5.05
$\Delta E_{\mathrm{S-L}}$,[b] kcal/mol	0.269	0.415	0.398	0.397	0.398	0.439	0.468

[a] For structures I, II, and III the result quoted is for 6-21G calculations. All others are 3-21G. [b] $\Delta E_{\mathrm{S-L}}$ is the SOMO–LUMO energy gap in the corresponding planar structures.

gles as compared to H–C–C angles.[23]

It should be noted that the above analysis applies to group orbital interactions in planar forms of the radicals. As pyramidalization occurs and the SOMO acquires more hybrid orbital character, the interactions should be altered. We find, however, as shown in Figure 5, no noticeable trends as geometry is changed. Indeed, in the three forms of the ethyl radical shown in Figure 5 there are no differences between planar and pyramidal forms in the calculated angles or lengths at the 3-21G level of approximation. We think this points up the care that must be taken in using any qualitative orbital interaction argument, particularly one which involves opposite forces acting to differing degrees. The analysis of Pross et al.[19] may be qualitatively correct, but it may also be difficult to apply, even in cases closely related to that for which it was derived.

Both $\cdot CMe_3$ and $\cdot SiMe_3$ adopt the pyramidal C_{3v} geometry as the lowest energy structure. The *tert*-butyl radical that has C_{3h} geometry is the lower in energy of the two planar structures. For $\cdot SiMe_3$ the planar C_{3v} geometry is lower than C_{3h}. The carbon radical has much shorter heavy-atom bond lengths than does the silicon analogue, and a van der Waals interaction may account for the difference in preferred planar geometry.

Molecular mechanics calculations[24] were performed on the $\cdot CMe_3$ and $\cdot SiMe_3$ radicals in each of its planar conformations to get a nonquantum mechanical estimate of the preferred geometries. Single shot calculations were performed by using the MM2 program operating on the minimized coordinates obtained in the Gaussian 80 calculations. The molecular mechanics program apportions the total energy into classical compression, bending, stretch bend, van der Waals, and torsional energies. It is the van der Waals energy in $\cdot CMe_3$ that shows the largest energy difference between the two planar structures. The other terms show small differences, although in each case the C_{3h} energy is lower than the corresponding energy in the planar C_{3v} form. When all 27 H···H van der Waals interactions (there are six types) are analyzed, one type present in planar C_{3v} $\cdot CMe_3$ is a destabilizing interaction. The $H_b \cdots H_b$ distance of H_b's pointing toward each other on adjacent methyl groups (see Figure 1) is 2.413 Å and has energy of +0.1714 kcal/mol. There are three such interactions of this type in the planar C_{3v} conformation. When the van der Waals energies for the 27 interactions in both planar geometries of $\cdot CMe_3$ are added, the C_{3h} structure is lower in van der Waals energy by 0.45 kcal/mol. In the case of CMe_3, C_{3v} may be raised in energy by van der Waals interactions, thus bringing the C_{3v} and C_{3h} energies closer together (only 0.04 kcal/mol separates planar C_{3v} and planar C_{3h} in 4-31G calculations). In $\cdot SiMe_3$, where the SiC lengths are longer, the H···H distances are thus greater. The van der Waals energies are small and stabilizing (the slope of the potential curve is smaller at large distances) and nearly equal when the 27 interactions in both C_{3h} and C_{3v} planar $\cdot SiMe_3$ are added. The van der Waals interactions thus do not have import in deciding the lower energy geometry in planar $\cdot SiMe_3$, and the C_{3v} structure is lower by virtue of other interactions in the radical.

The molecular mechanics program was also used to look at the energies of the three pyramidal structures of $\cdot SiMe_3$. Here the van der Waals energy is also not the major energy contribution to the preferred geometry. For each of the contributing terms the energy increases along the series C_{3v}(I) < C_3(II) < C_{3v} (III) (see Figure 1 for structures). Indeed, it is worth noting that the same order of stabilities of the $\cdot SiMe_3$ conformations (I–V) is predicted by molecular mechanics calculations (steric energy = 3.83, 5.70, 8.02, 11.04, 11.15 kcal/mol, respectively) and by the quantum mechanical calculations (relative energy = 0, 1.48, 3.13, 13.3, 13.6 kcal/mol, respectively).

The degree of pyramidalization in various radicals is a function of the substituents on the radical center. There could be uncertainties in comparing various measures of pyramidalization among symmetrical and unsymmetrical radicals. Specifically, there is more than one γ angle in an unsymmetrical radical. The ones cited in Table II for SiH_2X radicals are measured by using the plane defined by Si and the two hydrogens. The γ angle is then that between the plane and the Si–X bond. The vertical distance, $\hat{h}$, is defined by using idealized bond distances and is probably the most reliable measure of pyramidalization among the diverse radicals.

The replacement of H by electronegative atoms such as fluorine increases the degree of nonplanarity of carbon radicals, as indicated experimentally[25,26] and theoretically.[5i,6,13c,25] The same trend has been found for the silicon radicals experimentally[27] and theoretically.[13c] An explanation of this effect points out that electronegative substituents reduce the electronic charge density in the bond orbitals, increasing the s population of the lower energy orbital containing the odd electron and resulting in greater pyramidalization.[28] An alternative way of looking at the same effect would be to argue that highly electronegative atoms decrease bond pair–bond pair repulsions, resulting in narrower angles. Our results summarized in Table IV confirm the previous observations and indicate that the electronegative atom effect with fluorine is quite substantial, $\cdot SiF_3$ being by far the most pyramidalized silyl radical in our study.

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The effect of alkyl groups on silyl radical geometry is a controversial subject. ESR measurement of ^{29}Si couplings in $Me_nH_{3-n}Si\cdot$ were interpreted to mean that the radicals become less pyramidal with increasing Me substitution.[4b] Later measurements of α-proton couplings were interpreted to reinforce that conclusion.[4a] However, another group assigned positive rather than negative signs to the ESR α-proton couplings and concluded that there is a slight increase in deviation from planarity with increasing Me substitution.[4e] The β-proton couplings were interpreted as reinforcing that view. Our results are in better agreement with the second interpretation, as is evident in Table IV. The effects of Me substitution are much smaller than those of F substitution but are consistently in the direction of increasing pyramidalization, as measured by $\hat{h}$.

Inversion Barriers. Intuitively one might expect to find a relationship between the degree of pyramidalization in radicals with various substituents and the magnitudes of the inversion barriers in those radicals. Our results for the silyl radicals summarized in Table IV agree with that expectation qualitatively. Fluorine substituents, which have a great effect on degree of pyramidalization, also have a dramatic effect on the inversion barrier. A single methyl group does not significantly increase the barrier to inversion over that for $\cdot SiH_3$, but three methyl groups have an appreciable effect. Our calculated inversion barrier for $\cdot SiMe_3$ (13.3 kcal/mol) is considerably larger than that calculated for $\cdot CMe_3$ (1.23 kcal/mol)[7b] and somewhat larger than the experimentally estimated barrier for α-NpPhMeSi· (5.6 kcal/mol).[12] That last value may be smaller than would be expected for the simpler $\cdot SiMe_3$ due to steric effects.

The general character of our results, including the larger barriers for Si radicals compared to C radicals and the substituent effects on the barriers for silyl radicals, can be rationalized in terms of SOMO–LUMO interactions, as suggested by Cherry and Epiotis for AH_3 molecules.[3] The LUMO and SOMO will tend to interact, lowering the singly occupied level while raising the LUMO. If this lowering in energy is greater than the concomitant rise in energy of the E level, the pyramidal geometry will be favored. Perturbation theory predicts that if the symmetry is correct for mixing then the extent of mixing will depend upon how close these highest lying orbitals are in energy. As the energy difference between the SOMO and LUMO becomes smaller, there will be a greater mixing and a greater lowering in energy of the SOMO. Consequently, the planar structure that has a smaller SOMO–LUMO difference will have a larger barrier to inversion. The SOMO–LUMO levels and the lowering of the SOMO in going from a planar to pyramidal geometry is shown for $\cdot SiMe_3$ and $\cdot CMe_3$ in Figure 6. The calculational result is that the carbon radical, which has a large splitting (0.567 hartree), has a small inversion barrier, 1.49 kcal/mol. The splitting is much smaller in $\cdot SiMe_3$ (0.398 hartree) and the corresponding barrier to planarity much larger (13.3 kcal/mol).

Substituent effects on the barriers, as discussed above, also are well correlated to the magnitudes of the SOMO–LUMO splittings, as seen in Table IV. Replacing one hydrogen of $\cdot SiH_3$ with Me or F changes the SOMO–LUMO gap from 0.468 to 0.439 and 0.415 hartree, respectively, and raises the inversion barrier from 5.05 kcal/mol to 6.30 and 13.35 kcal/mol, respectively.

The process of inversion for $\cdot SiMe_3$ is not quite so simple as that for the other radicals studied here. In order for pyramidal C_{3v} $\cdot SiMe_3$ to invert through a planar structure and back to C_{3v}, the methyl groups must rotate at some point. It is worth inquiring whether this process is a synchronous rotation of the methyl groups through the C_{3h} planar structure or whether the inversion takes place independently of this rotation. In $\cdot CMe_3$, where the C_{3h} geometry is the lower in energy of the planar structures, inversion passes through the C_{3h} transition state with synchronous methyl group rotations. The silicon-centered radical has the C_{3v} geometry as the lower energy planar structure. Figure 7 shows the energy differences among five $\cdot SiMe_3$ structures. The $SiMe_3$ radical may pass through the lower energy planar C_{3v} geometry (IV) via one

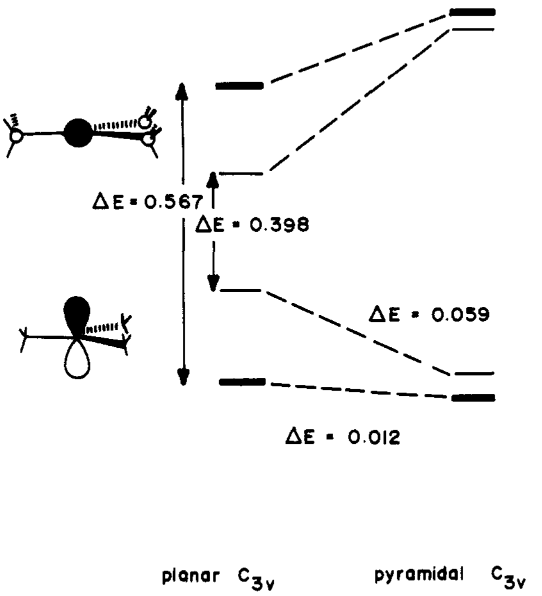

Figure 6. Lowering of the SOMO in the C_{3v} structures of $\cdot SiMe_3$ (light solid line) and $\cdot CMe_3$ (heavy solid line).

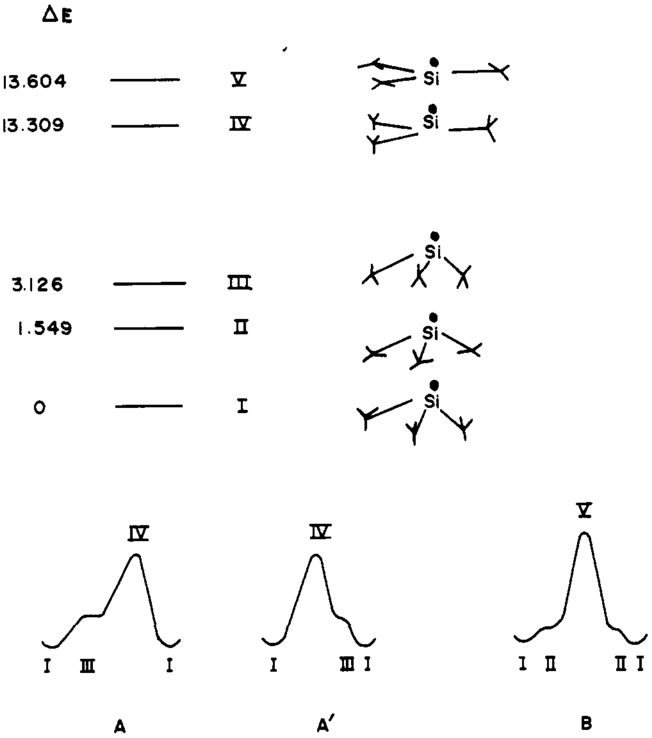

Figure 7. Possible inversion routes. In A or A′ there is a 60° rotation of the methyl groups and the radical passes through the planar C_{3v} geometry IV. In B there are 30° rotations of the methyl groups and the radical passes through the higher energy planar C_{3h} geometry V.

60° rotation of the methyl groups to structure III either before or after IV (routes A and A′). In route B, $\cdot SiMe_3$ would invert through the highest energy structure, planar C_{3h} (V), via 30° rotations to II and without passing through III. The results thus predict an inversion through the planar C_{3v} geometry with separate rotations of the methyl groups.

Conclusions

Trimethylsilyl radical has been calculated to have a pyramidal geometry with a barrier to planarity of 13.3 kcal/mol. This value is about 8 kcal/mol larger than that estimated experimentally for $\cdot SiMePhNp$-α. The calculations also show, however, a substantial substituent dependence for the degree of pyramidalization of the preferred geometry and for the barrier to planarity in the silyl radicals. The calculated barriers range from 5 ($\cdot SiH_3$) to 68 kcal/mol ($\cdot SiF_3$). Qualitatively, the substituent effects on barrier heights, as well as the relative energies of different geometries for methyl-substituted silyl radicals, can be predicted from SOMO–LUMO energy differences. Specifically, upon substitution of F for H in $\cdot SiH_3$ there is a marked increase in the degree of pyramidalization and in the inversion barrier. Substitution of Me for H produces a similar, although attenuated, effect.

When a CH_3 group is substituted on a planar carbon radical center, several geometric effects are observed that can be explained in terms of a hyperconjugative model like that used to explain the calculated geometries of planar CH_3NH_2.[19] The effects include methyl group tilt, relative CCH bond angles, and relative CH bond lengths. The former two effects are clearly present in methyl-substituted silyl radicals, but the latter effect is not. The hyperconjugative effect may be smaller in the silyl radicals than in the carbon analogues, and the geometric parameter hardest to distort, i.e., bond length, is not affected. It is not straightforward to extend the orbital interaction reasoning used for the planar radicals to their pyramidal forms, either for carbon or silicon radicals.

Molecular mechanics calculations indicate that the preference for a C_{3h} planar geometry over a C_{3v} one for the *tert*-butyl radical may have a steric origin in small repulsive van der Waals forces in the C_{3h} form. The van der Waals forces are much smaller in the trimethylsilyl radical, which prefers the planar C_{3v} form. Surprisingly, molecular mechanics calculations do a fair job of duplicating the quantum mechanical calculations in predicting the relative energies of all five planar and pyramidal geometries considered here for $\cdot SiMe_3$.

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Registry No. $H_3Si\cdot$, 13765-44-1; $H_iCH_oSi\cdot$, 51220-22-5; $H_2FSi\cdot$, 35427-70-4; trimethylsilyl radical, 16571-41-8; trifluorosilyl radical, 14835-14-4.

Electrophilic Halogen Exchange between Lewis Acids and Transition-Metal Perfluoroalkyl Complexes. Synthesis and Characterization of Transition-Metal α-Haloalkyl Complexes

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Facile halogen exchange takes place upon reaction of transition-metal perfluoroalkyl carbonyl complexes with BX_3 (X = Cl, Br, I). Treatment of $Mn(CO)_5CF_3$ with 1 equiv of BX_3 in a noncoordinating solvent affords $Mn(CO)_5CX_3$ (X = Cl, Br, I) in high yield under mild conditions. The stability of these new complexes decreases in the series Cl > Br > I. Mono- and dihalomethyl complexes, $Mn(CO)_5R$ (R = CHX_2, CH_2X; X = Cl, Br), were also prepared by this method from the appropriate fluoromethyl precursors. Application of the halogen-exchange reaction to other transition-metal systems enabled synthesis of $CpMo(CO)_3CX_3$ and $CpFe(CO)_2CX_3$ (X = Cl, Br). Regiospecific halogen exchange occurs at the carbon α to the metal center as shown by the synthesis of $Re(CO)_5CX_2CF_3$ (X = Cl, Br), $Mn(CO)_5CCl_2CF_3$, $CpMo(CO)_3CCl_2CF_3$, and $CpMo(CO)_3CCl_2C_2F_5$. The substituted ethyl complexes in CX_2CF_3 show hindered C–C bond rotation that is slow on the NMR time scale at room temperature. Further fluoride replacement is not observed when the above compounds are treated with additional BX_3 at room temperature. Similarly no exchange was observed when $Mn(CO)_5C(O)CF_3$ or $CpFe(CO)_2C_6F_5$ was treated with BCl_3. The ability of the transition-metal center to activate the α-C–F bond for halogen exchange results from the stabilization of the dihalocarbene complex which appears to be an intermediate in the exchange process.

Introduction

Perfluoroalkyl carbonyl complexes are readily prepared for nearly all of the late transition metals and have played an important role in the development of the chemistry of the metal–carbon bond.[1-3] These complexes are characterized by high thermal stability, and the perfluoroalkyl group is normally quite resistant to chemical attack. This parallels the known inertness of organic fluorocarbon compounds.[4,5] However, structural and spectroscopic

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