

The Rotational Barriers of Groups Containing Silicon in Substituted Benzenes. A Theoretical Approach to the Silicon Substituent Effect

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The potential energy profile for a number of derivatives of benzene substituted with the SiH_3 , SiH_2CH_3 , and CH_2SiX_3 ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{CH}_3$) groups was calculated at ab initio (HF/6-31G**/HF/6-31G*) level, and the energy barriers were estimated. The rotational barrier is low for the molecules with silicon directly bonded to the phenyl ring, but higher values are found for the CH_2SiX_3 groups, which depend on X as well. The hyperconjugative effect of the substituents was estimated from the natural bond orbital (NBO) theory of donor acceptor properties: the SiH_2CH_3 group was found to be electron-acceptor in character, and the CH_2SiX_3 were found to be electron-donor groups. The rotational barrier of these molecules is mainly determined by hyperconjugation, steric effects being smaller than in the analogous carbon derivatives. The Si–H and Si–C bonds display an electron-acceptor character of similar magnitude when silicon is attached to the phenyl ring, but the Si–C bond has a prevailing donor character when carbon is bonded to the phenyl ring.

INTRODUCTION

The internal rotation process of SiR_3 substituents, where R spans from the small H atom to bulkier groups, has been studied intensively.^{1–4} The understanding of the fundamentals of the structures of organosilicon compounds is important for their wide potential use in the industry of silicone polymers and silicon based ceramic materials⁵ and for new classes of biologically active compounds.⁶

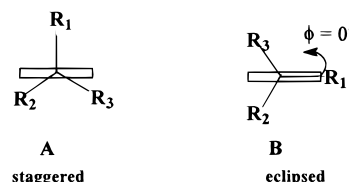
Analysis of the origin of the barrier for internal rotation around the Si–C bond can be employed to investigate the interactions between groups containing silicon and an unsaturated system and, in view of the possible d-orbital participation in bond formation in the former derivatives, enables comparisons to be made with the corresponding carbon compounds. The importance of hyperconjugative interactions in determining 3-fold barriers of the SiH_3 and CH_3 group bonded to a π system has been stressed.^{7,8} These contributions nevertheless amount to a very small residual effect in 6-fold barriers when these groups are attached to a phenyl ring.⁷

The predominant donor over acceptor character of the C–H bond has been deduced from experimental measurements^{9,10} and from a theoretical approach.¹¹ The donor and acceptor characters of the C– CR_3 bond ($\text{R} = \text{H}, \text{F}, \text{Cl}, \text{C}$) are comparable and one can slightly exceed the other as a function of the R atom.¹¹ A weak acceptor character has been attributed¹ to the SiH_3 group in phenyl silane on the basis of ^1H NMR measurements, and this effect, opposite to that of the CH_3 group, has been supported in other reports.^{8,12}

The conformational minimum of phenylsilane is staggered,^{7,13} A in Scheme 1, as in toluene, and the small rotational barrier, amounting to a few cal/mol, probably originates from steric repulsion effects.⁷

The barrier for internal rotation in $\text{PhCH}_2\text{SiX}_3$ molecules, with $\text{X} = \text{H}, \text{Cl}$, or CH_3 , amounts to a few kcal/mol, the conformational minimum is of type A ($\text{R}_1 = \text{SiX}_3$, $\text{R}_2 = \text{R}_3$

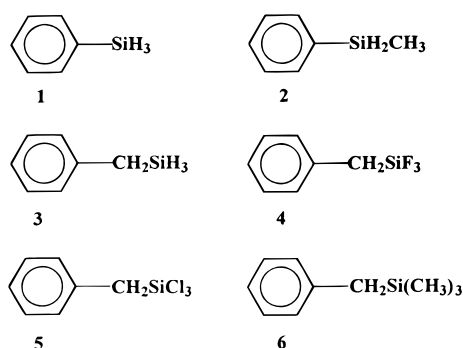
Scheme 1



= H) and its stabilization is attributed³ to the hyperconjugative effect. The rotational barriers of the molecules with $\text{X} = \text{H}$ and Cl are higher than those of the corresponding molecules in which carbon replaces silicon, and this feature has been attributed³ to the greater hyperconjugative ability of the C–Si bond with respect to the C–C bond. A different effect is observed when $\text{X} = \text{CH}_3$, because the barrier becomes lower than in the corresponding carbon derivative:^{2,3} this behavior has been interpreted^{2,3} as being due to a consistent decrease in steric effects in the rotational maximum of type B in the molecule containing silicon owing to the C–Si being longer than the C–C bond distance. Reduced steric effects in silicon compounds with respect to the analogous carbon derivatives have been reported¹⁴ for the conformational behavior of cyclohexyl derivatives as well. The X group in the CH_2SiX_3 rotor affects the hyperconjugative character of the C–Si bond³, becoming smaller when $\text{X} = \text{Cl}$ with respect to $\text{X} = \text{H}$ and CH_3 .

In addition to these reports at theoretical and experimental levels, which define unambiguously the rotational behavior of a number of vinyl and phenyl silicon compounds, it seems that a deeper systematic analysis of the importance of the hyperconjugative effect in determining the rotational barrier is still lacking. Quantitative tests on the relative hyperconjugative ability of Si–H and Si–C bonds and the effect of substituents bonded to silicon and carbon have not yet been carried out. Hyperconjugative ability is a molecular property that might influence the electrical conductivity of molecules containing silicon and their polymeric forms.

Scheme 2



The results of the present work aim to fill this gap. A number of silicon derivatives, listed in Scheme 2, were investigated at theoretical MO ab initio level in order to compare their conformational properties and the electronic effects acting within these molecules, in relation to the analogous carbon compounds.

COMPUTATIONAL DETAILS

The total molecular energy for the molecules **1–6** was calculated with the GAUSSIAN-94 series of programs¹⁵ on an IBM-6000 RISC workstation. The molecular geometries were fully relaxed at HF/6-31G*//HF/6-31G* level¹⁶ in order to locate the conformational minima. Other energy values were obtained by freezing the torsional angle ϕ at fixed values (0, 30, 45, and 90°) and relaxing all of the other coordinates in order to construct the potential energy profiles for internal rotation. Tables of geometrical parameters are not reported but are available from the author on request. A number of more significant bond distances are reported in Table 1.

For compound **1**, calculations introducing second-order Møller–Plesset perturbation theory,¹⁸ MP2/6-31G*//MP2/6-31G*, were carried out as well.

The hyperconjugative ability of the SiH₃, SiH₂CH₃, and CH₂SiX₃ (X = H, F, Cl, CH₃) rotors was tested by employing the natural bond orbital (NBO) scheme in the donor–acceptor approach¹⁹ applied to wave functions at HF/6-31G* level. The procedure was described in previous papers.^{11,20,21} Off-diagonal elements of the NBO Fock-matrix corresponding to selected interactions were set at zero. A single pass self-consistent field (SCF) energy is calculated from the new density matrix and compared with the total SCF molecular energy. The destabilization energy, $-\Delta E_{\pi}$, was averaged over the two frozen resonance structures assumed to have the same weight and to contribute to the same extent to the one-electron density matrix. The routines employed are those included in the GAUSSIAN-94 package.

van der Waals interactions were checked by employing the function parametrized by Allinger^{22,23} for molecular mechanics force field calculations.

RESULTS AND DISCUSSION

Potential Energy Profiles. The low barrier, $V_6 = 6.22$ cm⁻¹ (2.2 cal/mol), obtained experimentally²⁴ for compound **1** is not reproduced exactly by theoretical approaches. The HF/6-31G*, HF/6-311G*, and notably, MP2 levels, overestimate^{7,13} V_6 . Nevertheless, the correct minimum conformation of a staggered type is predicted.^{7,13} The rotational energy

profiles constructed for this molecule with total energy values at HF/6-31G* and MP2/6-31G* levels are reported in Figure 1a. Interpolation of the calculated energy values with a Fourier series (1) in V_3 and V_6 terms, gives the values reported in Table 2. These values are higher than experimental values, as reported previously.^{7,13}

$$V(\phi) = \frac{1}{2} \sum_n V_n (1 - \cos n\phi) \quad (1)$$

The energy profiles for compounds **2–6** are reported in Figures 2–6, the V_2 and V_4 terms according to eq 1 in Table 2. For these molecules the conformational minimum is the staggered conformation A and the rotational maximum conformation B ($R_2 = R_3 = \text{H}$, $R_1 = \text{SiH}_2\text{CH}_3$ or CH_2SiX_3). V_2 terms obtained from MO calculations for compounds **3** and **5** were discussed previously³ and the calculated values were found to be higher than the experimental estimates. The results reported here confirm this trend. The compounds with X = Cl and CH₃ have experimentally determined barriers³ of similar magnitude. The values of V_2 reported in Table 2 for compounds **3–6** show small, yet significant differences, and the barriers increase in the order F < H < Cl < CH₃. The V_2 term for the CH₂Si(CH₃)₃ rotor is significantly smaller than that of the CH₂C(CH₃)₃ rotor, and is in line with the experimental behavior of these two molecules.²

Comparison of the rotational profiles of the molecules examined reveals interesting differences. The most evident is that between compounds **2** and **3**, which differ in the relative position of the silicon atom and of the phenyl ring. The value of V_2 is rather low in **2** and increases markedly in **3**: the V_2 value of ethylbenzene¹¹ is within the values of these compounds. A further difference between these compounds is represented by the shape of the well and of the barrier: the well of compound **2** is broader than the barrier and this is due to the relatively large V_4 term²⁵ with respect to V_2 ($R = V_4/V_2 \cdot 100 = 21$), but in compound **3** $R \approx 2$. The absolute values of V_4 in these two compounds are nevertheless fairly close. For benzyl derivatives,¹¹ the V_4/V_2 ratio was thought to be an index of the presence of effects other than hyperconjugation contributing to the rotational barrier. This conclusion seems nevertheless to be valid until the barrier is mainly 2-fold because when the hyperconjugative effects of the three bonds of the CXYZ rotor have similar magnitude the V_2 term tends to be negligible and the V_4/V_2 ratio becomes meaningless. In compounds **2** and **3**, the contribution of the V_4 term is of similar absolute magnitude and should not, therefore, constitute an index of a significant presence of effects different from hyperconjugation in compound **2**.

In compounds **4**, **5**, and **6**, a contribution of effects different from hyperconjugation is expected on the basis of the behavior of the corresponding compounds¹¹ where silicon replaces the α -carbon atom. In the latter compounds the V_4/V_2 ratios are significantly greater.¹¹ Comparison of the V_4 and V_2 terms reported in Table 2 with those of the analogous carbon compounds reveals interesting differences. With the exclusion of compound **4**, the V_4 term is always greater in the carbon compound, confirming that in these derivatives steric effects should contribute to a greater extent to the rotational barrier. For compounds **2** and **3**, the effect on the rotational barrier of substituting silicon for carbon is

Table 1. Lengths (Å) of Bonds in the Rotating Group of Molecules **2–6** as a Function of Internal Rotation^a (Angle ϕ in Degrees)

compound	bond	angle ϕ			
		0	30	45	90
2	Si—C(sp ²)	1.887	1.887	1.886	1.885
	Si—C(sp ³)	1.887	1.888	1.888	1.889
	Si—H	1.480	1.481; 1.479	1.481; 1.479	1.479
3	C(sp ³)—Si	1.896	1.898	1.899	1.901
	Si—H	1.477; 1.477; 1.478	1.477; 1.477; 1.478	1.476; 1.477; 1.479	1.477; 1.477 1.480
	C(sp ³)—H	1.089	1.091; 1.087	1.090; 1.087	1.087
	C(sp ²)—(sp ³)	1.521	1.520	1.518	1.513
4	C(sp ³)—Si	1.852	1.853	1.853	1.853
	Si—F	1.574; 1.574; 1.574	1.573; 1.576; 1.575	1.573; 1.576; 1.575	1.573; 1.576; 1.573
	C(sp ³)—H	1.089	1.091; 1.087	1.090; 1.087	1.087
	C(sp ²)—C(sp ³)	1.522	1.521	1.520	1.518
5	C(sp ³)—Si	1.870	1.872	1.874	1.874
	Si—Cl	2.047; 2.047; 2.050	2.044; 2.050; 2.051	2.043; 2.050; 2.052	2.046; 2.046; 2.051
	C(sp ³)—H	1.089	1.090; 1.087	1.090; 1.086	1.087
	C(sp ²)—C(sp ³)	1.522	1.521	1.519	1.515
6	C(sp ³)—Si	1.907	1.910	1.911	1.911
	Si—C(sp ³)	1.895; 1.895; 1.894	1.892; 1.895; 1.896	1.891; 1.895; 1.896	1.892; 1.894; 1.892
	C(sp ³)—H	1.091	1.092; 1.088	1.092; 1.088	1.088
	C(sp ²)—C(sp ³)	1.522	1.520	1.517	1.512

^a In compound **1**, the bond distances are C—Si 1.882, Si—H 1.477 \pm 0.001 at HF/6-31G**/HF/6-31G* level and C—Si 1.878, Si—H 1.486 \pm 0.001 at MP2/6-31G**/MP2/6-31G* level and do not change on internal rotation. The experimental value of C—Si, from electron diffraction¹⁷ is 1.843 \pm 0.01 Å.

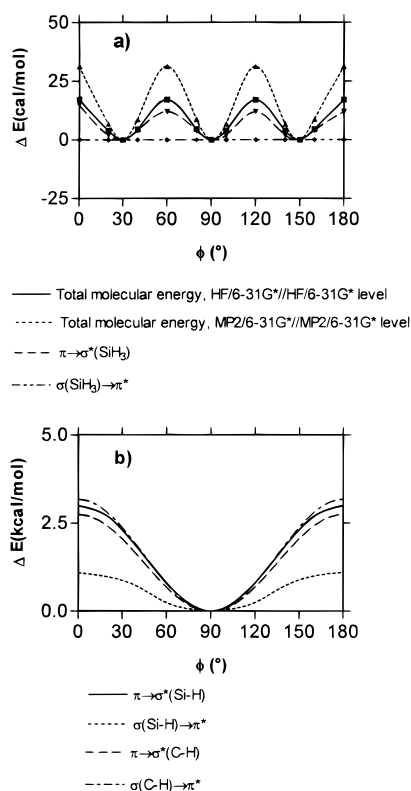


Figure 1. (a) Potential energy profiles for compound **1** at HF/6-31G**/HF/6-31G* and MP2/6-31G**/MP2/6-31G* level, hyperconjugative donor and acceptor effects of the SiH₃ group; (b) comparison of the hyperconjugative donor and acceptor characters of the Si—H bond in compound **1** with that of the C—H bond in toluene.

different in the α or β position (referring to the phenyl ring). Substitution at the α position decreases the barrier in the silicon compound, whereas β -substitution causes a sharp increase.

The V_2 terms in compounds **4** and **5** do not differ greatly from those of the analogous carbon compounds. The same does not hold for compound **6**, the V_2 term being lower than

in the analogous carbon derivatives, the barrier of which is most likely affected by the presence of strong through-space effects.^{11,26,27}

Hyperconjugative Character of the Si—C and Si—H Bonds. The electron donor and acceptor character of the Si—C bond in compounds **1–6** was examined within the framework of the NBO approach¹⁹ and the procedure described in previous papers^{11,20,21} was adopted. The stabilizing ΔE_π contribution due to selected interactions between localized σ orbitals of the rotating group and the π system, i.e., the electron donor $\sigma \rightarrow \pi^*$, electron acceptor $\pi \rightarrow \sigma^*$, and the total hyperconjugative interaction $\sigma \leftrightarrow \pi$, were calculated at the values of the rotational angle ϕ where the total molecular energy was computed. The profiles of ΔE_π for the different interactions referring to the whole rotating group are reported in Figures 1a–6a.

For compound **1**, the prevalent hyperconjugative effect of the SiH₃ group is of the donor type and is the result of the effect of three Si—H bonds. The rotational pattern of the hyperconjugative effect, Figure 1a, is of the same type as that of the total energy with smaller absolute values. The difference between the total energy and hyperconjugative stabilization has an absolute small value and does not allow the contribution of effects different from hyperconjugation to the rotational energy profile of this molecule to be considered.

For compounds **2–6**, a Fourier analysis with the truncated form of eq 1 was performed; the V_2^π and V_4^π terms are reported in Table 3. The V_4^π term is always a small fraction of the V_2^π term and the hyperconjugative effect shows an almost pure 2-fold behavior.

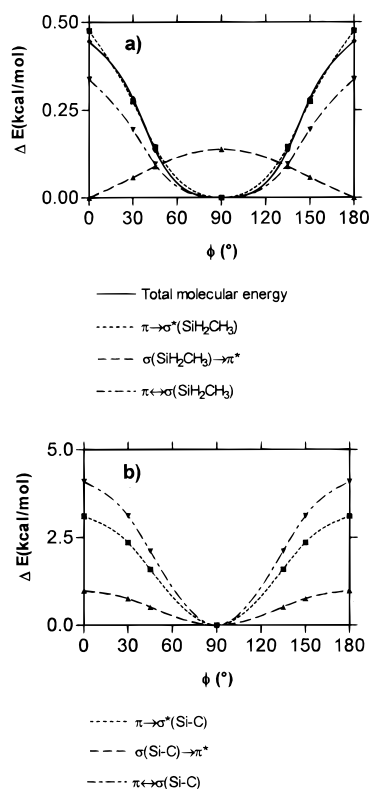
For the SiH₂CH₃ rotor, the donor and acceptor characters behave in the opposite way as a function of ϕ , as shown in Figure 2. The resultant hyperconjugative character of the group is acceptor, and hyperconjugative stabilization mirrors the shape of the total energy profile with the broad well.

The CH₂SiH₃ group displays opposite rotational behavior for the acceptor and donor hyperconjugative characters; the

Table 2. Total Molecular Energy E of the Conformational Minimum, Energy Barriers Referring to the Maximum of Potential Energy Profiles ΔE , and V_n Terms of the Truncated Fourier Series (eq 1); Energy Values Refer to Calculations at HF/6-31G**/HF/6-31G* Level

compound	E (au)	ΔE (kcal/mol)	V_0 (kcal/mol)	V_2 (kcal/mol)	V_4 (kcal/mol)	R^a
1	-520.780337 ^b	-0.017	^d			
	-521.615536 ^c	-0.031	^e			
2	-559.828044	0.446	0.449	-0.451 (-1.44) ^f	-0.096 (0.27) ^f	21
3	-559.816565	3.130	3.138	-3.142 (-1.44) ^f	0.064 (0.27) ^f	2
4	-856.617693	2.704	2.699	-2.696 (-2.52) ^f	-0.461 (0.26) ^f	17
5	-1936.692961	4.010	4.004	-4.000 (-4.08) ^f	0.552 (1.30) ^f	14
6	-676.957834	4.268	4.262	-4.258 (-5.48) ^f	0.495 (1.47) ^f	12

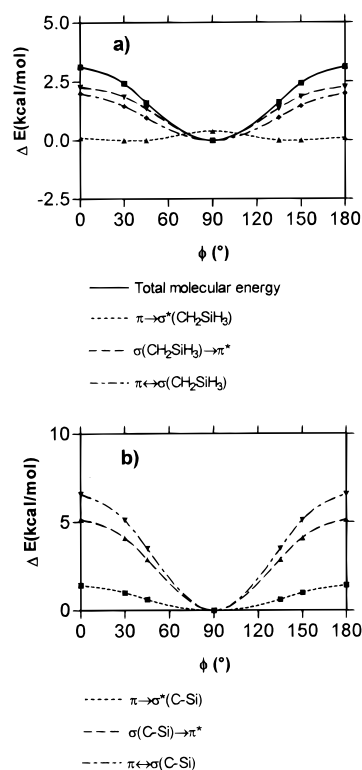
^a $R = (V_4/V_2) \times 100$. ^b -520.78034 au reported in ref 13. ^c MP2/6-31G**/MP2/6-31G* level. ^d $V_0 = 17.0$; $V_3 = 0.34$; $V_6 = -17.12$ cal/mol. ^e $V_0 = 30.9$; $V_3 = 1.04$; $V_6 = -31.4$ cal/mol. ^f Referring to the corresponding compound in which carbon replaces silicon (ref 11).

**Figure 2.** (a) Potential energy profiles for compound 2 at HF/6-31G**/HF/6-31G*, donor acceptor and total hyperconjugative effects of the SiH₂CH₃ group; (b) donor and acceptor and total hyperconjugative characters of the Si-C(H₃) bond in compound 2.

latter is now prevalent, however, and has the same shape (Figure 3a) as the total molecular energy.

Compounds 4–6 behave very similarly to compound 3 in regard to the hyperconjugative effects. The CH₂SiX₃ groups (X = F, Cl, CH₃) have a prevailing donor character displaying a rotational profile similar to that of the total molecular energy: the maximum of the profile relative to the hyperconjugative effect becomes progressively lower than that of the total molecular energy, the deviation increasing in the order F < Cl < CH₃. The presence of effects different from hyperconjugation is likely to account for this behavior.

Comparison of the hyperconjugative contribution of each bond forming the CH₂SiX₃ and SiH₂CH₃ rotors of these molecules affords a further insight into the rotational behavior of the whole group.

**Figure 3.** (a) Potential energy profiles for compound 3 at HF/6-31G**/HF/6-31G*, donor acceptor and total hyperconjugative effects of the CH₂SiH₃ group; (b) donor and acceptor and total hyperconjugative characters of the C-Si(H₃) bond in compound 3.

The rotational profiles of these effects were interpolated with a $B\cos^2\phi$ function and the coefficients B are reported in Table 4.

The maximum stabilizing contribution of the Si-H bond, Figure 1b, amounts to nearly 3 kcal/mol, and is averaged to a vanishingly small value in compound 1. In Figure 1b it is also possible to observe a comparison between the hyperconjugative effects of the Si-H and C-H bonds. The Si-H bond has an acceptor character higher than its donor character, yet for the C-H bond the donor and acceptor characters have similar magnitude. The donor character of the Si-H bond is close to the acceptor character of the C-H bond.

The Si-C(sp³) bond of compound 2 still displays a prevailing acceptor character, as can be observed in Figure

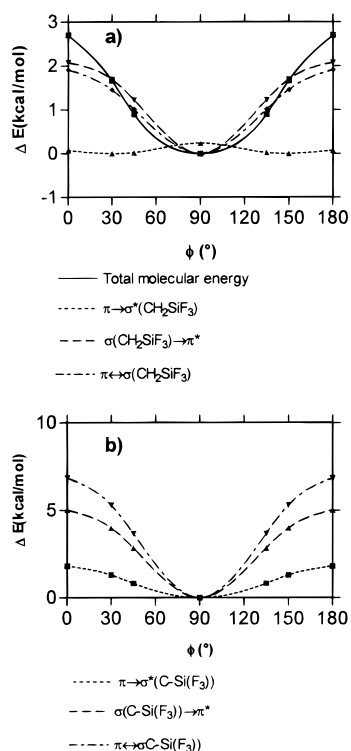


Figure 4. (a) Potential energy profiles for compound **4** at HF/6-31G*/HF/6-31G*, donor acceptor and total hyperconjugative effects of the CH_2SiF_3 group; (b) donor and acceptor and total hyperconjugative characters of the $\text{C-Si}(\text{F}_3)$ bond in compound **4**.

2b, and the data reported in Table 4 show that the donor/acceptor properties of the Si-H and Si-C bonds are quantitatively similar. This feature explains the origin of the small rotational barrier in compound **2**.

In compounds **3–6**, the C-SiX_3 bond displays marked prevailing donor properties and behaves in the opposite way with respect to the C-CX_3 bond.¹¹ This result can be verified from the data reported in Table 3. An even more interesting feature regarding the Si-C bond that stems from these results is that the resultant hyperconjugative character of this bond has an opposite sign, depending on which of the two atoms, carbon or silicon, is bonded to the unsaturated system. The conjugative character of the Si-CX_3 bond is strong for all the X considered (H , F , Cl , CH_3) and this explains the overall donor property of the CH_2SiCX_3 groups.

The conjugative character in the molecules examined can find a simple qualitative explanation in terms of the electronegativity of the atoms at the end of the bonds. In toluene, the mesomeric donor effect of the methyl group is commonly interpreted in terms of valence-bond electronic structures by assuming the $(\text{C}^{\delta-}-\text{H}^{\delta+})$ polarization of this bond due to the higher electronegativity of carbon (2.5) with respect to hydrogen (2.1) (the values refer to the Pauling electronegativity scale²⁸). In phenylsilane, the polarization $\text{Si}^{\delta+}-\text{H}^{\delta-}$ should be present (silicon electronegativity is 1.8) and the hyperconjugative effect is then expected to be of the prevailing acceptor type. When the Si-C bond is involved, the polarization of this bond is $\text{Si}^{\delta+}-\text{C}^{\delta-}$ and the acceptor character is expected when silicon is attached to the phenyl ring, although the global effect should be of donor type when carbon is bonded to the phenyl ring. Of course, this very crude approach does not explain more subtle differences that occur when the substituent X in the CH_2SiX_3 group is

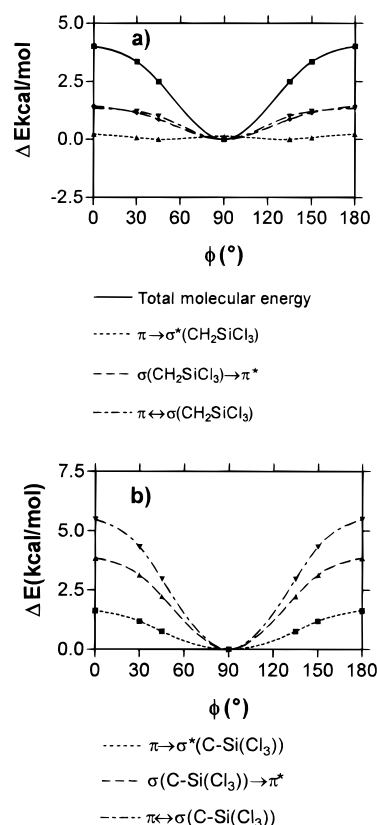


Figure 5. (a) Potential energy profiles for compound **5** at HF/6-31G*/HF/6-31G*, donor acceptor and total hyperconjugative effects of the CH_2SiCl_3 group; (b) donor and acceptor and total hyperconjugative characters of the $\text{C-Si}(\text{Cl}_3)$ bond in compound **5**.

changed. The hyperconjugative character decreases in the order $\text{X} = \text{CH}_3 > \text{H} > \text{F} > \text{Cl}$ and agrees with previous suggestions^{3,29} regarding the effect of the methyl and chlorine substituents.

The electronegative character of X (F , Cl) depresses the donor ability of the C-SiX_3 group and enhances the acceptor character. The fluorine atom mainly has the effect of increasing the acceptor character of the C-SiX_3 bond, and the chlorine atom markedly decreases the donor property. Thus, although the effect of fluorine may be interpreted as being mainly associated with the electronegativity of the atom, that of the chlorine atom is probably because Si and Cl belong to the same period and d-orbital overlap can draw electrons from chlorine to the silicon atom, thus making the Si-C bond less polar.

The NBO atomic charges, reported in Table 5, show that the carbon atom is the negative end and the silicon atom the positive end of the Si-C bond. The positive character of the silicon atom changes significantly in the molecules examined as a function of the attached CX_3 substituents. When $\text{X} = \text{F}$ the silicon atom has the highest positive character, but the CCl_3 group is less effective than the CH_3 group, despite the higher electronegativity of chlorine.

Rotational Behavior of Geometric Parameters. Changes in a number of bond distances as a function of ϕ are reported in Table 1. For compound **1**, the $\text{C}(\text{sp}^2)-\text{Si}$ and Si-H bond distances do not show appreciable variations (within 1×10^{-4} Å) on rotation either at HF/6-31G*/HF/6-31G* or at MP2/6-31G*/MP2/6-31G* level.

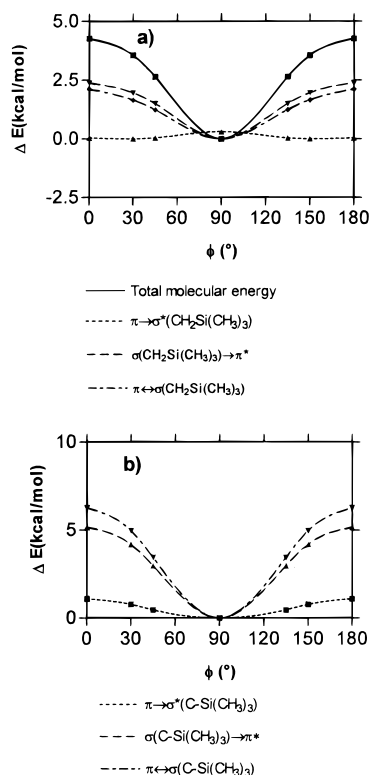


Figure 6. (a) Potential energy profiles for compound **6** at HF/6-31G**//HF/6-31G*, donor acceptor and total hyperconjugative effects of the $\text{CH}_2\text{Si}(\text{CH}_3)_3$ group; (b) donor and acceptor and total hyperconjugative characters of the $\text{C-Si}(\text{CH}_3)_3$ bond in compound **6**.

Table 3. Rotational Pattern of the Total Hyperconjugative Effect in Compounds **1–6** Expressed with the V_2^π and V_4^π Terms of a Truncated Fourier Series of Type (1)

compound	V_2^π (kcal/mol)	V_4^π (kcal/mol)
1	^a	
2	−0.337	−0.034
3	−1.986	0.226
4	−1.908	0.048
5	−1.420	0.126
6	−2.090	0.152

^a $V_6 = -9.4$ cal/mol.

For compound **2**, the $\text{Si-C}(\text{sp}^2)$ bond distance increases slightly from the minimum to the maximum rotational state, but those of $\text{Si-C}(\text{sp}^3)$ and Si-H display opposite behavior: the strengthening of the former in the conformational minimum causes the weakening of the latter bonds. For compound **3**, $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ bond elongation in the rotational transition state is marked, as is the corresponding shortening of the $\text{C}(\text{sp}^3)\text{-Si}$ and $\text{C}(\text{sp}^3)\text{-H}$ bonds by comparison with compound **2**. The changes in bond distances, Δd , exhibit a behavior almost parallel to that of the total molecular energy ΔE_{TOT} and to the hyperconjugative effect ΔE_π , as found previously for other conjugated molecular systems.^{11,30}

In compounds **4–6** the $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ bond displays the same qualitative behavior as in **3**. The $\text{C}(\text{sp}^2)\text{-Si}$ bond distance in **4** and **5** is shorter than in the other molecule and changes slightly on rotation: this bond thus seems to become stronger and less involved in the exchange of electrons with the phenyl ring when halogens are bonded to silicon. The chlorine atom bonded to silicon effectively decreases the hyperconjugative ability of the Si-CX_3 bond.^{3,29}

Table 4. Maximum Values^a of Donor/Acceptor Property (in kcal/mol Units) and Resultant Effect A^b of a Number of Bonds with Respect to a Phenyl Ring

bond	donor	acceptor	A
Si-H	1.10	2.99	1.89
C-H	3.17	2.74	−0.43
$\text{Si-C}(\text{H}_3)$	0.99	3.11	2.12
$\text{C-C}(\text{H}_3)$	3.18	3.09	−0.09
$\text{C-Si}(\text{H}_3)$	5.15	1.42	−3.73
$\text{C-C}(\text{H}_3)$	3.18	3.09	−0.09
$\text{C-Si}(\text{F}_3)$	5.03	1.83	−3.20
$\text{C-C}(\text{F}_3)$	2.16	4.27	2.11
$\text{C-Si}(\text{Cl}_3)$	3.85	1.64	−2.21
$\text{C-C}(\text{Cl}_3)$	1.68	4.91	3.23
$\text{C-Si}(\text{CH}_3)_3$	5.15	1.10	−4.05
$\text{C-C}(\text{CH}_3)_3$	2.85	3.62	0.77

^a B values were obtained interpolating the hyperconjugative effects with the $B\cos^2\phi$ function. ^b Representing the difference between acceptor and donor effects. Positive values attest to the resultant acceptor character of a bond.

Table 5. NBO Atomic Charges (Electrons) on Carbon and Silicon Atoms of the Substituent Groups in Compounds **1–6**

compound	group	C	Si
1	SiH_3	—	1.133
2	SiH_2CH_3	−1.165	1.3995
3	CH_2SiH_3	−0.915	1.135
4	CH_2SiF_3	−1.025	2.571
5	CH_2SiCl_3	−0.995	1.709
6	$\text{CH}_2\text{Si}(\text{CH}_3)_3$	−0.955	1.971

Comparison of the extent of Δd for the $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ bond as a function of ϕ in compounds **3–6** and that of the $\text{C}(\text{sp}^2)\text{-Si}$ bond in compound **2** with the corresponding energy changes in these compounds seems to suggest that the Δd values mirror the total energy barrier more closely than the hyperconjugative part of the total energy. This suggests that the changes in these distances are dictated by all of the effects contributing to the barrier and not only by hyperconjugative effects.

Through-Space Effects. Even if steric interactions between the atoms of the rotors and those of the phenyl ring in compounds **1–6** make a smaller contribution to the rotational barrier than in the analogous carbon compounds,^{2,3} effects different from hyperconjugation seem to affect their rotational barriers.

Because it appears rather difficult to make a quantitative estimate of these effects and their further factorization,¹¹ these contributions will be briefly discussed simply in terms of energy differences between hyperconjugation and total molecular energy, $\Delta E_{\text{st}} = \Delta E_{\text{TOT}} - \Delta E_\pi$. The values are reported in Table 6. In the silicon derivatives, through-space effects are much smaller than in the corresponding carbon derivatives, $\Delta E(\text{C})_{\text{st}}$. In compound **2**, steric interactions seem almost absent, but in its isomer **3**, where carbon is directly bonded to the phenyl ring, they are higher, while remaining lower than in ethylbenzene. The values of ΔE_{st} are not in proportion to the corresponding $\Delta E(\text{C})_{\text{st}}$ values, and this indicates that a different mixture of electrostatic and van der Waals interactions (when a model of through-space effects made up of these contributions is assumed) is probably active in the two series of molecules. An approximate estimate of van der Waals interactions in compounds **2** and **3**, employing the approach described in the

Table 6. Through-Space Effects ΔE_{st} (kcal/mol) for Compounds 2–6 and for the Analogous Carbon Compounds^a $\Delta E(C)_{st}$ Obtained as a Difference between the Total Rotational Barrier and the Hyperconjugative Contribution

compound	ΔE_{st}	$\Delta E(C)_{st}$
2	0.108	1.941
3	1.141	1.941
4	0.789	2.546
5	2.575	3.457
6	2.154	4.958

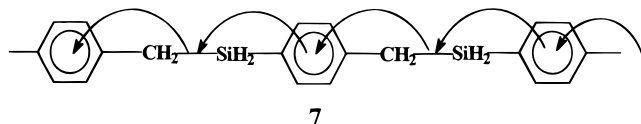
^a From ref 11.

Computational Details, gave contributions of 0.4 and 2.0 kcal/mol, respectively, showing that through-space effects are likely to be less important, even if not completely absent, in these molecules than in the analogous carbon compounds.

CONCLUSIONS

The theoretical approach applied to the silicon compounds here examined shows that the interactions of the silicon substituents with the phenyl ring are mainly of a hyperconjugative character. The SiH_2CH_3 group displays a small rotational barrier around the $\text{C}(\text{sp}^2)\text{—Si}$ bond, due to the similar conjugative effect of the Si—H and Si—C bonds, and the whole group is slightly electron acceptor in character. For the CH_2SiX_3 rotors, $\text{X} = \text{H, F, Cl, CH}_3$, which all possess a marked electron donor character, the rotational barriers increase with respect to the analogous carbon compounds (C replacing Si), except when bulky groups are bonded to silicon, which shows that steric effects are much greater in carbon derivatives.

The electronic effect of the Si—C bond changes sign depending on whether carbon or silicon is bonded to the phenyl ring.



This suggests that in a chain like that represented by compound 7, the prevalent electronic flow should be in one direction, and molecules of this type, with appropriate substitution introduced in the molecular skeleton in order to enhance the effect, are likely to behave as potential organic molecular semiconductors.

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