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An Ab Initio Molecular Orbital Study on Twisting in Silyl-Substituted Ethylene Cation Radicals

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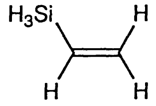
Twisting in two silyl-substituted ethylene cation radicals, the cation radicals of vinylsilane (**1**) and vinylidenebissilane (**2**), were investigated by ab initio UHF calculations with the 3-21G and 3-21G$^{(*)}$ basis sets. Both $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ were found to have twisted equilibrium structures, the twist angle being 29° and 42°, respectively. The planarization barriers evaluated for $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ are about 1 and 7 kcal mol^{-1}, respectively. The planar and 90°-twisted forms of $\mathbf{2}^{+\cdot}$ have comparable energies. The hyperconjugation of the C–Si bonds is reflected in the calculated molecular structures.

The possibility of twisting in olefin cation radicals has attracted considerable attention.[1,2] However, it was recently concluded, based on semiempirical UHF/AM1 calculations of hyperfine coupling constants for some alkyl-substituted ethylene cation radicals, that the only olefin cation radicals with a twisted structure are the ethylene cation radical, itself, and a series of trimethylsilyl-substituted ethylene cation radicals.[1] These cation radicals benefit from hyperconjugation of C–H or C–Si bonds, which stabilizes the positive charge, by twisting around the C–C bond. The ethylene cation radical was experimentally found to be twisted by about 25° in the gas phase with a planarization barrier of only 0.7—0.8 kcal mol^{-1} (1 cal=4.184 J);[3] considerable twisting in trimethylsilyl-substituted ethylene cation radicals was suggested based on their ESR spectra by Sakurai et al.[4] and Symons et al.[5] Consequently, the trimethylsilyl-substituted ethylene cation radicals are the only olefin cation radicals which have shown any marked twisted structure so far.

Stabilization of a positive charge center by β-C–Si bonds is now well recognized.[6] This stabilizing effect is orientation-dependent, since the β-C–Si bond interacts with the positive charge center hyperconjugatively.[6,7] Hence, the twist angle in silyl-substituted ethylene cation radicals may be determined by a compromize between the breaking of a one-electron π-bond and hyperconjugative stabilization of the positive charge. Although the hyperfine coupling constants of olefinic protons can be a good measure of the degree of twisting (as discussed in Refs. 4 and 5), a theoretical evaluation of the potential energy surface may be also desirable. This note reports the first ab initio level of calculations concerning the twisting in silyl-substituted ethylene cation radicals. Vinylsilane (**1**) and vinylidenebissilane (**2**) were selected as model compounds for a calculation, and the 3-21G[8] and 3-21G$^{(*)}$[9] basis sets and UHF formalism were employed. The latter basis set includes d-type polarization functions on silicon atoms.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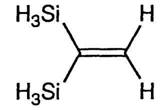
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Results and Discussion

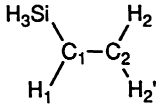
Vinylsilane Cation Radical ($\mathbf{1}^{+\cdot}$). The structures for the planar, twisted, and 90°-twisted forms were all optimized with the 3-21G and 3-21G$^{(*)}$ basis sets.

Table 1. Calculated Total Energies (a.u.) and Relative Energies (kcal mol^{-1}, in Parentheses) of Vinylsilane Cation Radical ($\mathbf{1}^{+\cdot}$)

Form	Symmetry	State	3-21G//3-21G	3-21G$^{(*)}$//3-21G	3-21G$^{(*)}$//3-21G$^{(*)}$
Planar	C_s(*syn*)[a]	$^2A''$	−365.83405(1.3)	−365.92949(1.3)	−365.92992(1.2)
	C_s(*anti*)[b]	$^2A''$	−365.83323(1.8)	−365.92867(1.8)	−365.92911(1.7)
Twisted	C_1[c]	^2A	−365.83616(0)	−365.93150(0)	−365.93190(0)
	C_1[d]	^2A	−365.83627(−0.06)	−365.93156(−0.04)	−365.93201(−0.07)
90°-Twisted	C_s(*syn*)	$^2A''$	−365.80929(16.9)	−365.90344(17.6)	−365.90403(17.5)
	C_s(*anti*)	$^2A''$	−365.80958(16.7)	−365.90376(17.4)	−365.90427(17.3)
	C_s(*syn*)	$^2A'$	−365.79801(23.9)	−365.89364(23.7)	−365.89412(23.7)
	C_s(*anti*)	$^2A'$	−365.79805(23.9)	−365.89364(23.7)	−365.89415(23.7)

a) One Si-H bond is synperiplanar to the C-C bond. b) One Si-H bond is antiperiplanar to the C-C bond. c) Planarity was assumed around the carbon atoms. d) No constraint was imposed.

Table 2. Structural Parameters of Vinylsilane Cation Radical ($1^{+\cdot}$) Obtained by UHF/3-21G and UHF/3-21G$^{(*)}$ (in Parentheses) Calculations[a]



	C_s planar (*syn*)[b]	C_1 twisted[c]	C_s 90°-twisted (*anti*)[d]
Bond lengths			
C_1-C_2	1.412(1.415)	1.384(1.386)	1.368(1.373)
C_1-Si	1.974(1.943)	1.988(1.958)	2.047(1.996)
C_1-H_1	1.080(1.081)	1.082(1.082)	1.078(1.081)
C_2-H_2	1.074(1.074)	1.076(1.076)	1.082(1.082)
C_2-H_2'	1.075(1.074)	1.077(1.077)	1.082(1.082)
Si-H(1)	1.472(1.460)	1.472(1.460)	1.472(1.462)
Si-H(2)	1.474(1.463)	1.474(1.463)	1.466(1.457)
Si-H(3)	1.474(1.463)	1.472(1.460)	1.472(1.462)
Bond angles			
C_2C_1Si	125.6(125.5)	125.4(125.1)	115.7(118.5)
$C_2C_1H_1$	115.9(116.1)	117.8(117.9)	130.2(127.4)
$C_1C_2H_2$	121.0(120.9)	121.5(121.5)	121.7(121.7)
$C_1C_2H_2'$	121.5(121.4)	121.2(121.3)	121.7(121.7)
$C_1SiH(1)$	105.0(105.2)	104.9(105.3)	104.9(105.2)
$C_1SiH(2)$	103.6(103.3)	102.4(101.9)	100.4(101.4)
$C_1SiH(3)$	103.6(103.3)	103.7(103.8)	104.9(105.2)
Dihedral angles			
$SiC_1C_2H_2$[e]	0.(0.)	29.3(29.5)	90.(90.)
$C_2C_1SiH(1)$	0.(0.)	−0.4(−0.6)	−59.9(−59.8)
$C_2C_1SiH(2)$	−120.4(−120.4)	−120.4(−120.4)	180.(180.)
$C_2C_1SiH(3)$	120.4(120.4)	120.4(120.3)	59.9(59.8)

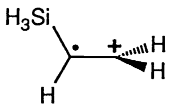
a) Bond lengths are in Å and angles are in degrees. b) One Si-H bond is synperiplanar to the C-C bond. c) The planar carbons were assumed. d) One Si-H bond is antiperiplanar to the C-C bond. e) The twist angle around the C-C bond.

The calculated energies are shown in Table 1, and the structures in Table 2.

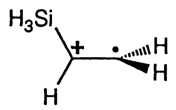
The structure for the planar form was optimized assuming C_s symmetry. Two conformations of the silyl group are possible. In the "*syn*" conformation, one Si-H bond is synperiplanar to the C-C bond, while one Si-H bond is antiperiplanar to the C-C bond in the "*anti*" conformation. The *syn* conformation was calculated to be more stable than the *anti* conformation by 0.5 kcal mol^{-1}, and was found to be the most favorable conformation.

Twisting of the planar cation radical around the C-C bond lowered the energy, and the structure of the twisted form was optimized assuming sp^2 hybridization (planarity) of the carbon atoms (Without this constraint, the energy was lowered by 0.06—0.07 kcal mol^{-1}). The twist angles at the 3-21G and 3-21G$^{(*)}$ optimized structures are 29.3° and 29.5°, respectively. The energy of the twisted form is lower than that of the planar form by 1.2—1.3 kcal mol^{-1}.

The structure of the 90°-twisted form was optimized assuming C_s symmetry. The *anti* conformation of the silyl group was slightly (0.2 kcal mol^{-1}) favored, and was found to be the most favorable. The energy of the 90°-twisted form is higher in energy than that of the twisted equilibrium structure by about 17 kcal mol^{-1}. The ground state of the 90°-twisted form is the



$^2A''$



$^2A'$

$^2A''$ state, which is formally regarded as being a "silylmethyl radical+methyl cation." The energy and structure of the $^2A'$ state, which is regarded as "silylmethyl cation+methyl radical," were also calculated. The $^2A'$ cation radical is higher in energy than the $^2A''$ cation radical by 6—7 kcal mol^{-1}. This result is in contrast to that for the methyl analogue, the propene cation radical.[10] The preference of the $^2A''$ state in $1^{+\cdot}$ is apparently due to a hyperconjugative stabilization of the positive charge by the C-Si bond; in the propene cation radical, the α-methyl group stabilizes the positive charge of the $^2A'$ state.

In summary, $1^{+\cdot}$ is twisted by about 29°, the planarization barrier is about 1 kcal mol^{-1}, and the barrier to rotation through the 90°-twisted form is about 17 kcal mol^{-1}.

Vinylidenebissilane Cation Radical ($2^{+\cdot}$). The structures for the planar, twisted, and 90°-twisted forms of $2^{+\cdot}$ were optimized only with the 3-21G basis set, while the energies were also evaluated with the 3-

21G$^{(*)}$ basis set in some cases, because for $\mathbf{1}^{+\cdot}$, both the 3-21G and 3-21G$^{(*)}$ basis sets gave similar structures, except that the latter gave slightly (0.03—0.05 Å) shorter C-Si bonds, and the 3-21G$^{(*)}$//3-21G$^{(*)}$, 3-21G$^{(*)}$//3-21G, and 3-21G//3-21G levels of the calculation all gave very similar results regarding the relative energies (See Tables 1 and 2). The results for $\mathbf{2}^{+\cdot}$ are shown in Tables 3 and 4.

The structure of the planar form was optimized assuming C_{2v} symmetry. The *syn* conformation of the silyl groups was favored by about 1 kcal mol^{-1}. The potential energy surface was found to be very flat against silyl-group rotation in the vicinity of the *syn* conformation.

Twisting of the planar cation radical lowered the energy, and the structure of the twisted form was optimized assuming C_2 symmetry. The twist angle at the optimized structure is 42.4°, which is quite large as an olefin cation radical. The energy of the twisted form is lower than that of the planar form by 7—8 kcal mol^{-1}.

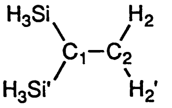
The structure of the 90°-twisted form was optimized first assuming C_{2v} symmetry. The *anti* conformation was slightly more stable (0.3 kcal mol^{-1}) than the *syn* conformation. When a C_2 symmetry was assumed, however, the energy was further lowered by about 0.2 kcal mol^{-1}. The energy of the 90°-twisted form is higher than that of the twisted equilibrium structure by 8—8.5 kcal mol^{-1}. As expected, the ground state of the 90°-twisted form corresponds to "disilyl-

Table 3. Calculated Total Energies (a.u.) and Relative Energies (kcal mol^{-1}, in Parentheses) of Vinylidenebissilane Cation Radical ($\mathbf{2}^{+\cdot}$)

Form	Symmetry	State	3-21G//3-21G	3-21G$^{(*)}$//3-21G
Planar	C_{2v}(*syn*)[a]	$^2B_1$	−654.39321(7.4)	−654.58321(7.6)
	C_{2v}(*anti*)[b]	$^2B_1$	−654.39158(8.5)	—
Twisted	C_2	^2B	−654.40508(0)	−654.59534(0)
90°-Twisted	C_{2v}(*syn*)	$^2B_1$	−654.39151(8.5)	—
	C_{2v}(*anti*)	$^2B_1$	−654.39199(8.2)	−654.58222(8.2)
	C_2	^2B	−654.39235(8.0)	—
	C_{2v}(*syn*)	$^2B_2$	−654.36337(26.2)	—
	C_{2v}(*anti*)	$^2B_2$	−654.36420(25.6)	—

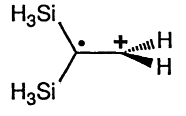
a) One Si-H bond is synperiplanar to the C-C bond. b) One Si-H bond is antiperiplanar to the C-C bond.

Table 4. Structural Parameters of Vinylidenebissilane Cation Radical ($\mathbf{2}^{+\cdot}$) Obtained by UHF/3-21G Calculation[a]

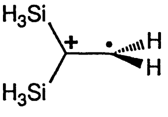


	C_{2v} planar (*syn*)[b]	C_2 twisted	C_2 90°-twisted
Bond lengths			
C_1-C_2	1.421	1.354	1.353
C_1-Si	1.974	1.994	1.998
C_2-H_2	1.075	1.079	1.082
Si-H(1)	1.474	1.474	1.472
Si-H(2)	1.476	1.473	1.471
Si-H(3)	1.476	1.473	1.474
Bond angles			
C_2C_1Si	119.9	121.9	123.0
$C_1C_2H_2$	121.7	121.9	121.9
$C_1SiH(1)$	106.2	104.8	106.0
$C_1SiH(2)$	104.3	104.9	104.1
$C_1SiH(3)$	104.3	103.6	103.9
Dihedral angles			
$SiC_1C_2H_2$[c]	0.	42.4	90.
$C_2C_1SiH(1)$	0.	−23.4	−30.0
$C_2C_1SiH(2)$	−120.6	−144.2	−150.3
$C_2C_1SiH(3)$	120.6	96.5	90.2

a) Bond lengths are in Å and angles are in degrees. b) One Si-H bond is synperiplanar to the C-C bond. c) The twist angle around the C-C bond.



$^2B_1$



$^2B_2$

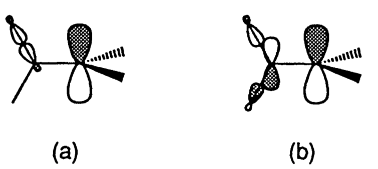
methyl radical+methyl cation" (the $^2B_1$ state in the C_{2v} cases). Another state, the $^2B_2$ state of the C_{2v} 90°-twisted form ("disilylmethyl cation+methyl radical") was also investigated, and was found to be higher in energy than the $^2B_1$ state by 17—18 kcal mol^{-1}. The energy difference between the two states is considerably larger than that between the $^2A''$ and $^2A'$ states of the C_s 90°-twisted form of **1**$^{+\bullet}$, and is also in contrast to that for the methyl analogue, 2-methylpropene cation radical.[11]

In summary, **2**$^{+\bullet}$ is twisted by about 42°, the planarization barrier is about 7 kcal mol^{-1}, and the barrier to rotation through the 90°-twisted form is about 8 kcal mol^{-1}. It should be noted that the planar and 90°-twisted forms have comparable energies.

Hyperconjugation of C-Si Bonds. As mentioned in the introduction part, the twisted equilibrium structures of **1**$^{+\bullet}$ and **2**$^{+\bullet}$ can be attributed to the hyperconjugative stabilization of the positive charge by the C-Si bond(s). The hyperconjugation effect of the C-Si bond(s) should be maximized at the 90°-twisted form where the overlap between the "vacant" p_π orbital of the carbon atom of $-CH_2$ and the C-Si σ orbital(s) becomes maximum, while the π conjugation between the two carbon atoms is maximized at the planar form. These two competing factors are considered to determine the degree of the twisting. Indeed, **2**$^{+\bullet}$ which has two silyl groups is more twisted and stabilized by twisting than **1**$^{+\bullet}$.

The hyperconjugation of the C-Si bond(s) is well reflected in the shape of the LUMO[12] of the 90°-twisted $^2A''$ state of **1**$^{+\bullet}$ and the 90°-twisted $^2B_1$ state of **2**$^{+\bullet}$, which are essentially the p_π orbitals of the carbon atom of the $-CH_2$ fragment combined out-of-phase with the C-Si σ orbital(s) (See Fig. 1).[13]

The hyperconjugation is also reflected in the calculated molecular structures. In Table 5, the C-C and C-Si bond lengths and the C-C-Si bond angle at several twist angles are shown (other structural parameters were optimized). As the twist angle is increased, the C-C bond becomes shorter (up to 60°),[14] while the C-Si bond(s) becomes longer. Considering the following resonance, this trend is attributable to increasing C-Si hyperconjugation.



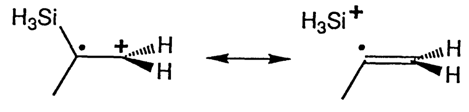
(a) (b)

Fig. 1. Schematic representation of the LUMO's of (a) C_s 90°-twisted $^2A''$ state of **1**$^{+\bullet}$, and (b) C_{2v} 90°-twisted $^2B_1$ state of **2**$^{+\bullet}$.

Table 5. UHF/3-21G Optimized Values of the C-C and C-Si Bond Lengths and C-C-Si Bond Angle in **1**$^{+\bullet}$ and **2**$^{+\bullet}$ for Various Values of the Twist Angle Around the C-C Bond

	Twist angle[a]	R(C-C)[b]	R(C-Si)[c]	∠CCSi[d]
1$^{+\bullet}$	0.0	1.412	1.974	125.6
	29.3	1.384	1.988	125.4
	60.0	1.364	2.009	123.7
	90.0	1.368	2.047	115.7
2$^{+\bullet}$	0.0	1.421	1.974	119.9
	30.0	1.364	1.992	121.8
	42.4	1.354	1.994	121.9
	60.0	1.348	1.995	122.4
	90.0	1.353	1.998	123.0

a) In degrees. b) The C-C bond length in Å. c) The C-Si bond length in Å. d) The C-C-Si bond angle in degrees.

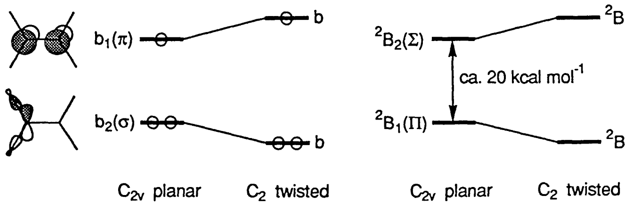


The change in the C-C-Si bond angle in **1**$^{+\bullet}$, which decreases as the twist angle is increased, is also attributable to increasing C-Si hyperconjugation. For **2**$^{+\bullet}$, however, the C-C-Si bond angle unexpectedly increases as the twist angle is increased; the reason for this is not clear.

It should be noted that silyl-substituted ethylene cation radicals are largely twisted by the electronic factor without any steric hindrance, because the trimethylsilyl groups were replaced by the silyl groups in the present calculations.

Orbital Mixing upon Twisting. In the above discussion, the preference of the twisted structures in **1**$^{+\bullet}$ and **2**$^{+\bullet}$ was interpreted using the hyperconjugation concept. Here, we see the same thing from a different point of view; we predict twisted equilibrium structures from the MO's of the planar form.

The HOMO ($3b_1$) and NHOMO ($8b_2$) of the neutral



(a) (b)

Fig. 2. σ-π Mixing upon twisting of the C_{2v} planar form of **2**$^{+\bullet}$: (a) Orbital description. (b) State description.

2 (C_{2v} planar) are energetically close to each other;16) the HOMO is associated with the C-C π bond, while the NHOMO with the two C-Si bonds (Fig. 2). Upon twisting of the molecule around the C-C bond, these two orbitals come to have the same symmetry and mix with each other. This orbital mixing leads to stabilization in the case of the cation radical, as shown in Fig. 2. If we use "state description" instead of "orbital description", the $^2B_1$ (Π) and $^2B_2$ (Σ) states of the C_{2v} planar $\mathbf{2}^{+\cdot}$ interact with each other upon twisting to lower the ground state energy (Fig. 2).17)

A similar discussion is also valid for $\mathbf{1}^{+\cdot}$. In this case, however, the energy difference between the 3a″ (π) and 13a′ (σ) orbitals (or the $^2A''$ (Π) and $^2A'$ (Σ) states) of the C_s planar form is larger than in **2**,18) and the interaction of the two orbitals (or states) is weak. This results in smaller stabilization upon twisting.

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10) UHF/3-21G calculations have shown that the 90°-twisted $^2A'$ state of the propene cation radical is more stable than the $^2A''$ state by about 16 kcal mol^{-1}.

11) UHF/3-21G calculations have shown that the 90°-twisted $^2B_2$ state of the 2-methylpropene cation radical is more stable than the $^2B_1$ state by about 28 kcal mol^{-1}.

12) The UHF LUMO of the 90°-twisted $^2A''$ state of $\mathbf{1}^{+\cdot}$ and the 90°-twisted $^2B_1$ state of $\mathbf{2}^{+\cdot}$ do not correspond to the SOMO in the RHF case, but to the RHF LUMO. This phenomenon seems to be characteristic of cation radicals in which the positive charge and unpaired electron are separated in different regions. The UHF result is quite natural in view of the most important valence-bond structure.

13) Since the LUMO is not occupied, it has no direct concern with stabilization of the cation radical. Nevertheless, its characteristic shape may be regarded as being a reflection of the hyperconjugation in which the cation center is partially filled by a flow of electrons associated with the C-Si bond(s); the relavent occupied MO, an in-phase combination of the p_π orbital of the carbon atom and the C-Si σ orbital(s), is less apparent due to other mixing. See also Ref. 7.

14) The ethylene cation radical itself also seems to show a similar trend. See Ref. 15.

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16) The orbital energies (3-21G) are −11.18 eV (HOMO) and −10.45 eV (NHOMO). The difference is 0.73 eV.

17) The energy of the $^2B_2$ (Σ) state calculated at the geometry for the $^2B_1$ (Π) state is −654.36133 a.u. and higher than the Π state by 20.0 kcal mol^{-1} (3-21G).

18) The orbital energies (3-21G) of the HOMO (3a″) and NHOMO (13a′) of **1** (C_s planar) are −10.38 eV and −12.09 eV, respectively (The difference is 1.70 eV), while the energy of the $^2A'$ (Σ) state of $\mathbf{1}^{+\cdot}$ calculated at the geometry for the $^2A''$ (Π) state is −365.76545 a.u. and higher than the Π state by 43.0 kcal mol^{-1} (3-21G).