

Comparison of Alkyl Substitution Effects on Singlet-triplet Splitting of Silylene with Carbene

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Full geometry optimizations have been carried out on singlet and triplet states of alkyl substituted acyclic silylene by B3LYP method using 6-311++G** basis set of the Gaussian 98 system of program. In contrast to carbene CH₂, the singlet state of silylene (SiH₂) is ground state. Similar to carbene, stability of singlet state is increased with substituting of alkyl groups on silylenic center. By comparing NBO charges on silylenic center of SiH₂ and other large substituted acyclic silylenes, the role of methyl group is electron withdrawing respect to hydrogen atom. Higher electronegativity of methyl group leads to stabilize the singlet respect to triplet state as well as decreasing the singlet-triplet splitting energies.

Key Words: Silylene, Carbene, Singlet-triplet splitting.

INTRODUCTION

Carbenes (CH₂) and silylenes (SiH₂), highly reactive intermediates, are extensively studied in organic chemistry¹⁻¹³. Generally, the carbenes and silylenes could be defined in terms of their electronic structure; singlet (σ^2 and/or π^2 configurations) and triplet ($\sigma\pi$ configuration) states. The reactivity of carbenes and silylenes can be predicted through determination of their singlet-triplet splitting. The stability of singlet state is depending on two factors. First, more electronegative substituents raise the stability of singlet state. Second, substituents which have electron pairs raise the stability of singlet state through electron donating *via* hyper-conjugation to the empty σ orbital. The triplet state, on the other hand, should be stabilized by substituents that are electropositive and/or bulky. In the present work, our goal is to obtain the quantitative information on the magnitude of singlet-triplet splitting in the simple acyclic silylenes and compared with carbenes.

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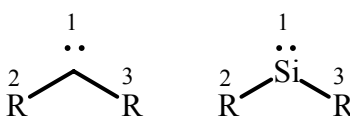
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METHOD OF CALCULATIONS

Geometry optimizations are carried out by B3LYP^{14,15} method using 6-311++G** basis set of the Gaussian 98 system of program¹⁶. In order to find energy minima, keyword FOPT are used. This keyword requests that a geometry optimization be performed. The geometry will be adjusted until a stationary point on the potential surface is found. Here, the Berny algorithm is employed for all minimizations using redundant internal coordinates¹⁷. For minimum state structures, only real frequency values have been accepted. For singlet states, the restricted RBecke3LYP is used while the unrestricted UBecke3LYP is used for triplet states.

RESULTS AND DISCUSSION

Full geometry optimizations are carried out by B3LYP method using 6-311++G** basis set of the Gaussian 98 system of program. In this work, the magnitude of singlet-triplet splitting is evaluated for the simple acyclic silylene and compared with carbene. The reactivity of silylenes is related to the singlet-triplet splitting. Therefore, we calculated the singlet-triplet splitting for simple acyclic silylenes: $C_nH_{2n+2}Si$ ($n = 0-6$). The total energies and energy differences between singlet and their corresponding triplet states, $\Delta E_{(t-s)}$ are calculated using B3LYP/6-311++G** level of theory (**Scheme-I** and Table-1). Since the lowest energy geometry for both singlet and triplet states is found to be the *trans* configuration, we focus our attention on *trans* configurations for all of $C_nH_{2n+2}Si$ ($n = 0-6$) compounds. The singlet-triplet splitting does not significantly change with substituting of more methyl groups on silylenic center ($C_nH_{2n+2}Si$ ($n = 7-9$)). So, for the sake of brevity, we exclude the results of more methyl substitutions.



Scheme-I. Simple acyclic carbenes and silylenes

In contrast to carbene CH_2 , the singlet state of silylene SiH_2 is ground state lying 20.408 kcal/mol higher in energy. This can be understood in terms of the molecular orbitals of the MH_2 ($M = C$ and Si) unit. The key point is the energy gap between the $2a_1$ (HOMO) and the $1b_1$ (LUMO) orbitals. The $2a_1-1b_1$ energy gap depends on four factors. First factor is related to the electronegativity of M . A lower electro-negativity of M increases the size of the atomic orbitals and lengthens the $M-H$ bonds, stabilizing the singlet state. Second factor that influences the HOMO-LUMO gap is the polarity of the $M-H$ bond. The $C-H$ bonds are nearly non-polar,

TABLE-1
 CALCULATED B3LYP/6-311++G** TOTAL ENERGIES AND ENERGY DIFFERENCES BETWEEN SINGLET AND THEIR
 CORRESPONDING TRIPLET STATES, $\Delta E_{(t-s)}$ FOR ACYCLIC CARBENES AND SILYLENES

| Compound | Singlet state | | | Triplet state | | | Singlet-triplet splitting (kcal/mol) |
|-----------------------------------|------------------------------------|---------------------------|----------------------------|------------------------------------|---------------------------|----------------------------|--|
| | Zero point energy (kcal/mol) | Total energy (Hartree) | Total energy (kcal/mol) | Zero point energy (kcal/mol) | Total energy (Hartree) | Total energy (kcal/mol) | |
| CH ₂ | 10.356 | -39.147 | -24554.330 | 10.754 | -39.166 | -24566.092 | -11.762 |
| H ₂ Si | 7.303 | -290.641 | -182369.699 | 7.529 | -290.608 | -182349.292 | 20.408 |
| C ₂ H ₄ | 29.169 | -78.495 | -49226.439 | 29.407 | -78.502 | -49231.107 | -4.668 |
| CH ₄ Si | 26.105 | -329.982 | -207037.801 | 26.498 | -329.946 | -207014.595 | 23.206 |
| C ₃ H ₆ | 47.093 | -117.838 | -73896.856 | 47.482 | -117.838 | -73896.109 | 0.747 |
| C ₂ H ₆ Si | 44.323 | -369.323 | -231706.495 | 45.131 | -369.282 | -231679.793 | 26.702 |
| C ₄ H ₈ | 64.944 | -157.164 | -98556.128 | 65.619 | -157.161 | -98553.858 | 2.270 |
| C ₃ H ₈ Si | 62.335 | -408.644 | -256362.515 | 63.214 | -408.604 | -256336.159 | 26.356 |
| C ₅ H ₁₀ | 82.795 | -196.490 | -123215.258 | 83.617 | -196.485 | -123211.855 | 3.403 |
| C ₄ H ₁₀ Si | 80.502 | -447.963 | -281017.246 | 81.385 | -447.925 | -280992.340 | 24.905 |
| C ₆ H ₁₂ | 100.646 | -235.814 | -147873.698 | 101.439 | -235.810 | -147870.393 | 3.305 |
| C ₅ H ₁₂ Si | 98.326 | -487.288 | -305675.924 | 99.163 | -487.250 | -305651.078 | 24.846 |
| C ₇ H ₁₄ | 118.361 | -275.139 | -172532.243 | 119.220 | -275.135 | -172528.889 | 3.354 |
| C ₆ H ₁₄ Si | 116.109 | -526.613 | -330334.572 | 116.966 | -526.575 | -330309.766 | 24.806 |

but the Si–H bonds are polarized in the direction $\text{Si}^+\text{--H}$. The result is to make the HOMO-LUMO gap greater than CH_2 and therefore this effect stabilizes the singlet state for SiH_2 relative to CH_2 . Third factor is related to the nonbonding electrons character. The heavier atoms prefer to have nonbonding electrons in atomic orbitals with a higher percentage of *s*-character. The higher *s*-character in the $2a_1$ orbital of SiH_2 relative to CH_2 suggests a relatively lower energy of this orbital and a higher HOMO-LUMO gap and stabilized singlet state. Fourth factor is the size of atom. because of the larger size of the lone pair orbital in SiH_2 , the electron-electron repulsion between the paired electrons in the $2a_1$ orbital of the singlet of SiH_2 is less respect to CH_2 , favoring the singlet state for the heavier elements.

Similar to CH_2 , substitution of a methyl group on silylenic center (CH_3SiH) increase the singlet-triplet splitting (23.206 kcal/mol). Substituting of two methyl groups on silylenic center leads to raise the singlet-triplet splitting (26.702 kcal/mol), where the singlet state is ground state. Substitution of three and four methyl groups on silylenic center ($\text{C}_3\text{H}_8\text{Si}$ and $\text{C}_4\text{H}_{10}\text{Si}$) leads to slightly decreasing the singlet-triplet splitting (26.356 and 24.905 kcal/mol, respectively) with singlet ground state. The singlet-triplet splitting does not significantly change with substitution of more methyl groups on silylenic center (from $\text{C}_4\text{H}_{10}\text{Si}$ to $\text{C}_6\text{H}_{14}\text{Si}$). Substitution of methyl groups on the silylenic center leads to accumulate the positive charge on silylenic center; stabilizing the singlet state and increasing the singlet-triplet splitting. Decreasing of singlet-triplet splitting from $\text{C}_2\text{H}_6\text{Si}$ to $\text{C}_6\text{H}_{14}\text{Si}$ is related to increasing the steric effects; leading the more stability of triplet state; and thus decreasing singlet-triplet splitting.

The geometrical parameters including bond lengths (R_1 – R_3) and bond angle (A_1) of singlet and triplet states for $\text{C}_n\text{H}_{2n+2}\text{Si}$ ($n = 0$ – 6) is presented (Table-2).

Similar to CH_2 , the singlet state of SiH_2 exhibits larger bond lengths than triplet SiH_2 . It is obvious that the singlet states of silylene generally utilize more *p* character in their bonds, which results in smaller H–Si–H bond angles. Decreased bond angles produce greater repulsion between the substituents, which is in turn reduced by lengthening the bonds. For methylsilylene, the bond length ($\text{CH}_3\text{Si–H}$) of singlet exhibits larger than triplet state and also the bond length ($\text{CH}_3\text{–SiH}$) of triplet is larger than singlet state. Generally, substituting of more methyl groups on silylenic center $\text{C}_n\text{H}_{2n+2}\text{Si}$ ($n = 3$ – 9) reveal that the bond length ($\text{CH}_2\text{–Si}$) of singlet is larger than singlet state.

The bond angle A_{213} for singlet state of methylenic and silylenic center is increased with substituting alkyl groups while this changes for triplet states is not observed.

TABLE-2
CALCULATED B3LYP/6-311++G** BOND LENGTHS ($R_{1,2}$, $R_{1,3}$) AND BOND ANGLE (A_{213}) OF SINGLET AND TRIPLET STATES FOR ACYCLIC CARBENES AND SILYLENES

| Compd. | Singlet state | | | Triplet state | | |
|-----------------------------------|---------------|-----------|-----------|---------------|-----------|-----------|
| | $R_{1,2}$ | $R_{1,3}$ | A_{213} | $R_{1,2}$ | $R_{1,3}$ | A_{213} |
| CH ₂ | 1.114 | 1.114 | 101.502 | 1.080 | 1.080 | 135.375 |
| H ₂ Si | 1.527 | 1.527 | 91.500 | 1.488 | 1.488 | 118.718 |
| C ₂ H ₄ | 1.455 | 1.110 | 106.323 | 1.464 | 1.083 | 134.888 |
| CH ₄ Si | 1.910 | 1.532 | 94.419 | 1.902 | 1.493 | 118.883 |
| C ₃ H ₆ | 1.471 | 1.471 | 112.641 | 1.468 | 1.468 | 133.731 |
| C ₂ H ₆ Si | 1.914 | 1.914 | 98.139 | 1.907 | 1.906 | 118.649 |
| C ₄ H ₈ | 1.467 | 1.473 | 112.928 | 1.472 | 1.470 | 134.063 |
| C ₃ H ₈ Si | 1.919 | 1.915 | 98.198 | 1.919 | 1.908 | 118.687 |
| C ₅ H ₁₀ | 1.469 | 1.469 | 113.265 | 1.472 | 1.472 | 134.532 |
| C ₄ H ₁₀ Si | 1.919 | 1.922 | 101.099 | 1.920 | 1.920 | 118.968 |
| C ₆ H ₁₂ | 1.468 | 1.468 | 113.265 | 1.471 | 1.473 | 134.587 |
| C ₅ H ₁₂ Si | 1.919 | 1.922 | 101.006 | 1.920 | 1.921 | 118.779 |
| C ₇ H ₁₄ | 1.468 | 1.468 | 113.265 | 1.471 | 1.471 | 134.725 |
| C ₆ H ₁₄ Si | 1.920 | 1.922 | 101.129 | 1.920 | 1.920 | 118.768 |

B3LYP/6-311++G** NBO charges on silylenic center (Si_1) is calculated for singlet and triplet states of $C_nH_{2n+2}Si$ (Table-3). By comparing NBO charges on silylenic center of SiH_2 and CH_3SiH for singlet state, the methyl groups donates less electron than does H to the silylenic center, consistent with most electronegativity of methyl group compared to hydrogen atom. This is in contrast to the conventional concept that the methyl group is more electron rich and has electron donating nature. Substituting more methyl groups on silylenic center $C_nH_{2n+2}Si$ ($n = 2-7$) show the increasing charge on Si_1 . Similar to carbene CH_2 the dipole moments of singlet and triplet states increase with substitution of one methyl group instead of hydrogen on silylenic center SiH_2 suggesting an electron withdrawing character for methyl group respect to hydrogen atoms.

In contrast to CH_2 , dipole moment of singlet state is generally increased from CH_4Si to $C_6H_{14}Si$.

The amount of singlet-triplet splitting is rationalized in terms of simple qualitative arguments based on the HOMO-LUMO gap and in s and p orbital occupancy (Table-4)¹⁸. Generally, the substitution of methyl groups on carbenic and silylenic center increase HOMO-LUMO gap. The increasing of HOMO-LUMO gap leads to more stability of singlet state.

TABLE-3
CALCULATED B3LYP/6-311++G** NBO CHARGES ON ATOMS AND
DIPOLE MOMENT OF SINGLET AND TRIPLET STATES FOR ACYCLIC
CARBENES AND SILYLENES

| Compd. | Singlet state | | | | Triplet state | | | |
|-----------------------------------|---------------|-------------------|-------------------|--------|---------------|-------------------|-------------------|--------|
| | Charge on C1 | Charge on C2 (H2) | Charge on C3 (H3) | Dipole | Charge on C1 | Charge on C2 (H2) | Charge on C3 (H3) | Dipole |
| CH ₂ | -0.112 | 0.056 | 0.056 | 2.062 | 0.907 | 0.046 | 0.046 | 0.690 |
| H ₂ Si | 0.589 | -0.294 | -0.294 | 0.203 | 1.124 | -0.062 | -0.062 | 0.121 |
| C ₂ H ₄ | -0.040 | -0.730 | 0.081 | 2.576 | 0.941 | -0.407 | 0.055 | 1.003 |
| CH ₄ Si | 0.785 | -1.167 | -0.306 | 1.009 | 1.203 | -0.510 | -0.063 | 0.932 |
| C ₃ H ₆ | 0.117 | -0.731 | -0.731 | 2.108 | 0.982 | -0.393 | -0.393 | 0.822 |
| C ₂ H ₆ Si | 0.967 | -1.165 | -1.165 | 1.213 | 1.286 | -0.509 | -0.509 | 0.779 |
| C ₄ H ₈ | 0.121 | -0.543 | -0.726 | 2.033 | 0.987 | -0.293 | -0.394 | 0.818 |
| C ₃ H ₈ Si | 0.981 | -0.946 | -1.165 | 1.267 | 1.283 | -0.386 | -0.514 | 0.853 |
| C ₅ H ₁₀ | 0.126 | -0.539 | -0.539 | 1.973 | 0.991 | -0.293 | -0.291 | 0.788 |
| C ₄ H ₁₀ Si | 0.993 | -0.952 | -0.943 | 1.396 | 1.282 | -0.392 | -0.392 | 0.890 |
| C ₆ H ₁₂ | 0.133 | -0.538 | -0.538 | 1.900 | 0.993 | -0.293 | -0.291 | 0.836 |
| C ₅ H ₁₂ Si | 0.999 | -0.948 | -0.943 | 1.304 | 1.286 | -0.392 | -0.391 | 0.934 |
| C ₇ H ₁₄ | 0.141 | -0.537 | -0.537 | 1.820 | 0.995 | -0.293 | -0.291 | 0.730 |
| C ₆ H ₁₄ Si | 1.004 | -0.948 | -0.940 | 1.348 | 1.290 | -0.392 | -0.392 | 0.971 |

TABLE-4
CALCULATED B3LYP/6-311++G** HOMO, LUMO (eV) AND HOMO,
LUMO SPLITTING OF SINGLET AND TRIPLET STATES FOR ACYCLIC
CARBENES AND SILYLENES

| Compound | Singlet state | | |
|-----------------------------------|---------------|--------|---------------------|
| | HOMO | LUMO | LUMO-HOMO splitting |
| CH ₂ | -0.261 | -0.142 | 0.119 |
| H ₂ Si | -0.246 | -0.123 | 0.123 |
| C ₂ H ₄ | -0.225 | -0.093 | 0.132 |
| CH ₄ Si | -0.227 | -0.104 | 0.123 |
| C ₃ H ₆ | -0.207 | -0.073 | 0.134 |
| C ₂ H ₆ Si | -0.215 | -0.088 | 0.127 |
| C ₄ H ₈ | -0.207 | -0.073 | 0.134 |
| C ₃ H ₈ Si | -0.213 | -0.087 | 0.126 |
| C ₅ H ₁₀ | -0.207 | -0.072 | 0.135 |
| C ₄ H ₁₀ Si | -0.209 | -0.085 | 0.124 |
| C ₆ H ₁₂ | -0.206 | -0.072 | 0.135 |
| C ₅ H ₁₂ Si | -0.209 | -0.085 | 0.124 |
| C ₇ H ₁₄ | -0.206 | -0.071 | 0.135 |
| C ₆ H ₁₄ Si | -0.209 | -0.085 | 0.124 |

Conclusion

The magnitude of singlet-triplet splitting is evaluated for the simple acyclic silylene and compared with carbene. In contrast to carbene CH₂, the singlet state of silylene SiH₂ is ground state lying 20.408 kcal/mol higher in energy. Similar to CH₂, the substitution of a methyl group on silylenic center (CH₃SiH) increase the singlet-triplet splitting. Substitution of two methyl groups on silylenic center leads to raise the singlet-triplet splitting where the singlet state is in ground state. Substitution of methyl groups on the silylenic center leads to accumulate the positive charge on silylenic center stabilizing the singlet state and increasing the singlet-triplet splitting. Decreasing of singlet-triplet splitting from C₂H₆Si to C₆H₁₄Si is related to increasing the steric effects leading the more stability of triplet state and thus decreasing singlet-triplet splitting.

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