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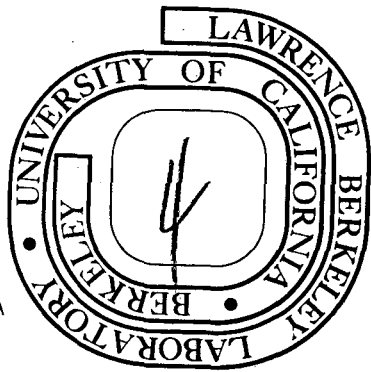
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Singlet-Triplet Energy Separation for Silaethylene*

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In 1972 Barton and McIntosh¹ reported the results of low-temperature trapping experiments designed to analyze the pyrolysis products of 1,1-dimethyl-1-silacyclobutane. Among the products they observed are unstable species possessing a sharp infrared band at 1407 cm^{-1} . This band was assigned to the 1,1-dimethyl-1-silaethylene molecule $(\text{CH}_3)_2\text{Si}=\text{CH}_2$, which had previously been identified as an unstable intermediate by Flowers and Gusel'nikov.² During the past two years there have been at least five ab initio theoretical studies³⁻⁷ of the parent compound $\text{H}_2\text{Si}=\text{CH}_2$, designed to test the assignment of Barton and McIntosh¹ and to investigate the delicate question⁸ of whether or not silaethylene is a diradical species. Available experimental data has been interpreted⁸ to imply that while the Si=C double bond is dipolar, silaethylene is a $p_\pi-p_\pi$ bonded species and not a diradical.

Among the previous theoretical studies, Strausz, et al.,^{4,6} were the first to examine both the lowest singlet and triplet states of silaethylene. They carried out complete structural predictions at the minimum basis set (MBS) self-consistent-field level of theory. Using a much larger sp basis, single calculations at the two equilibrium geometries predict the singlet state to lie lower by 9.6 kcal/mole. Finally, Strausz, Robb, Theodorakopoulos, Mezey, and Csizmadia⁶ estimated that correlation energy corrections would raise $\Delta E(T_1-S_0)$ to ~ 16 kcal.

The most recent theoretical study, that of Ahlrichs and Heinzmann,⁷ should be the most reliable. Using a double zeta (DZ) basis set, the geometry of singlet $\text{H}_2\text{Si}=\text{CH}_2$ was fully optimized. Assuming several parameters to be unchanged, the structure of triplet silaethylene was subsequently predicted. With the geometries thus obtained a larger basis set (including polarization functions) was used for Ahlrichs and Heinzmann's final calculations. In these a single-configuration SCF description of the triplet state was adopted and a two-configuration SCF approximation assumed for the singlet. In this manner the triplet state was predicted to lie 27.9 kcal above the singlet ground state.

Recent ab initio studies⁹⁻¹² of the methylene molecule, another system where the lowest singlet and triplet states are quite close energetically, have shown that such singlet-triplet separations are very sensitive to both basis set and correlation corrections. In light of the critical role of silaethylene in silicon-carbon chemistry, we decided to push this molecule to the current theoretical state of the art.

Beginning with the minimum basis SCF structure of Csizmadia and co-workers,⁴ the singlet and triplet equilibrium geometries were redone using a standard double zeta basis:¹³ $\text{Si}(11s\ 7p/6s\ 4p)$, $\text{C}(9s\ 5p/4s\ 2p)$, $\text{H}(4s/2s)$. The predicted structures are seen in the Figure. Our singlet equilibrium geometry is similar to that predicted by Ahlrichs with a slightly smaller basis: $r_e(\text{Si-C}) = 1.69\ \text{\AA}$, $r_e(\text{Si-H}) = 1.48\ \text{\AA}$, $r_e(\text{C-H}) = 1.08\ \text{\AA}$, $\theta(\text{HSiH}) = 115^\circ$, $\theta(\text{HCH}) = 112^\circ$. The largest difference is for the HCH angle, which we predict to be 115° , or 3° larger than Ahlrichs. For the

triplet state, the only previous nearly complete structural determination is that of Strausz, Gammie, Theodorakopoulos, Mezey, and Csizmadia. Their structure agrees quite well with ours except for the SiH_2 rocking angle, which they apparently assumed to be 30° . We predict 49.7° for this angle, in good agreement with Ahlrichs's value of 45° . Thus we can conclude that the structures of singlet and triplet silaethylene are now well-characterized from theory.

At the DZ SCF level of theory the triplet state of silaethylene is predicted to lie 13.7 kcal above the singlet. This agrees rather well with the value 12.4 kcal reported by Ahlrichs and Heinzmann. When we add to the DZ basis d functions centered on C (orbital exponent $\alpha = 0.75$) and Si ($\alpha = 0.6$), the SCF $\Delta E(T_1-S_0)$ value increases somewhat, to 16.7 kcal.

The most unique feature of the present paper is our nearly complete variational treatment of the valence shell correlation energy of $\text{H}_2\text{Si}=\text{CH}_2$. This was accomplished using the direct CI method¹⁴ developed by Lucchese¹⁵ as a part of the BERKELEY system¹⁶ of minicomputer-based programs. In all calculations the six lowest occupied SCF orbitals (corresponding to Si 1s, 2s and 2p and C 1s) were "frozen", i.e., held doubly-occupied in all configurations. With this restriction, the DZ calculations included all single and double excitations relative to the respective SCF reference configurations. This amounts to a total of 3284 1A_1 configurations and 7394 $^3A''$ configurations. When the DZ basis was augmented with d functions on carbon and silicon, it was necessary to delete the six highest virtual orbitals from the CI. This is a reasonable approximation, since these six highest virtual orbitals are localized in the core regions of the molecule. In this way the CI's of all single and double excitations include 4097 1A_1

configurations and 9759 $^3A''$ configurations.

The DZ CI value of $\Delta E(T_1-S_0)$ is seen in the Table to be 31.6 kcal. After the addition of d functions, the singlet-triplet separation increases again, to 34.7 kcal. However the true $\Delta E(T_1-S_0)$ will be even larger since unlinked cluster effects (arising from higher than double excitations) will be greater for the 1A_1 state than the $^3A''$ state. Using Davidson's correction¹⁷ this difference is predicted to be 3.8 kcal, yielding a final theoretical $\Delta E(^3A''-^1A_1)$ of 38.5 kcal. Assigning an uncertainty of 5 kcal/mole to this prediction, it is seen that all previous theoretical studies have placed the lowest triplet state of silaethylene too low in energy.

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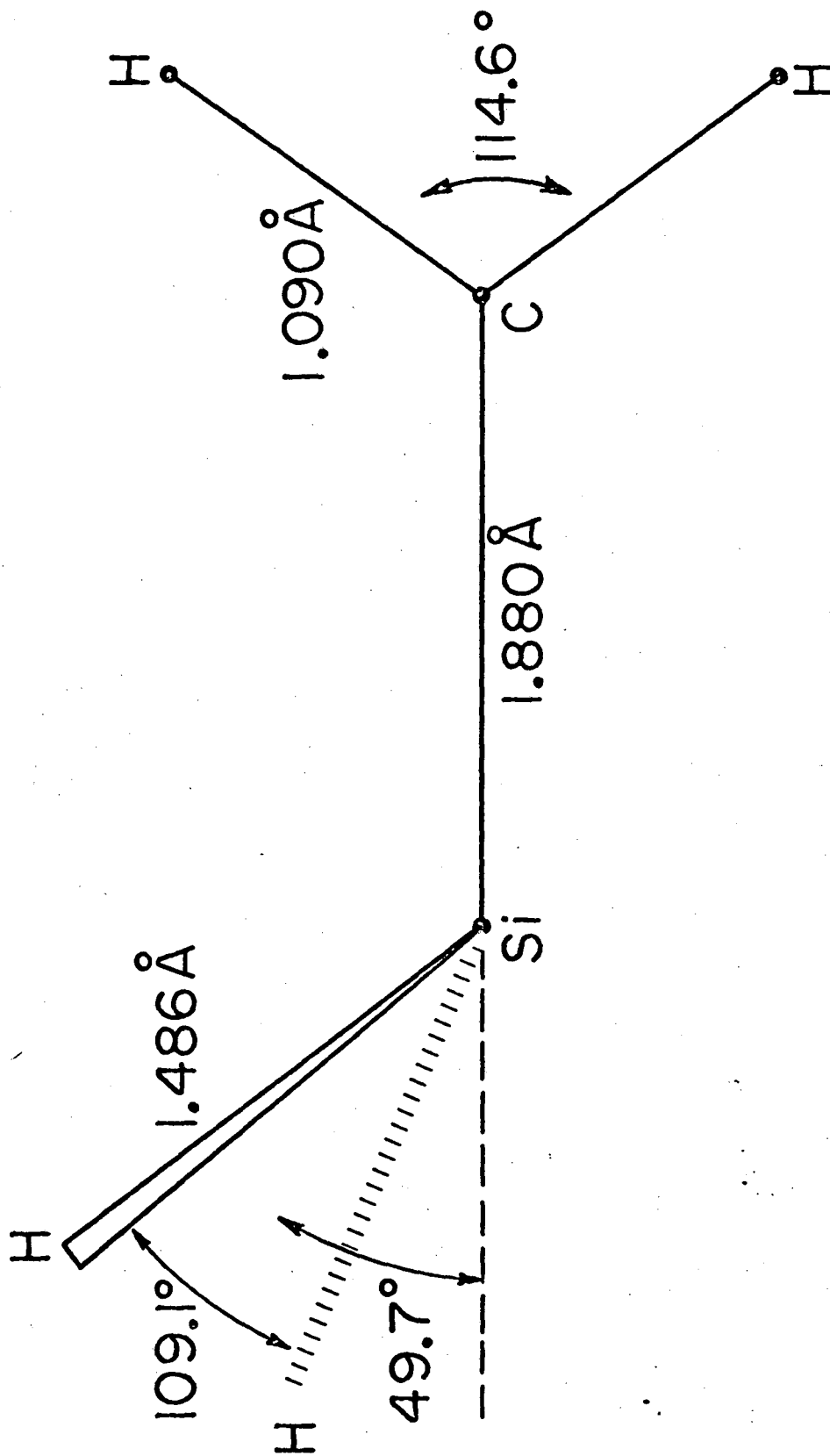
Figure Caption

Predicted equilibrium geometries for triplet and singlet silaethylene. For the former, the rocking angle, 49.7° is defined as the angle between the C-Si axis and the HSiH plane.

Table. Absolute and relative energies of singlet and triplet silaethylene.

Level of Theory	Singlet Energy, hartrees	Triplet Energy, hartrees	$\Delta E(T_1-S_0)$ kcal/mole
Double zeta (DZ) Self-consistent-field	-328.99730	-328.97551	13.7
Double zeta (DZ) Configuration interaction	-329.16408	-329.11367	31.6
DZ + d (C,Si) Self-consistent-field	-329.04356	-329.01690	16.7
DZ + d (C,Si) Configuration interaction	-329.26117	-329.20581	34.7

Triplet Silaethylene



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