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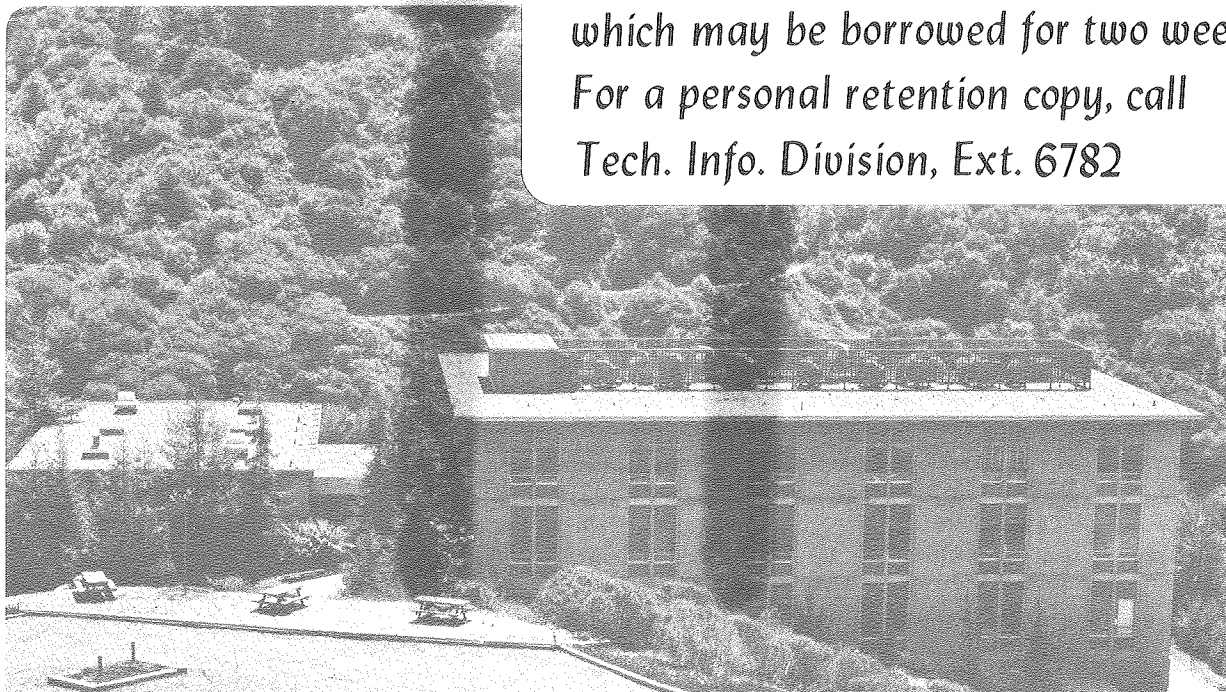
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THEORETICAL CHALLENGE TO THE EXPERIMENTALLY DETERMINED
GEOMETRICAL STRUCTURE OF DIMETHYLSILAETHYLENE

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Abstract

The equilibrium geometries of $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ and $\text{H}_2\text{Si}=\text{CH}_2$ have been determined at the self-consistent-field level of electronic structure theory using a double zeta basis set augmented with d functions on all heavy atoms. For the parent silaethylene, large scale configuration interaction (6920 configurations) demonstrates that electron correlation effects do not qualitatively alter the predicted structure. On this basis it is concluded that the experimental electron diffraction geometry of Mahaffy, Gutowsky, and Montgomery is likely to be seriously incorrect. Specifically the theoretical prediction for the dimethylsilaethylene $\text{Si}=\text{C}$ distance is 1.692 \AA , while the range of experimental values presented was $1.815 - 1.835 \text{ \AA}$.

In a recent communication to this journal, Mahaffy, Gutowsky and Montgomery¹ (MGM) presented an experimental molecular structure for 1,1 dimethylsilaethylene (DMSE), based on their electron diffraction data. Their work was of particular interest, inasmuch as it represented the first experimental structural study of any molecule containing a carbon-silicon double bond.² The most significant finding of MGM was an extremely long Si=C double bond, namely $1.83 \pm 0.04 \text{ \AA}$, or only 0.08 \AA shorter than their observed Si-C single bond, $1.91 \pm 0.02 \text{ \AA}$. For comparison, the typical C=C double bond (1.35 \AA) is 0.19 \AA shorter than the typical C-C single bond (1.54 \AA). If this long Si=C distance of 1.83 \AA is correct, one would likely infer that the π bond in DMSE is exceptionally weak.

MGM noted an apparent discrepancy between theory and experiment. For the parent unsubstituted silaethylene $\text{H}_2\text{Si}=\text{CH}_2$, MGM cited about a dozen quantum mechanical predictions^{3,4} of the Si=C bond distance, and these vary from 1.63 \AA to 1.75 \AA . Of these the most complete study⁴ was carried out at the self-consistent-field (SCF) level of theory and employed a double zeta (DZ) basis set of contracted gaussian functions. Since the predicted Si=C bond distance of 1.715 \AA is so much less than the experimental DMSE value of 1.83 \AA , one is logically left with three alternatives:

(a) the two methyl substituents greatly increase the Si=C distance in DMSE relative to the parent $\text{H}_2\text{Si}=\text{CH}_2$.

(b) the theoretical predictions for the Si=C bond distance in $\text{H}_2\text{Si}=\text{CH}_2$ are all incorrect

(c) the experimental Si=C distance in DMSE is in error.

Of course it is also possible that some superposition of these three effects might lead to the 0.115 Å gap between theory for H₂Si=CH₂ and experiment for DMSE.

In the present communication we report theoretical results which drastically reduce the possibility that points (a) or (b) above could be responsible for the discrepancy between theory and experiment. First, an explicit optimization of the geometrical structure of DMSE has been completed. Furthermore, this equilibrium geometry was determined at a level of theory higher than any previous structural optimization of even the parent H₂Si=CH₂. To the double zeta (DZ) basis⁵ used by Hood and Schaefer⁴ was added a set of d functions on each heavy atom. These polarization functions were assigned orbital exponents $\alpha = 0.75$ (carbon) and $\alpha = 0.60$ (silicon). The designation of this DZ+d basis set is then Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), H(4s/2s).

The predicted theoretical structure for DMSE is seen in the Figure. The relative orientations of the two methyl groups was arbitrarily chosen to maintain point group C_{2v}, but the barriers to rotation about these Si-C single bonds should be quite small. Figure 1 shows that the predicted Si=C bond distance, 1.692 Å, falls far outside the range 1.83 ± 0.04 Å provided by the experimental electron diffraction study.¹ The predicted Si-C single bond distance, 1.873 Å, is also shorter than experiment, 1.91 ± 0.02 Å, but in this case the disagreement is much less severe. None of the other geometrical parameters of DMSE were determined by MGM,¹ but the predicted theoretical values are all quite consistent with chemical intuition.⁶ Furthermore, a steadily increasing body of

comparisons^{7,8} between theory and experiment would suggest a typical reliability of $\pm 0.01 \overset{\circ}{\text{Å}}$ for bond distances predicted at the DZ+d SCF level of theory.

To assess the relationship between the structures of DMSE and the parent silaethylene, the latter equilibrium geometry was theoretically determined in a manner precisely the same as that described above for DMSE. This DZ+d SCF structure for the parent is illustrated in the middle of the Figure. The Figure shows that at the DZ+d SCF level of theory, the Si=C bond distances of $\text{H}_2\text{Si}=\text{CH}_2$ and $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ are identical ($1.692 \overset{\circ}{\text{Å}}$) to within one-thousandth of an angstrom. This would certainly appear to dispense with the possibility, suggested by MGM,¹ that the Si=C distance is significantly longer in DMSE.

The only remaining satisfactory explanation of the experimental DMSE geometry is that the DZ+d SCF level of theory systematically predicts Si=C distances much too short. This possibility has been examined by explicitly determining the structure of $\text{H}_2\text{Si}=\text{CH}_2$ using highly correlated⁹ wave functions. Using the DZ+d basis set, configuration interaction (CI) was carried out including all single and double excitations relative to the Hartree-Fock reference configuration. With the six core orbitals (C 1s, Si 1s, 2s, $2p_x$, $2p_y$, $2p_z$) constrained to be doubly occupied in all configurations, this approach yields a total of 6,920 $^1\text{A}_1$ configurations.

The DZ+d CI structure of silaethylene shown at the bottom of the Figure demonstrates clearly that electron correlation has little effect on the predicted Si=C bond distance. The theoretical distance is $1.705 \overset{\circ}{\text{Å}}$, or only $0.013 \overset{\circ}{\text{Å}}$ longer than the analogous SCF result. For the

above-discussed comparison of the silaethylene and DMSE structures, one anticipates that the DMSE Si=C bond distance will also be $\sim 1.70 \text{ \AA}$. Based on previous experience^{7,8} we suggest that the exact (unknown) Si=C bond distance r_e for the unsubstituted silaethylene is $1.705 \pm 0.03 \text{ \AA}$. To our thinking this prediction causes serious doubt upon the assumptions made by MGM¹ in extracting the Si=C distance in DMSE from the reported electron diffraction data.¹⁰

It should be noted that theoretical geometry predictions for molecules containing the second-row atoms Al, Si, P, S and Cl have been much less thoroughly calibrated than those for hydrocarbons and other first-row molecules.⁷⁻⁹ However, the most complete comparison, that of Collins, Schleyer, Binkley, and Pople,¹¹ suggests that even without polarization functions and CI, a double zeta basis set is unlikely to yield bond distance errors greater than 0.1 \AA . Furthermore, for thioformaldehyde (isoelectronic with silaethylene), our DZ basis set yields a C=S bond distance of 1.637 \AA ,¹² in reasonable agreement with experiment,¹³ 1.611 \AA . For the same molecule, with a DZ basis set augmented by sulfur d functions, Flood and Boggs¹⁴ predicted $r_e(\text{C}=\text{S}) = 1.600 \text{ \AA}$. Therefore it appears extremely unlikely that the level of theory employed here results in a large error in the C=Si bond distance of DMSE.

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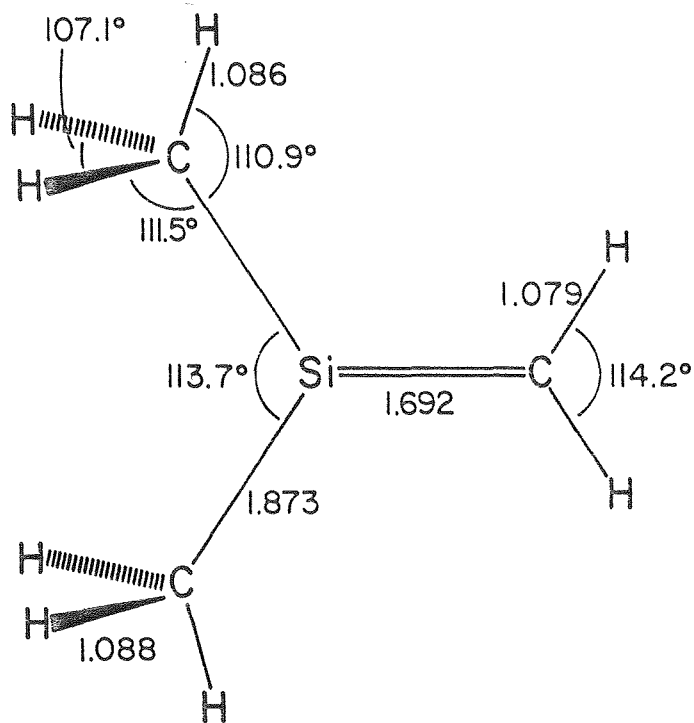
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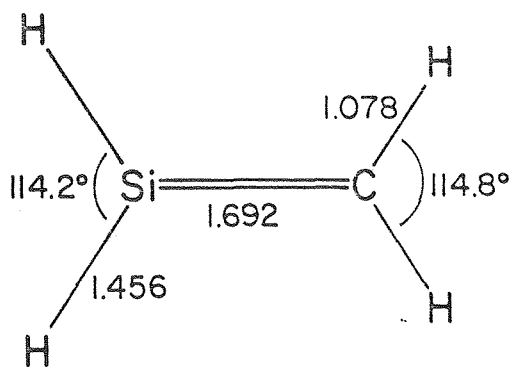
Figure Caption

Theoretical equilibrium geometries for 1,1 dimethylsilaethylene (DMSE) and the parent unsubstituted silaethylene.

DZ+d SCF



DZ+d SCF



DZ+d CI

