On the Structure of the Si₂H₄ Ground State: Singlet Silysilylene*

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Abstract: Ab initio SCF-MO calculations in a 4-31 Gaussian basis set for Si₂H₄ suggest that its electronic ground state structure corresponds to singlet silysilylene rather than planar disilene, which would be expected by analogy with the chemistry of ethylene.

Introduction

We have undertaken ab initio SCF-MO calculations to sketch the structure and thermochemistry of silicon hydrides, and to outline the similarities and differences with the well-explored chemistry of hydrocarbons. The chemistry of silicon hydrides is of intrinsic interest to chemists, and may support research in two areas of interest to solid-state physicists; the reconstruction of cleaved silicon crystal surfaces and the structure of amorphous silicon bearing hydrogen.

Silanes are the silicon analogues of saturated hydrocarbons. Silane (SiH₄), disilane (Si₂H₆), and polysilanes up to at least Si₆H₁₄ have been prepared. The higher polysilanes are thermally unstable with respect to dehydrogenation and the formation of amorphous silicon. This is in contrast to the thermal decomposition of saturated hydrocarbons which produce volatile unstrained hydrocarbons such as ethylene (C₂H₄) as major products.

The pyrolysis of disilane produces silane and silylene (SiH₂), which inserts like singlet methane in a Si-H bond of another disilane molecule to form trisilane (Si₃H₈). The pyrolysis of trisilane is postulated to produce silysilylene (HSiSiH₃) in a singlet electronic spin state rather than disilene (H₂Si=SiH₂), the silicon analogue of ethylene. Wulf, Goure, and Barton have reached a similar conclusion for methylated disilene, that trimethylsilylmethylsilylene.

In the quantum chemical computational studies reported here, we compute the structure and relative stability of disilene, both planar and bent, and of both singlet and triplet silysilylene.

Theoretical Methods

We have estimated the total energy of disilane and its isomers by constructing an SCF-MO determinantal wave function for all the molecular electrons. A contracted Gaussian orbital basis set of the 4-31G type developed previously for the silicon atom in disilane is employed. The 4-31G basis contains a separate contraction (fixed linear combination) of four Gaussian functions to represent the core Is, 2s, and 2p orbitals of silicon. The 3s and 3p valence shell orbitals of silicon are both represented by an inner contraction of three Gaussian functions and a single outer Gaussian. Common Gaussian exponents are employed in the 2s-2p contractions and in the 3s-3p contractions. The silicon 4-31G basis we have used has exponents optimized with respect to the energy of disilane. For hydrogen we employ the standard 4-31G basis.

To compute the SCF-MO wave function and total energy, we employed the computer program GAUSSIAN-70.11 Wave functions of the restricted Hartree-Fock (RHF) type are computed for closed-shell species such as disilene and singlet silysilylene. The unrestricted Hartree-Fock (UHF) method is applied to triplet silysilylene.

Applied to disilane in the staggered configuration with assumed tetrahedral bond angles, minimization of the total energy with respect to the two bond lengths r(Si-Si) and r(Si-H) gives an equilibrium geometry with r(Si-Si) = 2.352 Å and r(Si-H) = 1.492 Å, in good agreement with the observed bond lengths of 2.331 ± 0.003 and 1.492 ± 0.003 Å, respectively.

Computational Results

We have studied the relative stability of several isomeric structures of Si₂H₄ by varying geometry parameters until the computed total energy is a minimum, subject to the constraints characteristic of each structure. The values of geometry parameters which minimize the total for the several structures are listed in Table I.

The equilibrium geometry of planar disilene, with the assumed D₃h point group of ethylene illustrated in Figure 1, was computed first. The computed Si-Si double bond length (2.083 Å) is 0.27 Å shorter than the computed Si-Si single bond of disilene, while the Si-H bond length of disilene is only 0.01 Å shorter than that computed for disilane. The computed disilene is 114.4° is about 2° smaller than the LiCH of ethylene.

When the constraint of planarity is removed, planar disilene relaxes to the trans-bent form, of point group S₂, illustrated in Figure 1, with the SiH₂ groups at each end bent up and down by the angle θ = 12.9° from the molecular plane and the Si-Si and Si-H bonds lengthened by about 0.01 Å. This trans-bent form of disilene is computed to be 0.5 kcal more stable than the planar form. This is in contrast to both the observed and computed planar geometry of ethylene. No lowering of energy was found for a cis-bent form of disilene.

In view of the suggestion by experimentalists, that the ground state of Si₂H₄ may be singlet silysilylene, as shown in Figure 1, we have computed the stability of that structure with assumed tetrahedral angles and the computed Si-H bond length of disilane in the silyl group. We find the equilibrium structure of singlet silysilylene to have a zSiSiH of 92.1° with both the Si-Si and Si-H bond lengths to be about 0.05 Å longer than those in disilane. The hydrogen atom on the di- valent silicon is in the staggered geometry relative to hydrogen atoms of the silyl group. This singlet silysilylene is computed to be 8.6 kcal more stable than planar disilene.

Minimizing the energy of the UHF wave function for triplet silysilylene, we find zSiSiH to be 117.7° with the Si-Si and Si-H bond lengths closer to those of disilane.

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Our computations give the silylsilylene triplet state to be 4.3 kcal more stable than the singlet state. It is well established by the computational studies of Meadows and Schaefer that a single configuration SCF-MO wave function, without polarization functions in the basis, as are those we have computed here, underestimates the stability of singlet SiH₂ relative to triplet SiH₂ by 15.4 kcal. Thus we believe that singlet silylsilylene is more stable than triplet silylsilylene by about 11.1 kcal. Moreover, we estimate triplet silylsilylene to be less stable than planar disilene by 2.5 kcal/mol.

The energy eigenvalues for planar disilene, trans-bent disilene, and singlet silylsilylene are collected in Table II.

It is to be expected that the correlation energy for the π bond of planar disilene and the corresponding weakly coupled electron pair of the trans-bent form will be greater than that of the lone pair of the divalent silicon of singlet silylsilylene. However, preliminary generalized valence bond calculations on these systems suggest that the energy order which we find here will not be changed by a better account of electron correlation.

We have made preliminary tests of the effect of the addition of d basis functions to silicon and find that the relative energies of the three structures studied here changed by less than 1 kcal.

**Conclusions**

Ab initio computations in a 4-31G basis set for Si₃H₄ suggest that its ground state is singlet silylsilylene rather than planar disilene. This supports an earlier hypothesis by Sefcik and Ring. It is supporting evidence for the recent conclusion by Wulff, Goure, and Barton, that tetramethyldisilene rearranges to trimethylsilylmethylsilylene.

**References and Notes**

(1) A more comprehensive account of this work was given in a talk by Lawrence C. Snyder titled "A Quantum Chemist's View of Silicon Chemistry Related to Silicon Surface Reconstruction", which was presented at the Pauling Award Symposium, honoring John Pople, Nov 5, 1977, at the University of Oregon, Eugene, Oregon.


(11) W. J. Hehe, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE No. 236, GAUSIAN-70 ab initio SCF-MO Calculations on Organic Molecules.


(16) L. C. Snyder, J. W. Moskowitz, and Z. Wasserman, to be published.