On the Structure of the Si_2H_4 Ground State: Singlet Silylsilylene[†]

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Abstract: Ab initio SCF–MO calculations in a 4-31 Gaussian basis set for Si_2H_4 suggest that its electronic ground state structure corresponds to singlet silylsilylene 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.[1] 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[2] and the structure of amorphous silicon bearing hydrogen.[3]

Silanes are the silicon analogues of saturated hydrocarbons. Silane (SiH_4), disilane (Si_2H_6), and polysilanes up to at least Si_6H_{14} have been prepared.[4] The higher polysilanes are thermally unstable with respect to dehydrogenation and the formation of amorphous silicon.[5] This is in contrast to the thermal decomposition of saturated hydrocarbons which produce volatile unsaturated hydrocarbons such as ethylene (C_2H_4) as major products.

The pyrolysis of disilane produces silane and silylene (SiH_2), which inserts like singlet methylene in a Si–H bond of another disilane molecule to form trisilane (Si_3H_8).[6] The pyrolysis of trisilane is postulated to produce silylsilylene ($HSiSiH_3$) in a singlet electronic spin state rather than disilene ($H_2Si=SiH_2$), the silicon analogue of ethylene.[6] Wulff, Goure, and Barton[7] have reached a similar conclusion for methylated disilene, that tetramethyldisilene rearranges to trimethylsilylmethylsilylene. This is in contrast with the chemistry of unsaturated hydrocarbons, where ethylene is more stable than either singlet or triplet methylmethylene.

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 silylsilylene.

Theoretical Methods

We have estimated the total energy of disilene 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[8] developed previously for the silicon atom in disilane is employed.[9,10] The 4-31G basis contains a separate contraction (fixed linear combination) of four Gaussian functions to represent the core 1s, 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.[8]

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 silylsilylene. The unrestricted Hartree–Fock (UHF) method is applied to triplet silylsilylene.

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 $r_e(Si-Si) = 2.352$ Å and $r_e(Si-H) = 1.492$ Å, in good agreement with the observed bond lengths of 2.331 ± 0.003 and 1.492 ± 0.003 Å, respectively.[12]

Computational Results

We have studied the relative stability of several isomeric structures of Si_2H_4 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 D_{2h} 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 disilane, while the Si–H bond length of disilene is only 0.01 Å shorter than that computed for disilane. The computed disilene ∠HSiH (114.4°) is about 2° smaller than the ∠HCH of ethylene.[13]

When the constraint of planarity is removed, planar disilene relaxes to the trans-bent form, of point group S_2, illustrated in Figure 1, with the SiH_2 groups at each end bent up and down by the angle $\theta = 12.9°$ 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 Si_2H_4 may be singlet silylsilylene, 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 silylsilylene to have a ∠SiSiH 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 divalent silicon is in the staggered geometry relative to hydrogen atoms of the silyl group. This singlet silylsilylene is computed to be 8.6 kcal more stable than planar disilene.

Minimizing the energy of the UHF wave function for triplet silylsilylene, we find ∠SiSiH to be 117.7° with the Si–Si and Si–H bond lengths closer to those of disilane.

Table I. Computed Si_2H_4 Structures

structure	total energy, au	r_{Si-Si}, Å	r_{Si-H}, Å	∠HSiH, deg	∠θ, deg	∠SiSiH, deg
disilene planar	−579.3287	2.083	1.477	114.4	0	
disilene bent trans	−579.3293	2.102	1.485	115.7	12.9	
silylsilylene singlet	−579.3424	2.408	1.506			92.1
silylsilylene triplet	−579.3492	2.317	1.497			117.7

Table II. Computed Total Energy and Eigenvalues for Si_2H_4 Structures

	structure		
	disilene		silylsilylene
eigenvalue	planar	bent-trans	singlet
16	−0.247	−0.251	−0.286
15	−0.434	−0.432	−0.382
14	−0.460	−0.456	−0.470
13	−0.495	−0.491	−0.471
12	−0.629	−0.630	−0.609
11	−0.741	−0.740	−0.730
10	−4.224	−4.226	−4.212
9	−4.225	−4.226	−4.214
8	−4.226	−4.227	−4.215
7	−4.226	−4.228	−4.233
6	−4.226	−4.228	−4.233
5	−4.228	−4.229	−4.234
4	−6.112	−6.114	−6.107
3	−6.112	−6.114	−6.119
2	−68.712	−68.714	−68.711
1	−68.712	−68.714	−68.721

Figure 1. Structures of Si_2H_4: from top to bottom, planar disilene, trans-bent disilene, and silylsilylene, respectively.

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[14] 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 SiH_2 relative to triplet SiH_2 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.
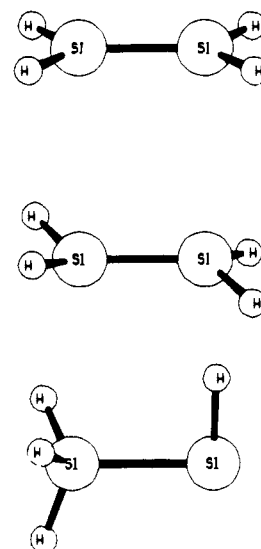
The energy eigenvalues for planar disilene, trans-bent disilene, and singlet silylsilylene are collected in Table II.

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.[15] 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.[16]

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 Si_2H_4 suggest that its ground state is singlet silylsilylene rather than planar disilene. This supports an earlier hypothesis by Sefcik and Ring.[6] It is supporting evidence for the recent conclusion by Wulff, Goure, and Barton,[7] that tetramethyldisilene rearranges to trimethylsilylmethylsilylene.

References and Notes

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