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# Molecular and Electronic Structure of $Si_3H_6$

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**Abstract:** The ground state of disilylsilylene ($(SiH_3)_2Si$) is predicted to be the closed-shell ($^1$A in $C_2$ symmetry) state, about 6 kcal/mol below the lowest triplet ($^3B_1$ in $C_{2v}$ symmetry) at the MP4/6-31G(d)//3-21G* level of theory. A second triplet with a very small Si–Si–Si angle ($^3$A in $C_2$ symmetry) is found to be more than 30 kcal/mol above the ground state. The global minimum on the $Si_3H_6$ ground-state surface is predicted to be trisilacyclopropane, 18.3 and 9.7 kcal/mol, respectively, below $(SiH_3)_2Si$ and $SiH_3SiH{=}SiH_2$.

There has been considerable experimental[1,2] and theoretical[3-5] interest recently in devising substituents that preferentially stabilize singlet or triplet states of silylenes. It has been established[1,3] that in the parent compound $SiH_2$ the ground-state closed-shell singlet is 14–18 kcal/mol below the $^3B_1$ state. It is clear that lone-pair-containing electronegative substituents (e.g., F, OH, $NH_2$) stabilize the closed-shell state,[2,4] while the introduction of highly electropositive substituents results in a triplet ground state. Thus, both HLiSi[5b,5c] and $SiLi_2$[5a] have been predicted by ab initio calculations with large basis sets and highly correlated wave functions to have triplet ground states.

Since Li may not be the most accessible substituent experimentally, it is of interest to investigate alternative electropositive substituents that might preferentially stabiilze triplet states. The substituent investigated in the present work is the silyl group, giving rise to disilylsilylene.

An ancillary interest here is the relative energies of several $Si_3H_6$ isomers. For the hydrocarbon analogues, the global minimum of $C_3H_6$ is propene, with cyclopropane 7 kcal/mol higher in energy.[6] Based on ethylene vs ethylidene,[7] the carbenes are expected to be approximately 70 kcal/mol above propene. Since the Si=Si double bond is much weaker than the C=C bond[8-10] and since silylenes appear to be considerably more stable than carbenes,[11] the order of stability of the silicon isomers may different from that of the hydrocarbons.

## Computational Approach

All structures were fully optimized with use of analytically determined gradients at the self-consistent field (SCF) level with the 3-21G* basis set.[12] Closed- and open-shell molecules were treated with restricted (RHF)[13] and unrestricted (UHF)[14] Hartree–Fock procedures, respecitvely. Diagonalization of the matrices of energy second derivatives verified that all predicted structures are indeed minima on their respective potential energy surfaces. Energy differences were obtained at the 3-21G* structures by using two larger basis sets and wave functions, which include correlation corrections. The 6-31G(d)[15] energy differences have been obtained with full fourth-order Moller Plesset (MP4)[16] perturbation theory, while those for the larger MC-311G(d,p) basis set[17] were calculated with MP2 wave functions. Previous calculations have shown that calculations at this level are not significantly different from the results of second-order configuration interaction/multiconfigurational SCF (SOCI/MCSCF) calculations.[3a,5a] The calculations described in this paper were carried out on the North Dakota State University IBM 3081D and the San Diego Supercomputer Center Cray XMP/48 using the appropriate versions of GAUSSIAN82.[18]

## Results and Discussion

The 3-21G* structures of the lowest singlet and triplet states of disilylsilylene are summarized in Table I. Note that the closed-shell $^1$A state is twisted from $C_{2v}$ into $C_2$ symmetry, while the $^3B_1$ state retains $C_{2v}$ symmetry at its optimal geometry. As noted in earlier studies of silylenes,[1-5] the triplet Si–X bond lengths (in this case X = Si) are shorter than those in the closed-shell

**Table I.** Structures of Disilylsilylene[a]

| | $^1$A ($C_2$) | $^3B_1$ ($C_{2v}$) | $^3$A ($C_2$) |
|---|---|---|---|
| *R*(SiSi) | 2.392 | 2.327 | 2.492 |
| *R*($SiH_a$) | 1.479 | 1.477 | 1.479 |
| *R*($SiH_b$) | 1.481 | 1.478 | 1.476 |
| *R*($SiH_c$) | 1.484 | 1.478 | 1.473 |
| *A*(SiSiSi) | 93.7 | 125.2 | 71.3 |
| *A*($H_a$SiSi) | 112.6 | 108.8 | 97.9 |
| *A*($H_b$SiSi) | 113.7 | 110.9 | 118.9 |
| *A*($H_c$SiSi) | 105.5 | 110.9 | 110.4 |
| dih($H_a$SiSiSi) | 196.9 | 180.0 | 197.3 |
| dih($H_b$SiSiSi) | 123.6 | 119.8 | 117.2 |
| dih($H_c$SiSiSi) | 242.0 | −119.8 | 244.8 |

[a] Bond lengths in angstroms; angles in degrees. $H_a$, $H_b$, and $H_c$ refer to the three hydrogens on each silyl group. $H_b$ and $H_c$ are symmetrically equivalent in the ($C_{2v}$) $^3B_1$ structure. *R*, *A*, and dih refer to bond lengths, bond angles, and dihedral angles, respectively.

**Table II.** Relative Energies (kcal/mol)

| | $(SiH_3)_2Si$ | | | $SiH_3SiH{=}$ $SiH_2$ | *c*-$(SiH_2)_3$ | $SiH_3SiH_2SiH$ |
|---|---|---|---|---|---|---|
| | $^1$A | $^3B_1$ | $^3$A | | | |
| | | | | 6-31G(d) | | |
| SCF | 0.0 | −7.9 | 31.7 | −1.1 | −11.9 | 0.5 |
| MP2 | 0.0 | 2.6 | 33.9 | −9.9 | −20.6 | 1.2 |
| MP3 | 0.0 | 4.6 | | −8.1 | −18.4 | 1.0 |
| MP4 | 0.0 | 5.8 | | −8.6 | −18.3 | 1.0 |
| | | | | MC-311G(d,p) | | |
| SCF | 0.0 | −8.0 | | −1.6 | −12.0 | |
| MP2 | 0.0 | 3.0 | | −9.7 | −19.9 | |

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state. As expected, the central Si–Si–Si angle is close to 90° in $^1A$ and opens to 125.2° in $^3B_1$. The latter may be compared with 118.4°, 118.2°, and 124.7° in silylene,[3a] dimethylsilylene,[5a] and di-*tert*-butylsilylene,[5a] respectively.

A second low-lying triplet state with a very small bond angle has been predicted in both $Li_2Si$[5a] and HSiLi.[5b] In both cases the structure was interpreted as a weakly bound complex between silicon and the diatomic moiety. A similar structure has been found on the $SiH_2$ surface[5c,d] but with relatively much higher energy. The structure of the analogous $^3A$ state (in $C_2$ symmetry) is shown in Table I. As observed for the lithium compounds, this structure has a very small central Si–Si–Si angle of 71.3° and a rather long Si–Si bond. This gives rise to a nonbonded Si–Si distance of 2.905 Å, roughly 0.55 Å longer than a typical Si–Si single bond. Thus, the nonbonded Si–Si interaction is apparently much less than the analogous Li–Li or Li–H interactions in the previously studied compounds.

The relative energies of the three $(SiH_3)_2Si$ states are summarized in Table II. At the SCF level, $^3B_1$ is predicted to be about 8 kcal/mol lower in energy than $^1A$ with both basis sets. As expected,[3-5] the addition of correlation corrections preferentially stabilizes the singlet state, with the result that the order of stability of the two states is reversed. Since the relative energy predictions at the SCF and MP2 levels are nearly independent of basis set, MP4 calculations were only carried out with the smaller basis set. (The basis set independence of such predicted energy differences has been noted previously.[5a]) The closed-shell singlet state is predicted to be about 6 kcal/mol lower in energy than $^3B_1$. In previous calculations, SOCI/MCSCF singlet–triplet splittings in silylenes have been found to be within 2 kcal/mol of those predicted at the MP4 level with the same basis sets;[3a,5a] thus, it is expected that MCSCF-based calculations will not significantly alter the results presented here.

The second triplet state is found to be more than 30 kcal/mol above the singlet at the MP2/6-31G(d) level, so higher level calculations on $^3A$ were not pursued. The relative energies of the two triplet states are similar to those found earlier by Rice and Handy[3d] for the parent $SiH_2$ and much larger than those predicted for $Li_2Si$[5a] and HSiLi.[5b] The expectation value of the $S^2$ operator for the $^3A$ state is 2.027; thus, the UHF wave function for this state is very close to a pure triplet, for which $\langle S^2\rangle = 2.0$. This is in contrast to the UHF wave function for $^3A_2$ $Li_2Si$,[5a] in which $\langle S^2\rangle = 2.78$.

The structures of the isomers of disilylsilylene are illustrated in Figure 1. Silyldisilene is predicted to have $C_s$ symmetry, with a planar disilene moiety; however, the same level of theory predicts the parent disilene to be planar as well.[10] It is likely that a larger basis set and the incorporation of correlation corrections in the geometry prediction will lead to a slightly nonplanar structure,[19] but small deviations from planarity are not expected to significantly alter the relative energies.

The relative energies of the $Si_3H_6$ isomers are summarized in Table II. At the SCF level silyldisilene is predicted to be slightly more stable than disilylsilylene. Addition of correlation corrections widens this gap, with the final prediction that the double-bond-containing species is nearly 10 kcal/mol lower in energy than the silylene isomer. The three-membered ring is also stabilized by the inclusion of correlation corrections and is predicted to be the global minimum on the ground-state $Si_3H_6$ surface. This is in contrast with the analogous $C_3H_6$ surface, for which propene is the global minimum, several kilocalories per mole lower in energy than cyclopropane.[6] This reflects once again the relative thermodynamic instability of the Si=Si π bond. The remaining isomer, $SiH_3SiH_2SiH$, is predicted to be very slightly (1 kcal/mol) above $(SiH_3)_2Si$.

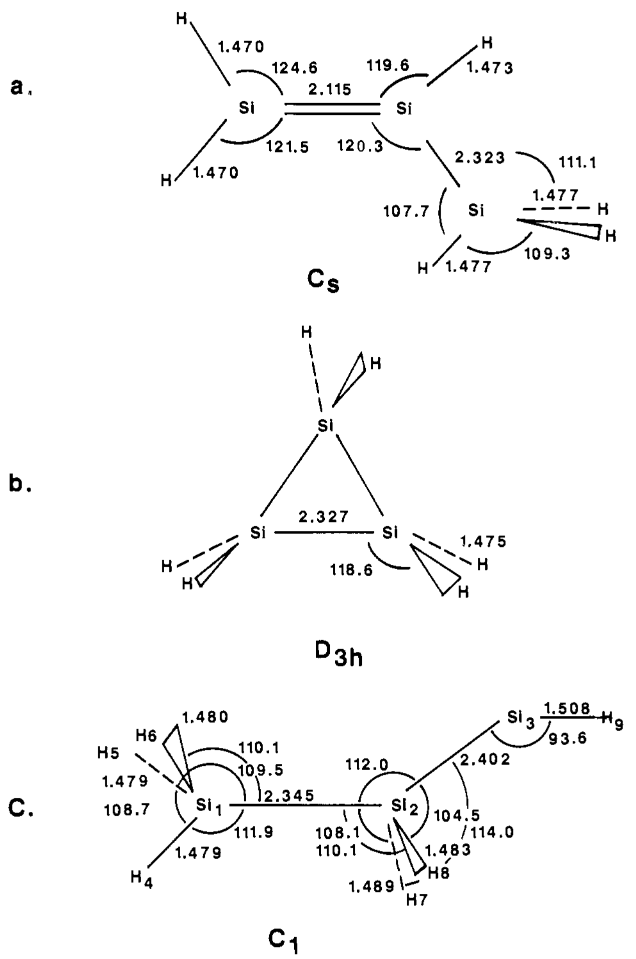

Figure 1. 3-21G* structures of (a) silyldisilene, (b) Trisilacyclopropane, and (c) $SiH_3SiH_2SiH$ [$A(H_6SiH_4) = 108.4°$, dih($H_4SiSiSi$) = 177.6°, dih(HgSiSiSi) = 158.9°].

## Conclusions

The singlet closed-shell ground state of $(SiH_3)_2Si$ is predicted to be only 6 kcal/mol below the lowest triplet state. This may be compared with predicted splittings of 17–19 kcal/mol in the parent $SiH_2$,[3] 23–25 kcal/mol in $(CH_3)_2Si$,[4,5] and 73–74 kcal/mol in $SiF_2$,[4] at similar levels of theory. This trend, which clearly reflects the effect of the electronegativities of the substituents, is highlighted by the introduction of lithium substituents, which actually reverse the order of stability of singlet and triplet states.[5] Monosubstituted silylenes, HSiX with X = Li,[5] $SiH_3$,[4c,d] $CH_3$,[4,5] NH2,[4] OH,[4] and F,[4] also fit into this overall trend. However, note that at the MP4/6-31G(d) level of computation, the singlet–triplet splittings in HSiF, HSiOH, and $HSiNH_2$ are within 2 kcal/mol of each other, with the amino substituent having the largest splitting. This is consistent with the suggestion regarding methylene chemistry made by Feller, Borden, and Davidson[20] that lone pair–π interactions are also important in stabilizing the singlet state.

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The global minimum on the $Si_3H_6$ potential energy surface is trisilacyclopropane. This is in contrast with the hydrocarbon analogues, for which propene is the global minimum on the $C_3H_6$ surface, and reflects the relative strengths of the Si-Si vs C-C $\pi$ bonds,[10] as well as the smaller strain in the three-membered silicon ring.[21]

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# Magnetic Properties in Terms of Localized Quantities. 7. Application to Nitrogen NMR Shifts

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**Abstract:** Magnetic susceptibility and NMR chemical shift tensors for various classes of nitrogen-containing molecules are calculated by means of the IGLO method. The compounds studied are the amines $NH_m(CH_3)_{3-m}$ ($m$ = 0, 1, 2, 3), $C_6H_5NH_2$, the three-membered ring aziridine ($(CH_2)_2NH$), the nitriles $CH_3CN$ and $C_6H_5CN$, the isonitrile $CH_3NC$, diazomethane ($CH_2NN$), hydrazine ($N_2H_4$), and some diazenes RN=NR (R = H, $CH_3$). Generally the agreement between theory and experiment is good, with the exception of nitrogen atoms in NN multiple bonds. It is found that the calculated NMR chemical shifts of nitrogens involved in NN double bonds are too paramagnetic, even in the limit of near Hartree-Fock quality of the basis sets. Because of the large magnitude of the deviations between theory and experiment, gas-to-liquid shifts or asymmetry effects cannot explain the differences. We conclude that correlation effects, which are neglected in the IGLO method as well as in any other theory of coupled Hartree-Fock type, are likely to play an important role in the calculation of NMR shifts for nitrogen atoms involved in NN multiple bonds.

## I. Introduction

Nitrogen NMR spectroscopy is becoming more and more an indispensable tool for the identification of bioorganic molecules and the investigation of their reaction mechanisms. The experimental difficulties due to quadrupolar nuclei ($^{14}N$) or low abundance ($^{15}N$) have been overcome by the advent of new techniques.[1,2]

On the theoretical side, however, only very few ab inito methods are capable of calculating magnetic properties of molecules having more than a few first-row atoms. Conventional coupled Hartree-Fock or finite perturbation methods, though applicable in principle, cannot be used because of the computational problems connected with the choice of a single gauge origin describing the external magnetic field. Therefore only methods that use local gauge origins, i.e., Ditchfield's GIAO,[3] Hansen and Bouman's LORG,[4] and our IGLO approach,[5] are expected to give results of reasonable accuracy when they are applied to large molecules.

We have shown that the IGLO method (IGLO stands for individual gauge for localized molecular orbitals) provides detailed and reliable information on magnetic susceptibility and chemical shift tensors of small- to medium-sized molecules.[6] It has been used to assign the principal axes of chemical shift tensors in highly strained hydrocarbons[7] and to answer some unresolved questions in carbocation chemistry,[8] and recently it has been applied successfully to compounds containing silicon and phosphorus[9] and to a number of boranes and carboranes.[10]

In this paper we present calculations on second-order properties of some representative nitrogen compounds, covering approximately the whole range of nitrogen NMR shifts. In our calculations we cannot distinguish $^{15}N$ from $^{14}N$ NMR shifts. Experimentally the primary isotope effect is of the order of 0.1 ppm[1,2] and hence negligible for our purposes.

Due to the lone-pair electrons at nitrogen, its NMR chemical shifts are somewhat more difficult to calculate than are those for carbon. In order to check the convergency of the calculated properties when enlarging the basis we performed calculations with rather large basis sets. Experiences from these basis saturation tests are used in the accompanying paper on five- and six-membered heterocycles,[11] where we could not afford such large bases.

This paper is organized as follows: In section II we briefly describe the IGLO ansatz, sign conventions, basis sets and geometries used, and the problem of referencing relative chemical shifts. In section III magnetic susceptibility tensors are given, and in sections IV and V nitrogen and carbon chemical shifts are discussed. Our conclusions are summarized in section VI.

## II. Computational Method and Reference Standards

The IGLO method for the ab initio calculation of second-order magnetic properties is essentially of coupled Hartree-Fock (CHF)

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