

Ab Initio Studies on the Silicon Compound: On the Electronic Structure of Disilene Reconsidered

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Received September 30, 1986

Abstract: This paper presents a study of the electronic structure of disilene through unrestricted Hartree-Fock, generalized valence bond perfect pairing, and complete-active-space self-consistent-field methods. We have found that the restricted Hartree-Fock solution of disilene undergoes a triplet instability and that the electronic structure of disilene is a weak singlet diradical. The optimized geometry of disilene is further shown to be a strongly trans-bent C_{2h} structure. Finally, the basis set dependencies on the optimized geometries appearing in the previous works are proven to be artificial.

Considerable attention has recently been paid to the multiple bonding in silicon from both experimental and theoretical viewpoints.¹ In particular, disilene, Si_2H_4 , has attracted interest from the theoretical chemistry arena,²⁻¹² because it is the most fundamental of the silicon-silicon double bonded species and because it shows an unusual preference for a trans-bent C_{2h} structure rather than a planar D_{2h} structure as is apparent in the carbon analogue ethylene.^{2-6,9-11} Furthermore, its carbenoid isomer silylsilylene was found to exhibit "sudden stability" comparable to that of disilene.²⁻⁶

The calculated geometrical structure of disilene, especially the trans-bent angle α formed by the HSiH plane and Si-Si bond, strongly depends on the basis set used.²⁻⁶ The energetics among disilene isomers are significantly affected by the incorporation of the electron correlation corrections.^{3,6} Recently, Krogh-Jespersen reported that the trans-bent angle of disilene is also affected by an inclusion of the electron correlation effect through the Møller-Plesset perturbation calculations terminating at the second order (MP2).^{6a} He also showed that the triplet state is close to the singlet state in disilene.^{6b} This fact suggests that the restricted Hartree-Fock (RHF) solution may undergo a triplet instability¹³ and that a more advanced method is required beyond the RHF level to describe adequately the electronic structure of disilene. Since the convergence of the Møller-Plesset perturbation series is expected to be slow in such a system, an MP2 approach is also not considered to be effective.

Method of Calculation

In the present work, we apply the symmetry-broken unrestricted Hartree-Fock (UHF),¹³ generalized valence bond perfect pairing (GVB),¹⁴ and four electrons in four orbitals complete-active-space self-consistent-field (CASSCF)¹⁵ methods on the electronic structure of di-

Table I. RHF and UHF 6-31G** Total Energies, Orbital Overlap, and Diradical Character of Disilene at RHF Optimized Geometries^a

structure	method	energy (au)	orbital overlap	diradical character
D_{2h}	RHF	-580.082 772	1	0
D_{2h}	UHF	-580.085 709	0.808	2.2
C_{2h}	RHF	-580.082 780	1	0
C_{2h}	UHF	-580.085 929	0.802	2.4

^aOptimized C_{2h} structure is shown in Table II, and optimized D_{2h} structure is as follows: $R_{Si-Si} = 2.126 \text{ \AA}$, $R_{Si-H} = 1.467 \text{ \AA}$, and $\angle HSiH = 116.4^\circ$.

silene. The calculations were performed by GAMESS¹⁶ and GAUSSIAN82¹⁷ programs. The UHF instabilities are checked by the procedure proposed by Seeger and Pople.^{13b} The basis sets used here were the standard split-valence type 3-21G and split-valence plus polarization type 6-31G**.^{18,19}

Results and Discussions

Table I compares the 6-31G** total energies obtained by the RHF and UHF methods at RHF optimized geometries. The orbital overlap between the α -spin part HOMO and the β -spin part HOMO is also shown in Table I. The orbital overlap is, of course, unity when the RHF solution is used. The diradical character is defined by¹³

$$\text{diradical character [\%]} = 100 \left(1 - \frac{2x}{1 + x^2} \right)$$

where x is the orbital overlap. The diradical character as a result of the existence of the UHF instability clearly shows that the disilene species has weak singlet diradical character.^{13c} The RHF solution undergoes a triplet-type instability, and the resultant UHF solution is a spin-density-wave (SDW) type.^{13a} The energy gain from this symmetry breaking is about 1.9 kcal/mol (0.003 au) in both cases, although it is slightly larger in the C_{2h} structure. Accordingly, the energy separation between C_{2h} and D_{2h} structures becomes 0.1 kcal/mol which is considerably larger than the 0.005 kcal/mol in the RHF case.

Any system undergoing an instability should be described by multiconfiguration SCF (MC-SCF) wave functions, at least by the two-configuration SCF wave function.^{13c} Although such a calculation was already performed by Ohta et al.⁷ and Gordon

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Table II. Optimized Structures and Total Energies of Disilene^a

method	basis set	$R(\text{Si}=\text{Si})$	$R(\text{Si}-\text{H})$	$\angle\text{HSiH}$	α^b	total energy
RHF	3-21G	2.149	1.477	114.9	15.7	-577.038 617
RHF	6-31G**	2.128	1.467	115.3	5.8	-580.082 780
UHF	3-21G	2.282	1.486	110.8	40.9	-577.050 689
UHF	6-31G**	2.277	1.478	109.8	43.7	-580.095 216
GVB(2)	3-21G	2.234	1.486	110.7	38.5	-577.067 107
GVB(2)	6-31G**	2.233	1.478	109.7	40.9	-580.110 828
GVB(4)	3-21G	2.248	1.486	110.8	38.0	-577.073 790
GVB(4)	6-31G**	2.248	1.477	109.9	40.4	-580.117 474
CASSCF	3-21G	2.239	1.483	112.3	33.1	-577.081 612
CASSCF	6-31G**	2.236	1.475	111.8	36.3	-580.123 389

^a Bond lengths are in Å and angles in deg. Energies are given in au. ^b Angle formed by HSiH plane and Si—Si bond.

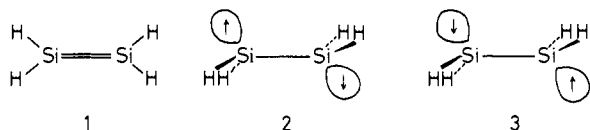
et al.,⁸ they did not refine the RHF optimized geometries.

In Table II, the optimized structures of disilene are shown at RHF, SDW-UHF, GVB, and CASSCF levels. In the GVB calculation, one pair and two pairs are correlated (GVB(2) and GVB(4), respectively, in Table II), and in the CASSCF, the number of configuration state functions is 12 under C_{2h} symmetry. The geometries are fully optimized with the energy gradient method²⁰ with the threshold value for the residual force being 0.0005 hartree/bohr.

The geometries derived from the SDW-UHF, GVB, and CASSCF methods are quite different from those obtained by the RHF method. Among these, the CASSCF result is the most reliable. In the RHF level calculations, the trans-bent angle α shows large basis set dependency, i.e., 15.7° at the 3-21G level and 5.8° at the 6-31G** level, being consistent with previous works.²⁻¹¹ Except for the RHF case, the other three methods give similar α values, 30–40°. The diradical character increases from 2.4% for the RHF/6-31G** structure to 13.0% for the CASSCF/6-31G** structure. The trans-bent angle α increases so as to stabilize the diradical electronic structure. The experimental values of α are 18 and 0° in tetramesityldisilene and *trans*-1,2-di-*tert*-butyldimesityldisilene, respectively.

The silicon-silicon bond lengths are longer than that of the RHF case, reflecting the diradical character of the Si-Si bond, even though it is still shorter than that of the single bond. This fact suggests that some double bond character remains in disilene. The present Si-Si bond length is longer than the X-ray structure, 2.14–2.16 Å, of the substituted disilene in the solid phase.²¹ The H-Si-H bond angle is most important. This angle is very close to the tetrahedral angle of 109.471° independent of the basis set and the theory used. If the angles became completely tetrahedral, the trans-bent angle α should be 54.74°.

Therefore, the electronic structure of disilene involves a contribution not only from the ethylene-like double bonded structure **1** but also from the diradical structures (or dangling bond structure) **2** and **3**. Contour plots of the GVB pair orbitals shown in Figure 1 represent these "diradical orbitals". We note that the sum of the contours from Figure 1, top plus bottom, is identical for the two Si atoms. This is the characteristic feature of the



electronic structure of disilene and is a reason for the high reactivity of disilene compared with ethylene.

The diradical character seems to increase when the silicon atom is replaced by germanium or tin atoms, because in these species the HOMO-LUMO gap is expected to be smaller than that in disilene.¹⁰ Indeed, an X-ray structure of substituted distannene

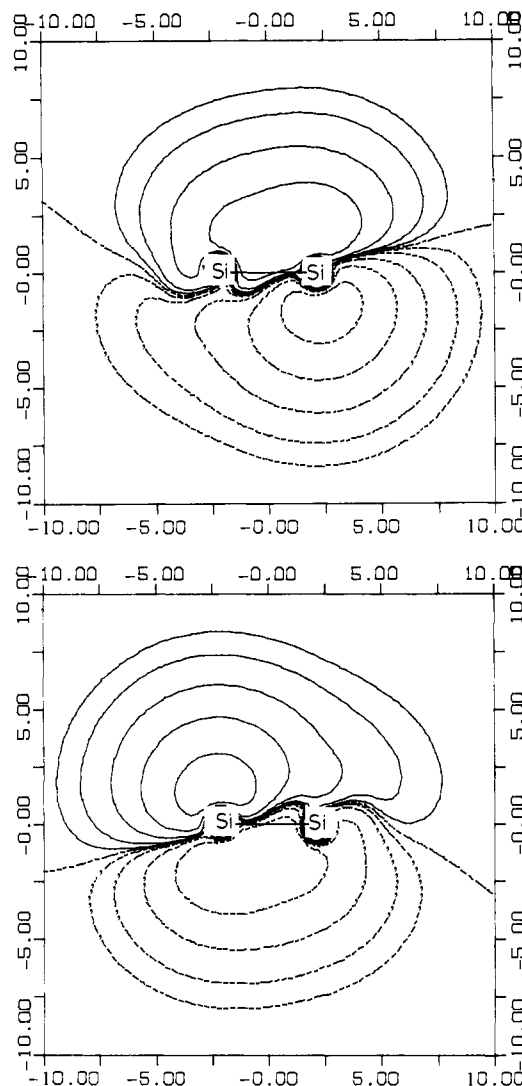


Figure 1. Contour plots of the GVB pair orbitals representing "diradical" orbitals by the GVB(4)/6-31G** calculation at GVB(4)/6-31G** optimized geometry.

has suggested that distannene features no double bond and is dimeric in the solid phase.²²

Conclusions

We have studied the electronic structure of disilene by means of the UHF, GVB, and CASSCF methods and three principal results have been confirmed in the present work.

(1) The RHF solution of disilene undergoes a triplet instability, and disilene is a class of compound having weak singlet diradical character.

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(2) The optimized geometries of disilene with correlated wave functions became strongly trans-bent C_{2h} structures.

(3) The basis set dependencies of the optimized geometries of disilene are proven to be artificial in the RHF treatment in all previous work that did not involve a contribution from the diradical structures.

On the basis of these results, we feel that the full potential surface of the Si_2H_4 system as well as that of the other silicon double bonded systems should also be reconsidered.

Note Added in Proof. After finishing this manuscript, the work by Olbrich appeared.²³ His optimized structure of disilene at CPF level is consistent with the present work.

Acknowledgment. The author thanks Prof. Shigeru Nagase of Yokohama National University and Prof. Shigeki Kato of the University of Tokyo for stimulating discussions and suggestions.

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An ab Initio MO Study of Isomers of HNS_2 and HNO_2

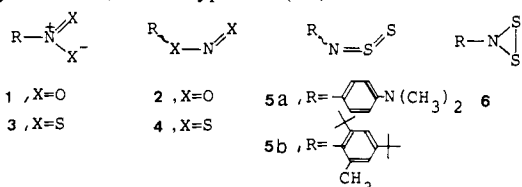
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Abstract: A systematic comparison of the geometry and stability of many possible isomers of HNO_2 and HNS_2 has been carried out. The geometry optimization at the HF/4-31G* level and the energetics at the MP3/6-31G** level show for HNS_2 that, although *N*-thiosulfinylamine, $H-N=S=S$, is the most stable, several other isomers may exist within a reasonable energy range. This suggests a wider variety of chemistry of RNS_2 than is known, in which only *N*-thiosulfinylamines are established. For HNO_2 , only the nitrous acid $H-O-N=O$ and the nitro compound $H-N(=O)_2$ are reasonably considered as thermodynamically stable. This difference of sulfur compounds compared with the oxygen analogues has been attributed to the availability of sulfur d orbitals for facile hypervalency. The preferred stability of *Z* isomers relative to *E* isomers and the barrier for $E \rightarrow Z$ isomerization have been discussed. An assignment of vibrational spectra has been proposed for some isomers.

I. Introduction

Although nitro compounds **1** and nitrites **2** are among the most important classes of nitrogen-containing compounds and have been extensively studied,¹ the corresponding sulfur analogues **3** and **4** have been yet unknown. Some years ago Barton² and some of the present authors³ reported that attempted syntheses of dithionitro compounds **3** resulted in the formation of *N*-thiosulfinylamines **5**, a new type of S(IV) thiocumulene.⁴



In a series of studies on *N*-thiosulfinylamines, we reported the photoreaction of **5b** leading to the formation of sulfur diimide ($R-N=S=N-R$) and proposed the reaction mechanism involving a thionitroso intermediate ($R-N=S$) which is most likely to be formed from dithionitro compound **3** or dithiaziridine **6**, both isomeric to **5**.^{3b} Our recent studies on the detailed mechanism of the photoreaction of **5b** have also revealed the initial photoisomerization of (*Z*)-**5b** to (*E*)-**5b** and thermal reversion of (*E*)-**5b** to (*Z*)-**5b**.⁵

However, the detailed nature of these reactions is far from determined. Indeed, the relative stabilities or geometrical structures of the various possible isomers of the compounds RNS_2 are not known. Especially the fact that *N*-thiosulfinylamine **5** so far is the only stable compound known to exist among possible RNS_2 isomers is of great interest in view of the well-known facts

that both nitro compounds **1** and nitrites **2** are stable chemical species in the case of oxygen analogues.

In order to give an insight to the chemistry of RNS_2 ($R = H$ as a model) in connection with the experimental studies which have been already done and will be done in the future about this new series of compounds, we carried out an ab initio MO study. We tried to explain the structure, vibrational frequencies, hypervalency of the sulfur atoms as well as the isomerization between *Z* and *E* isomers. In order to compare sulfur and oxygen compounds, we also carried out calculations for various isomers of HNO_2 .

II. Computational Details

All calculations were carried out for closed-shell singlets. Geometries were fully optimized at the Hartree-Fock (HF) level with the split valence + polarization 4-31G*⁶ basis set by using the analytical energy gradient method.⁶ The harmonic vibrational frequencies were calculated

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