

ELECTRONIC STRUCTURE OF THE DISILENYL RADICAL ANION*

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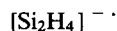
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According to quantum chemical calculations, the anion radical of disilene adopts a *syn*- or *anti*-pyramidal geometry. The former is not a stable entity on the electronic hypersurface and it decreases further in energy by rotation of the Si—Si bond. Energy optimization of various structural alternatives reveals for the anion radical an Si—Si bond slightly longer than a single bond. The *anti* geometry prefers a C_{2h} geometry whereas the *syn* geometry resembles a silylene coupled with a silylene radical anion. The fragmentation of disilene into two silylene units is less exothermic for the neutral species than for the anion (radical), as examined by the *ab initio* calculations.

INTRODUCTION

The formation of radical anions in polysilanes is now well established, owing to the pioneering work of West.¹ In comparison, the reduction of disilene and investigations of its ESR spectroscopic properties have been reported only recently,²

In this work, we investigated the electronic hypersurface of the disilene anion radical, **1**:



1

We considered in detail the evaluation of the rotational barrier in **1** and computation of the electron affinity of disilene. These aspects yield valuable information of the thermodynamic stability of the anion radical formed.

METHODOLOGY

All quantum chemical calculations were performed with the set of Gaussian 92 programs.^{3a} For the closed-shell species the RHF approximation and for the doublets the UHF approximation⁴ was used. The 6–31 + g(d, p) basis set⁵ was employed throughout. Electron correlation corrections were calculated by the MP4SDTQ approximation⁶ (here abbreviated to MP4 approximation), utilizing the frozen core approximation. The reliability of the UHF results was checked by com-

puting the expectation values of $\langle S^2 \rangle$ from the UHF calculations. For all doublets under investigation the values of $\langle S^2 \rangle$ are in the range of 0.75–0.77, which indicates a very low spin contamination (for further discussion on this aspect, see also Ref. 3b).

RESULTS AND DISCUSSION

Qualitative considerations

It is useful to start the discussion from planar disilene. Its frontier orbital system⁷ consists of a π and π^* orbital with corresponding $\sigma(\sigma_+, \sigma_-)$ below (above) them. Within D_{2h} symmetry they refer to $b_{1u}(\pi)$, $b_{2g}(\pi^*)$, $a_g(\sigma, \sigma_+)$ and $b_{3u}(\sigma_-)$ irreducible representations⁷ [Figure 1]. For the discussion of *anti*-pyramidalization, only the σ_+ and σ_- orbitals are of relevance.⁷ Hence the σ orbital is omitted in Figure 1.

Let us consider how π and π^* of planar **1** mix with the σ_+ and σ_- orbitals during the planar to *anti* distortion. In the *anti* structure, the overlap between π and σ_- (both are of b_u symmetry) and that between π^* and σ_+ (both are of a_g symmetry) are non-zero. Consequently, orbital mixing occurs between π and σ_- and between π^* and σ_+ on bending. Owing to this orbital mixing, the π and π^* levels are lowered upon the planar to *anti* distortion (the quantum chemical calculations on disilene are numerous; for a survey, see Ref. 8a, and for later work see Ref. 8b; a general valence

* Dedicated to Professor O. J. Scherer on the occasion of his 60th birthday.

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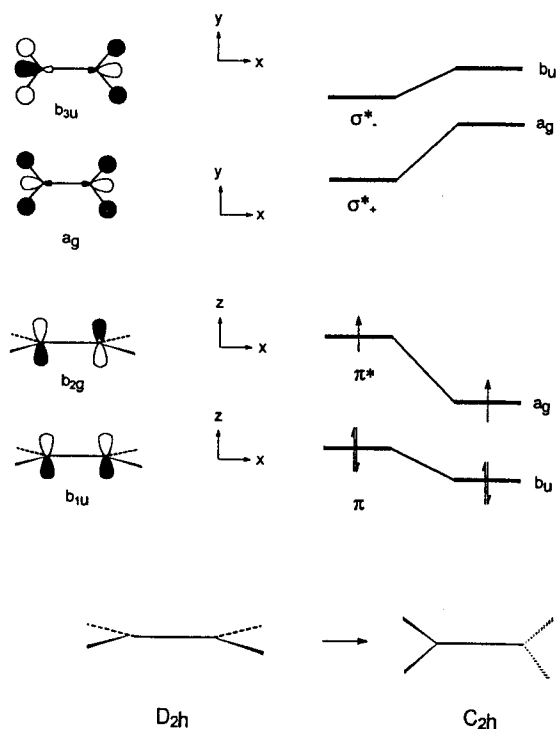


Figure 1. Orbital correlation diagram for *anti*-pyramidalization in disilene

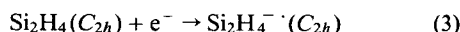
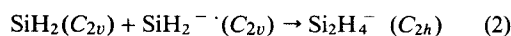
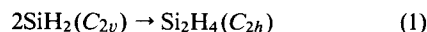
bond analysis of *trans*-bending at double bonds has been given by Trinquier and Malrieu^{8c}). In the case at hand, one can differentiate between two cases: (a) in the (neutral) disilene, Si₂H₄ (*D*_{2h}), the σ and π level is doubly occupied ($|\sigma\bar{\sigma}\pi\bar{\pi}\rangle$), giving rise to a weak second-order Jahn–Teller interaction between the π and σ^* orbitals, by lowering to *C*_{2h} symmetry; (b) additional occupation of the π^* orbital in the anion ($|\sigma\bar{\sigma}\pi\bar{\pi}\pi^*\rangle$) causes an additional distortional force,

by mutual interaction of π^* with σ^* orbitals. Consequently, *anti*-pyramidalization of the silylene units is exerted more strongly in the anion (radical) than in the neutral compound.

Fragmentation processes and electron affinities

The absolute energies [in atomic units (au)] of the investigated species are given in Table 1. Relative energies, which yield valuable information on the various fragmentation processes, are listed in Table 2.

The stability of disilene and its radical anion towards fragmentation into silylene units is estimated by the energy balances for reactions (1)–(4):



The stability of disilene is determined by reaction (1) and that for its corresponding anion by reaction (2). The reaction processes (3) and (4) result in the stabilities for formation of the corresponding anion radicals from the neutral species. In other words, they refer to the electron affinity of the parent disilene [reaction (3)] or the silylene [reaction (4)]. Negative values in Tables 1 and 2 correspond to an exothermic reaction balance. The values at the RHF level parallel those at the electron correlation level (MP4). Additional contributions by zero-point vibrational energies alter the results only to a minor extent.

There is another aspect which should be discussed here. The energy balances, reactions (1)–(4), were determined by a comparison of the results for closed-shell and open-shell species (doublets). The former were calculated by the RHF and the latter by the UHF approximation. The wavefunction resulting from the latter procedure may suffer from spin contamination.^{3b} We examined this aspect by analysis of the expected

Table 1. Absolute energies (au) and lowest energy vibrations (cm⁻¹)

Structure	Symmetry ^a	RHF (UHF) ^b	MP4 ^c	ZPE ^d	ν (cm ⁻¹)
Si ₂ H ₄	<i>D</i> _{2h}	-580.084213	-580.315642	0.033080	-87, <i>a_g</i>
	<i>C</i> _{2h}	-580.084233	-580.316062	0.033254	99, <i>a_g</i>
Si ₂ H ₄ ⁻	<i>D</i> _{2h}	-580.066371	-580.301787	0.029242	-927, <i>b_{3u}</i>
	<i>C</i> _{2h}	-580.113209	-580.344438	0.030431	214, <i>a_u</i>
SiH ₂	<i>C</i> _{2v}	-290.003734	-290.109156	0.012543	1121, <i>a₁</i>
SiH ₂ ⁻	<i>C</i> _{2v}	-290.023700	-290.134637	0.011442	1059, <i>a₁</i>

^a Orientation of structures according to the standard orientation conventions.³

^b RHF/6-31 + g(d, p) for closed shell and UHF/6-31 + g(d, p) for doublet species.

^c MP4SDTQ/6-31 + g(d, p)//RHF(UHF)/6-31 + g(d, p).

^d Zero point vibrational energy contribution.

Table 2. Reaction energies (kcal mol⁻¹)

Reaction	RHF (UHF) ^a	MP4 ^b	ZPE/MP4 ^c
(1)	-48.2	-61.4	-56.3
(2)	-53.9	-63.3	-59.2
(3)	-18.2	-17.8	-19.6
(4)	-12.5	-16.0	-16.7

^a RHF (UHF)/6-31 + g(d, p).^b MP4SDTQ/6-31 + g(d, p)//RHF(UHF)/6-31 + g(d, p).^c Level (b) plus zero point vibrational energy contribution.

values of $\langle S^2 \rangle$ resulting from the UHF calculations. In all cases the values of $\langle S^2 \rangle$ are in the range 0.75–0.77. On this basis,^{3b} spin contamination in the doublet species is nearly zero.

Interestingly, the dimerization reaction (2) is slightly more exothermic than reaction (1). At first glance it seems surprising that the anion of disilene is more stable towards dissociation of the Si—Si bond than the neutral disilene. A rationale for this effect is given later. Reactions (3) and (4) are sizably exothermic, at all levels of sophistication. They reveal a strong electron affinity of the species SiH₂ and Si₂H₄. Our results on the electron affinities of disilene are in accord with recent theoretical investigations.⁹

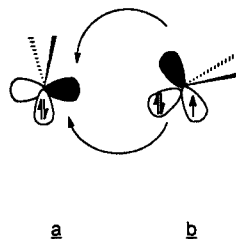
Rotational barrier

Of particular interest is the rotational barrier in **1**. From an experimental viewpoint,² detailed information on this aspect is not possible. We examined it by detailed quantum chemical investigations. Relative energies for the various rotational conformers are given in Table 3. A corresponding list of the structural parameters resulting from energy optimization is presented in Table 4.

The conformer of **1** lowest in energy is the anti-pyramidalized structure. In other words, **1** strongly prefers a *C*_{2h} geometry. The preference for deviation from planarity is fairly large. At the best computational level (ZPE/MP4) it results in -26.1 kcal mol⁻¹ (1 kcal = 4.184 kJ) in favour of the anti-pyramidal conformation. For comparison, the corresponding energy difference for the parent disilene is only -0.12 kcal mol⁻¹. Here the operation of only a small anti-pyramidalization force has been established by MCSCF calculations.¹⁰

The Si—Si distance in the anion radical (*C*_{2h}, Si—Si = 2.365 Å) is longer than in the parent disilene (*C*_{2h}, Si—Si = 2.131 Å). The strong pyramidalization force is also witnessed in the strongly diminished tilting angle α . Rotation of one silylene unit (determined by the angle θ) from the anti ($\theta = 180^\circ$) to the syn ($\theta = 0^\circ$) conformer causes a stretching of the Si—Si bond. However, most noticeable is the fact that α_1 and α_2 adopt sizably different values. It is most strongly pronounced in the syn conformation ($\alpha_1 = 97.6^\circ$, $\alpha_2 = 144.6^\circ$). Here the Si—Si bond is also longer than a corresponding single bond (2.36 Å, estimated from covalent bond radii¹¹).

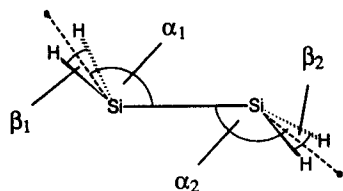
On this basis, one may describe this conformer as a donor-acceptor (a-b) complex of a silylene, **a**, with a

Table 3. Rotational barrier in **1** (kcal mol⁻¹)

θ (°)	Symmetry	UHF ^a	MP4 ^b	ZPE/MP4 ^c	ν (cm ⁻¹)
0	<i>C</i> _{2v}	13.0	12.6	12.1	-1013, <i>b</i> ₂
0	<i>C</i> ₁	6.0	8.5	8.3	-206
30	<i>C</i> ₁	5.3	7.9	7.6	-88
60	<i>C</i> ₁	4.3	6.9	7.0	157
82.8	<i>C</i> ₁	4.1	6.7	6.7	109
90	<i>C</i> ₁	4.1	6.7	6.6	43.4
120	<i>C</i> ₁	3.6	5.3	5.2	-209
150	<i>C</i> ₁	1.1	1.0	0.9	144
180	<i>C</i> _{2h}	0.0	0.0	0.0	214, <i>a</i> _u

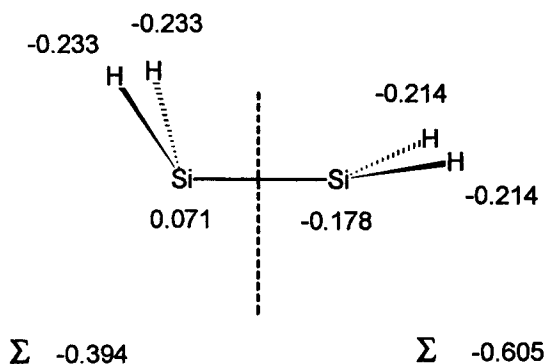
^a UHF/6-31 + g(d, p). Values of $\langle S^2 \rangle$ are in the range 0.75–0.77.^b MP4SDTQ/6-31 + g(d, p)//UHF/6-31 + g(d, p).^c Level (b) plus zero point vibrational energy contribution.

Table 4. Relevant geometric parameters (bond lengths in Å, bond angles in degrees) of the disilene anion radical

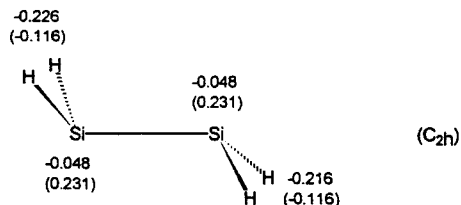


θ ($^\circ$)	Si—Si	α_1	α_2	β_1	β_2
0	2.417	97.6	144.6	97.0	103.4
30	2.411	97.4	144.6	96.9	103.2
60	2.403	98.1	144.7	96.7	102.9
82.8	2.406	99.1	144.9	96.5	102.5
90	2.407	99.3	144.7	96.4	102.4
120	2.405	100.8	135.6	96.8	101.4
150	2.370	115.9	116.4	99.8	99.9
180 (C_{2h})	2.365	116.5	116.5	100.1	100.1
Si_2H_4 (C_{2h})	2.131	170.	170.	115.1	115.1

silylene anion, **b**, as shown. This view is in accord with an analysis of the Mulliken population, indicated as follows.



The strongly flattened silylene unit possesses more negative charge than the strongly pyramidalized silylene unit. In contrast, in the *anti* conformation the charge is equally distributed over all equivalent atoms. In the structure shown, the values in parentheses are corre-



sponding values for (neutral) disilene. A comparison of both sets of values indicates distribution of negative charge over both the silicon and the hydrogen atoms. All hydrogen (silicon atoms) are equivalent within C_{2h} symmetry. Hence they bear equal charges.

On this basis, it is plausible that the *syn* conformation (C_1) is [at the best computational level (ZPE/MP4)] $8.3 \text{ kcal mol}^{-1}$ less stable than the C_{2h} symmetrical *anti* conformer ($\theta = 180^\circ$). The C_{2v} symmetrical *syn* conformer is even $12.1 \text{ kcal mol}^{-1}$ higher in energy. Another stable rotational isomer appears for $\theta = 82.8^\circ$. According to the vibrational analysis it refers to an energy minimum on the electronic hypersurface and is $6.7 \text{ kcal mol}^{-1}$ less stable than the *anti* conformer. The geometric parameters (Table 4) reveal a geometry intermediate between $\theta = 0^\circ$ and $\theta = 180^\circ$.

The charge distribution analysis also makes it apparent why the formation of the anion from two silylene units [reaction (2)] is slightly more exothermic than reaction (1). The negative charge can be equally distributed over the hydrogens. Concomitantly, the Si—H bonds are elongated in **1** (C_{2h} symmetry, Si—H = 1.513 \AA) as compared with the parent C_{2h} symmetrical Si_2H_4 (Si—H = 1.467 \AA).

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