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Stability and Reactivity of the Si–C Double Bond

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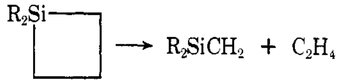
Abstract: Properties of the Si=C group are investigated by means of quantum mechanical ab initio computations of the lowest singlet and triplet states of $SiCH_4$ and the cycloaddition of $SiCH_4$ to 1,3-disilacyclobutane, $Si_2C_2H_8$. Extended basis sets are employed and effects of electron correlation are included. The pertinent results are (1) $SiCH_4$ has a planar π-bonded singlet ground state about 28 kcal/mol below the lowest triplet which has perpendicular structure; (2) the bond strength of the Si–C $2p\pi$–$3p\pi$ bond as determined by the rotational barrier is ~46 kcal/mol; (3) the barrier for the cycloaddition is less than 14 kcal/mol and the reaction energy ~−76 kcal/mol, indicating great reactivity of the Si=C group which results from the considerable bond polarity.

I. Introduction

One of the most striking features of silicon chemistry is the complete absence of compounds with multiple bonds of $p\pi$–$p\pi$ type that are stable under the usual conditions. However, the existence of short-lived intermediates of the form $R_2SiCR'_2$ has been concluded, e.g., from the pyrolysis of silaolefins;[1-5] an almost up-to-date review of this and related problems has been given by Gusel'nikov et al.[1] A typical case is the thermal decomposition of monosilacyclobutanes which yields 1,3-disilacyclobutanes and ethane, where kinetic data support the following mechanism.[6,7]


(1)


(2)

Whereas the mechanism (1, 2) seems to be generally accepted, there has been much discussion and speculation concerning the electronic structure of the intermediate R_2SiCH_2. The problem here is the relative stability of the π-bonded closed shell (singlet) structure with polarized Si–C bonds

$$R_2Si^{\delta+}{=}C^{\delta-}H_2 \qquad (3)$$

vs. the open-shell triplet 1,2-diradical state

$$R_2\dot{S}i{-}\dot{C}H_2 \qquad (4)$$

From experiments one has, in our opinion, so far not been able to establish beyond doubt which of the two structures (3) or (4) is the more stable one, although preference is usually given to (3).[1-5]

It was the aim of the work described in this paper to investigate the stability of the Si–C double bond by means of quantum mechanical ab initio calculations. For this purpose we first performed elaborate computations for the molecule $SiCH_4$, which is, at least from the computational point of view, the simplest conceivable compound of this class. Generation and trapping of $SiCH_4$, which turned out to be a very reactive intermediate, has been reported by Golino[5b] et al. With these computations we first of all want to decide whether (3) or (4) is more stable—it turns out that (3) is ~28 kcal/mol lower in energy than (4)—and furthermore determine properties of $SiCH_4$ like bond polarity, π-bond strength, etc., which provide hints on the chemical behavior of this molecule.

We finally investigated the reaction

$$2SiCH_4 \rightarrow Si_2C_2H_8 \text{ (1,3-disilacyclobutane)} \qquad (5)$$

which is a model case for (2), to determine the corresponding barrier ΔE_B and reaction energy ΔE. These results then provide detailed answers to the question of the stability and reactivity of the Si–C double bond in $SiCH_4$ and also for related compounds.

After completion of the present study Strausz, Gammie, Theodorakoupoulos, Mezey, and Czismadia[8] (SGTMC) have published an ab initio investigation of the lower electronic manifold of $SiCH_4$. Our results are partly in considerable disagreement with those of SGTMC, who predict the triplet to be 1.4 kcal/mol lower in energy than the singlet. This as well as other deviations from the present results can be attributed to the rather small basis set and the methods used by SGTMC, who have neglected effects of electron correlation.

II. Method of Computation

Most results reported in the present paper (e.g., geometrical parameters for the various states of $SiCH_4$, barrier and reaction energy for reaction 5) were obtained by means of closed and open shell RHF computations, which certainly are sufficiently accurate for this purpose. However, the correlation energy—by definition neglected on the HF level—has in general a pronounced influence on the energy difference between closed shell singlet and open shell triplet states.[9] The correlation energy of the π-bonded ground state of C_2H_4 exceeds the corresponding one for the lowest triplet (vertical excitation) by ~20 kcal/mol[9] and similar relationships have to be expected for $SiCH_4$. The rather pronounced influence of electron correlation stems in part from the fact that for the ground state one has a considerable admixture of the low-lying doubly substituted configuration $\Psi(\pi^2 \rightarrow \pi^{*2})$ where the bonding π MO is replaced by the antibonding π^* MO, whereas a corresponding configuration is clearly missing for the π,π^* triplet state.

We therefore perform a 2 × 2 CI for the closed shell singlet

$$^{S}\psi_{CI} = C_1\psi_{SCF} + C_2\psi(\pi^2 \rightarrow \pi^{*2}) \qquad (6)$$

$$^{S}E_{CI} = \langle {}^{S}\psi_{CI}|H|{}^{S}\psi_{CI}\rangle \qquad (7)$$

and compute the singlet-triplet separation $\Delta E_{S\rightarrow T}$ according to

$$\Delta E_{S\rightarrow T} = {}^{T}E_{SCF} - {}^{S}E_{CI} \qquad (8)$$

The π^* MO is determined by a previously described method[10] which is virtually identical with an MC-SCF procedure for the trial function $^{S}\psi_{CI}$ specified in eq 6.

A situation similar to the one just described is encountered in the computation of the rotational barrier ΔE_r about a double bond. ΔE_c provides a rather direct measure for the strength of the corresponding π-bond ΔE_π

$$\Delta E_\pi \sim \Delta E_r \qquad (9)$$

since the latter is broken in the perpendicular case (twist angle $\theta = 90°$) whereas the σ bond remains essentially unchanged. It is well known that the SCF approximation fails completely to give a proper description of $E(\Theta)$, energy as function of the twist angle.[9] This problem and the corresponding literature have recently been reviewed by Staemmler.[11] The failure of the SCF model results from two facts. First of all the wave function changes smoothly from a normal closed shell state for the π-bonded case to an open shell configuration for the twisted molecule, where one has two singly occupied AOs (coupled to a singlet) which are mutually orthogonal. Treating the latter case as a closed shell system is clearly unreasonable which explains the errors (~60 kcal/mol corresponding to 100% error for C_2H_4) obtained in such a procedure. The second difficulty is due to effects of electron correlation. For the computation of ΔE_r we have to consider only the planar and the perpendicular cases which may be treated within the RHF approximation as closed and open shell states. In complete analogy to $\Delta E_{S\rightarrow T}$ we now expect again a nonnegligible influence of a correlation effects. In analogy to eq 8 we compute ΔE_r according to

$$\Delta E_r = {}^{S}E_{RHF}(\theta = 90°) - {}^{S}E_{CI}(\theta = 0°) \qquad (10)$$

This approach—which is virtually equivalent to the "double configuration SCF" procedure of Wood[12]—has been proposed and tested by Staemmler[11] who showed that it yields ΔE_r with an error of a few kcal/mol.

In using (8) and (10) for the computation of $\Delta E_{S\rightarrow T}$ and ΔE_r we have accounted for a fraction of correlation effects only. However, previous work[11,12] as well as the discussion of results for C_2H_4, see Table II, indicates that this procedure gives more reliable results than the SCF method, and that deviations from experiments are probably a few kcal/mol only.

All calculations were carried out in using contracted Gaussian type functions, mainly taken from Huzinaga's tables.[13] Orbital exponents η for the additional polarization functions were the same as optimized previously for related molecules.[14,15] The following three basis sets were used.

Basis I
  Si: (11s, 7p, 1d/7s, 4p, 1d), η (d) = 0.4
  C: (9s, 5p, 1d/5s, 3p, 1d), η(d) = 0.7
  H: (4s, 1p/2s, 1p)
    η(p) = 0.433 for Si-bonded H
    η(p) = 0.75 for C-bonded H
Basis II
  Si: (10s, 6p/6s, 4p)
  C: (8s, 4p/4s, 2p)
  H: (4s/2s)
Basis III

This is identical with basis II, except for the contraction of Si AOs

Si: (10s, 6p/6s, 3p)

Most of the computations for $SiCH_4$ were performed with basis II and then checked with the larger basis I. The smallest basis (III) was employed in the study of reaction 5 only. We note that this basis (III) is still of "double ζ quality" since we have two adjustable linear parameters for each valence shell AO.

III. Results and Discussion

A. Results for C_2H_4. In order to get an idea of the reliability of our approach we discuss briefly for C_2H_4 the CI results for ΔE_r, the vertical and adiabatic $\Delta E_{S\rightarrow T}$ (obtained according to eq 8 and 10) in connection with experimental facts.

The results obtained with the extended basis I for the vertical $\Delta E_{S\rightarrow T}$ of 99.3 kcal/mol, see Table II, differs by 2.3 kcal/mol from the experimental value of 97.1 kcal/mol. For ΔE_r an experimental value of 65 kcal/mol seems to be generally accepted.[16] Owing to effects of zero-point vibrations this amounts to a difference of 66–67 kcal/mol in electronic energies (the "perpendicular" N ($^1B_1$) state corresponds to a maximum of the potential as a function of the twist angle θ). The present result (64.2 kcal/mol) differs by 2–3 kcal/mol from the just mentioned value.

Experimental evidence for the adiabatic $\Delta E_{S\rightarrow T}$ is quite uncertain. Merer and Mulliken[16] very cautiously state "... spectroscopic evidence suggests that the (0,0) band ... may lie near 20.000 cm^{-1} (~57 kcal/mol)". This would mean that the electronic energy of the triplet (^3A_2T) is ~10 kcal/mol below the singlet (^1B_1N) arising from the same electronic configuration. However, Buenker and Peyerimhoff[9] note "... it seems clear that the $^1B_1$–$^3A_2$ splitting is quite small, probably not greater than 0.10 eV" (2.3 kcal/mol). The ordering of these states is not known experimentally. Extended CI calculations consistently[9] predict $^1B_1$ to be lower than $^3A_2$, which would mean that the adiabatic $\Delta E_{S\rightarrow T}$ is in any case larger than ΔE_r (~65 kcal/mol). The present result, $E_{S\rightarrow T}$ = 62.8 kcal/mol (adiabatic), appears to be quite reasonable and differs by 1.2 kcal/mol only from the most extended CI result, 64 kcal/mol.[9]

To sum up: if comparison with experiments (ΔE_r, vertical $\Delta E_{S\rightarrow T}$) or large scale computations (adiabatic $\Delta E_{S\rightarrow T}$) is possible, the limited CI results, obtained from eq 8 and 10 for the corresponding ΔE, are in error by ~3 kcal/mol for C_2H_4. This agreement could be fortuitous and the situation may be different for $SiCH_4$. However, in any case we expect our CI results to be closer to experiment than those of the SCF treatment.

B. Properties of $SiCH_4$. We first determined the geometrical parameters and energies for the lowest lying singlet state (planar, $\theta = 0°$), the triplet state (perpendicular, $\theta = 90°$), and transition state for the rotation about the Si–C axis. The results are collected in Table I. The geometry of planar $SiCH_4$ was computed with basis II. A reoptimization of the Si–C distance with the larger basis I affected this parameter by 0.015 Å only. For the twisted geometry we only varied the Si–C distance and the "flap angles" ϕ_{Si} (and ϕ_C) between the $H_2Si(H_2C)$ plane and the Si–C axis (with basis I). All other parameters were kept as for the planar geometry. A reoptimization of ∠HSiH for the triplet had a negligible effect on the energy (0.5 kcal/mol).

Table I. Computed Energies^a and Structure Parameters for $SiCH_4$

		Planar^{b,c} Singlet	Planar^{b,c} Triplet	Perpendicular^b Singlet^d	Perpendicular^b Triplet^e
Basis I^f	E_{SCF}	−329.0439	−328.9699	−328.9948	−329.0226
	$E_{CI}{}^g$	−329.0671			
Basic II^f	E_{SCF}	−328.8743	−328.8062	−328.8279	−328.8546
	$E_{CI}{}^g$	−328.9017			
Si-C, Å		1.69		1.85	1.85
θ^h		0°		90°	90°
$\phi_{Si}{}^i$		0°		35°	45°
$\phi_C{}^i$		0°		0°	0°

[a] au. [b] Remaining structure constants (optimized for the planar singlet): SiH = 1.48 Å, CH = 1.08 Å, ∠HSiH = 115°, ∠HCH = 112°. [c] Optimized geometry for the singlet. [d] Transition state for rotation around SiC axis. [e] Lowest triplet state. [f] See text. [g] See eq 6 and 7. [h] Twist angle. [i] "Flap angle" of SiH_2 and CH_2 group with SiC axis.

Table II. Comparison of Properties of C_2H_4 and $SiCH_4$^{a}

			Rot. barrier ΔE_r	Vert $\Delta E_{S\to T}$	Adiabatic $\Delta E_{S\to T}$, kcal/mol
$C_2H_4{}^d$	SCF^b	Basis I	48.2	83.3	46.8
		Basis II	45.7	84.5	44.5
	CI^c	Basis I	64.2	99.3	62.8
		Basis II	63.6	102.4	62.5
		B.P.^{e}	62	100	64
		Exp	65^f	97.1^g	
$SiCH_4$	SCF^b	Basis I	30.8	46.4	13.4
		Basis II	29.1	42.7	12.4
	CI^c	Basis I	45.4	61.0	27.9
		Basis II	46.3	59.9	29.6
	SGTMC^h		81.9		−1.4
	Dewar et al.^{i}		42.3		

[a] See footnotes of Table I and text. [b] ΔE as obtained on RHF level. [c] ΔE as defined in eq 8, 10. [d] Results taken in part from ref 11. [e] Reference 9. [f] Reference 23. [g] Reference 24. [h] Reference 8. [i] Reference 18.

The results collected in Tables I and II first of all show that the planar π-bonded structure is the ground state of $SiCH_4$, which is 27.9 kcal/mol below the triplet; compare $\Delta E_{S\to T}$ for the (large) basis I in Table II. The result of SGTMC,[8] who obtain the triplet to be 1.4 kcal/mol lower than the singlet, results from basis set deficiencies—which will be discussed below in context with the charge distribution—and from the neglect of correlation effects which contribute ~15 kcal/mol to $\Delta E_{S\to T}$.

We note that the results obtained from basis sets I and II, which differ essentially in the polarization functions included in I, are in surprisingly close agreement with each other both for C_2H_4 and $SiCH_4$. This shows that dAOs on Si are not of particular importance and play about the same role as for C, at least as far as properties as ΔE_r and $\Delta E_{S\to T}$ are concerned.

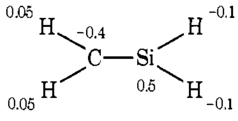
The computed geometrical parameters given in Table I do not show unexpected features. The Si-C distance for the perpendicular geometry (1.85 Å) is virtually identical with the one in $SiCH_6$ (1.857 Å[17]), as it should be since one has a single bond in these cases. The SiH_2 flap angle for the singlet (Φ_{Si} = 35°) and the triplet (Φ_{Si} = 45°) state of perpendicular $SiCH_4$ express the well-known tendency of second-row atoms for increased p character in valence AOs as compared to the first row.

The SiC distance for the planar π-bonded $SiCH_4$ (1.69 Å) is 0.16 Å shorter than for the single bond; the corresponding shortening from C–C to C═C is roughly 0.14 Å. This clearly indicates a certain strength of the SiC $p\pi$–$p\pi$ bond. Accepting ΔE_r as a measure for the bond strength of the π bond we get, compare eq 9 and 10,

$$\Delta E_\pi(\mathrm{SiC}) \sim 46 \text{ kcal/mol} \qquad (11)$$

This is not too different from the MINDO/3 result of Dewar et al.[18] of 42.3 kcal/mol, but in disagreement with the value of SGTMC,[8] who obtained 82 kcal/mol. This discrepancy is mainly due to the fact that SGTMC treated twisted $SiCH_4$ as a closed shell case and further neglected effects of electron correlation.

We have then investigated the charge distribution of the ground state of $SiCH_4$. This was done by application of a recently described population analysis[19] which is based on the occupation numbers of MAOs (modified AOs). This method has the advantage of giving virtually basis set independent results.[19] The following charge distribution was obtained from basis I for the molecular geometry given in the first column of Table I.



These numbers show the expected polarity of the Si-C group which results from the different electronegativities of C and Si.

Let us discuss some consequences of this polarity on the $p\pi$–$p\pi$ bond in $SiCH_4$. For this purpose we decompose the bonding π MO $\Psi\pi$ according to

$$|\Psi\pi\rangle = a_1|2p\pi_C\rangle + a_2|3p\pi_{Si}\rangle$$

where $|2p\pi_C\rangle$ and $|3p\pi_{Si}\rangle$ denote the (normalized) partial sums of AO contributions located on C and Si to $|\Psi\pi\rangle$. The accumulation of electronic charge at the carbon end leads to an increased screening of nuclear charge and, hence, to an extension of $|2p\pi_C\rangle$ as compared to the isolated atom 2p AO. The reverse effect takes place for the corresponding silicon AO, of course. This leads to an adjustment of the size of AOs actually forming the π bond which increases overlap and bond strength, and relieves the "mismatching" of corresponding π AOs on C and Si which has been thought to be the main reason for the weakness of SiC $p\pi$–$p\pi$ bond.[20,21] Quantitatively we find an increase of the overlap from $S = 0.18$ for unperturbed AOs[20] to $S = \langle 2p\pi_C|3p\pi_{Si}\rangle = 0.33$ for basis II (without d AOs) and $S = 0.38$ for basis I.

Quite similar conclusions can be drawn from the contour diagram of the π MO in $SiCH_4$, Figure 1, and the corresponding difference density plot of $\Delta\rho$ given in Figure 2. Figure 1 shows in fact the almost perfect size adjustment of the $p\pi$ AOs on C and Si. At first glance this diagram looks almost like that of a covalent bond. However, the difference density, Figure 2, shows a reduction of π-electron density, $\Delta\rho < 0$, on the silicon end, and an accumulation of charge on the carbon end and, of course, in the bond region. The $\Delta\rho$ plot also indicates the extension of the carbon $2p\pi$ AO, since $\Delta\rho < 0$ near the nucleus but $\Delta\rho > 0$ at larger distances from the carbon atom.

The accumulation of charge at C raises also the orbital energy and explains the rather small (in absolute value) SCF orbital energy of $SiCH_4$, $\epsilon_\pi = -0.316$ au, as compared to $\epsilon_\pi = -0.379$ au for C_2H_4.

The STO-4G basis set used by SGTMC[8] contains no flexibility that would allow size adjustment of AOs taking place on bond formation. Since these effects are more important for the π-bonded structure than for the perpendicular singlet or triplet state (where the singly occupied MOs are located on Si and C), minimum basis sets underestimate the stability of planar SiH_4 (singlet) as compared to the twisted singlet or triplet states.

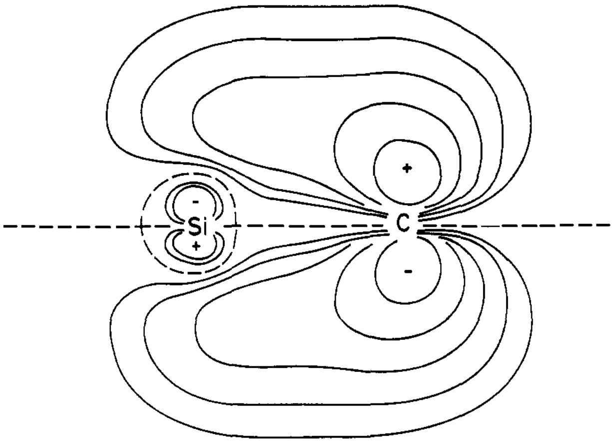


Figure 1. Contour lines of ψ, the bonding π MO in $SiCH_4$. Lines plotted correspond to the following values: $\psi = 0.0$ (broken), ± 0.05, ± 0.07, ± 0.1, ± 0.14, ± 0.2 (in au).

This explains the discrepancy between the adiabatic $\Delta E_{S\rightarrow T}$ obtained on the SCF level by SGTMC (-1.4 kcal/mol) and by the present authors (13.4 kcal/mol, basis I).

C. Cycloaddition of Silaethene $SiCH_4$ to 1,3-Disilacyclobutane. In order to obtain direct information on the reactivity of the Si-C double bond we have finally investigated reaction 5 which can always take place if $SiCH_4$ is formed. The computations were performed mainly with basis III, which yields the SCF energy for $SiCH_4$ that is merely 4 kcal/mol higher than for basis II; compare Table I.

$$E_{SCF} = -328.8682 \text{ au} \qquad (12)$$

In order to determine the reaction energy ΔE we first had to estimate the geometrical parameters of the unknown molecule $Si_2C_2H_8$. Following the electron diffraction results of Vilkov[22] for SiC_3H_8 and $Si_2Cl_4C_2H_4$ we assumed (all distances in Å): CH = 1.13, SiH = 1.48, SiC = 1.89, $\angle$HCH = 110°, $\angle$HSiH = 109°, $\angle$SiCSi = 95.5°, $\angle$CSiC = 84.5°. In order to reduce computation time we further assumed D_{2h} molecular symmetry and, hence, a coplanar arrangement of the "heavy atoms", although $Si_2C_2H_8$ is expected to have a nonplanar SiC frame. We than obtained

$$Si_2C_2H_8\text{: } E_{SCF} = -657.8502 \text{ au} \qquad (13)$$

which together with (12) gives a reaction energy $\Delta E = -71$ kcal/mol for reaction 5.

Since d AOs should be of importance for the description of electron densities if bond angles deviate considerably from tetrahedral angles (especially for C), we next performed computations in which a d set on Si (η(d) = 0.4) and on C (η(d) = 0.7) were included for reactants and products. We then obtained, as expected, a slightly larger reaction energy for the cycloaddition.

$$\Delta E = -76 \text{ kcal/mol} \qquad (14)$$

The correct ΔE should be rather larger in absolute value than indicated in (14), since we have used the optimized geometry for reactants but only an estimated one for the product. Our results prove in any case the strong exothermicity of reaction 5 and we considered that it was not worthwhile to perform further computations—e.g., optimization of geometrical parameters of $Si_2C_2H_8$—to refine our result for ΔE.

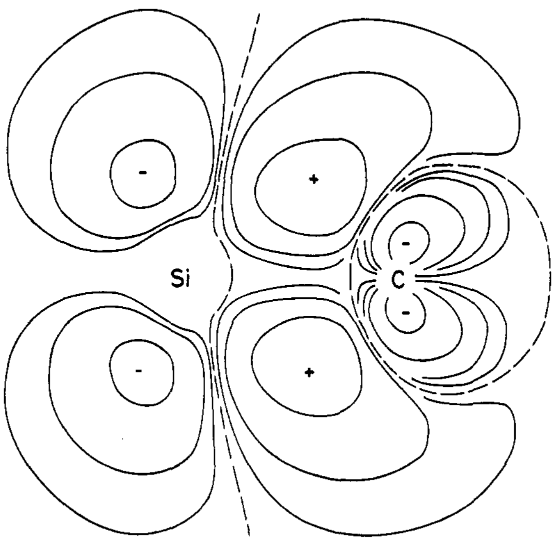


Figure 2. Contour lines of the difference density $\Delta\rho = 2|\psi|^2 - |\psi_a|^2 - |\psi_b|^2$, where ψ denotes the bonding MO in $SiCH_4$, and ψ_a, ψ_b the valence π AO of C and Si. Lines plotted correspond to $\Delta\rho = 0.0$ (broken), ± 0.001, ± 0.003, ± 0.01, ± 0.03 (in au).

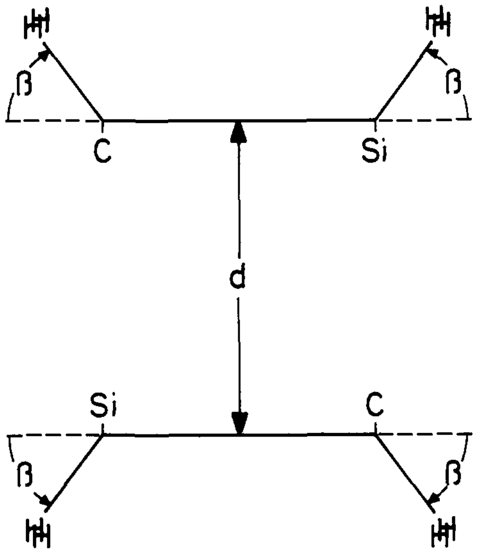


Figure 3. Geometry and parameters considered for the cycloaddition of $SiCH_4$ to $Si_2C_2H_8$.

We finally performed a series of computations to determine the reaction path and the barrier ΔE_B for (5). Since a thorough investigation of the total hypersurface is prohibitive by the enormous requirements of computation time, we considered the head-to-tail arrangement only and further imposed the following restrictions (see also Figure 3): (1) molecular symmetry C_{2h} along the entire reaction path; (2) $\angle$SiCSi = $\angle$CSiC = 90°; (3) the internal structure parameters of the reacting silaethene molecules, including the angle β, were varied in a concerted way. We have introduced a deformation parameter x, $0 \leq x \leq 1$, such that $x = 0$ corresponds to free $SiCH_4$ as given in Table I, and $x = 1$ to the assumed geometry of the product described above. Linear interpolation was performed for $0 < x < 1$.

Within these restrictions we then performed a series of computations for various x and d, defined in Figure 3, from which the reaction path (and corresponding energies) collected in Table III was extracted.

The features of the energy along the reaction coordinate may be rationalized at least qualitatively in the following way. As the undistorted $SiCH_4$ molecules approach we first find a shallow minimum at $d \sim 5$ Å, which results from attractive dipole-dipole forces. The increasing overlap of charge clouds then causes an increase in energy due to exclusion principle effects. The transition state occurs at $d \sim 2.9$ Å, $x \sim 0.25$ (corresponding to a flap angle $\beta \sim 11°$), where the π-electron clouds are shifted to form the new Si-C bonds. The transition

Table III. Reaction Path and Energies for Reaction 25

d, Å[a]	x[a]	ΔE, kcal/mol[b]
∞	0	0.0
5.3	0	−0.3
3.7	0	+1.8
3.2	0	+8.3
2.9	0	+11.2
2.9	0.25	+13.9
2.6	0.5	+1.0
2.3	0.5	−31.9

[a] See Figure 3 and text. [b] Energies relative to separated reactants, $E(\infty) = -657.73\,64$ au; see eq 12.

state occurs quite early in the reaction, which is also not unexpected. The energy then decreases rapidly as d decreases and the new Si–C bonds are formed.

The computed barrier for reaction 5 is

$$\Delta E_B \sim 14 \text{ kcal/mol} \qquad (15)$$

The correct barrier is certainly smaller since a relaxation of the constraints imposed, especially the symmetry C_{2h} with coplanar arrangements of silicon and carbon atoms, can only lead to a path with a smaller barrier. We further note that we have not accounted for correlation effects in studying reaction 5. Especially the attractive dispersion forces should cause a slight decrease of ΔE_B. Since the computed barrier of ~14 kcal/mol is relatively small anyway we decided not to perform additional computations, however.

IV. Summary

The main conclusions emerging from the investigations reported in the present study can be summarized in the following way.

(1) A surprisingly strong Si–C pπ–pπ bond is formed in silaethene $SiCH_4$. The π-bond strength $\Delta E_\pi \sim 46$ kcal/mol amounts to roughly 70% of the corresponding value in C_2H_4, if the rotational barrier ΔE_π is accepted as a measure of ΔE_π.

(2) The 1,2-diradical triplet of $SiCH_4$ is computed to be ~28 kcal/mol higher in energy than the π-bonded ground state.

(3) The polarity of the Si=C group and the rather low-lying π^* MO (as measured by the rather small vertical $\Delta E_{S\rightarrow T}$ of 61 kcal/mol which is only ~60% of the corresponding value in C_2H_4) indicate a considerable reactivity of Si=C, despite the relative strength of the π bond.

(4) This conclusion is confirmed by the small barrier (less than 14 kcal/mol) found for the cycloaddition of $SiCH_4$ to $Si_2C_2H_8$, and also the large reaction energy of 76 kcal/mol. We note that the corresponding cycloaddition of C_2H_4 to cyclobutane along the reaction path considered above is Woodward–Hoffmann forbidden. The considerable polarity of the Si=C group relieves the symmetry restriction and the reaction is no longer forbidden.

These conclusions are in part similar to the qualitative results obtained in previous semiempirical investigations.[20,21]

One may finally speculate under which conditions an $R_2Si{=}CR_2$ could be stable. Terminal groups like R = CH_3 or $C(CH_3)_3$ would certainly help to some extent, but since the four-membered ring in 1,3-disilacyclobutane can quite easily accommodate large substituents, this effect should be not too pronounced. Flowers and Gusel'nikov[7] have in fact estimated the activation energy for the cycloaddition of $Me_2Si{=}CH_2$ to be about 11 kcal/mol, which fits within the results of the present study.

The main reason for the reactivity of the Si=C group seems to be the great polarity of the bonds. An attempt to change this polarity by appropriate substituents would invariably weaken the π bond (mismatching of 3pπ and 2pπ AOs), decrease $\Delta E_{S\rightarrow T}$, and consequently enhance reactivity.

After submission of the present paper, Chapman et al.[25] have published the infrared spectrum of matrix isolated 1,1,2-trimethylsilaethene (in argon at 8 K). Although it was not possible to assign the SiC double bond stretching vibration, the authors point out that the spectrum strongly suggests a planar configuration of 1,1,2-trimethylethene. This would be in accord with the results of the present theoretical study.

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