THE STABILITY AND NATURE OF AN Si-C DOUBLE BOND.

AN AB INITIO MO STUDY FOR 1,1-DIMETHYLSILAETHYLENE

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Summary. Several properties of $Me_2Si=CH_2$(I) are calculated for the first time using the ab initio MO method. (I) is found to be substantially more stable than the isomers $MeSi-CH_2Me$(II) and $Me_2HSi-CH$(III), in contrast to the case of the parent compound ($H_2Si=CH_2$). The geometry and vibrational frequencies are predicted.

The generation and characterization of silicon-carbon double-bonded intermediates are currently among the most active areas of organosilicon chemistry [1]. A large number of papers have appeared to indicate indirectly the transient existence of such intermediates, very often $Me_2Si=CH_2$, largely by kinetic and trapping experiments. The intermediates are very reactive toward self-dimerization and polar regents. In contrast, only a few reports are available at present which claim the spectroscopic observation of the intermediates. Mass spectral evidence [2] supporting the existence of $Me_2Si=CH_2$ in the gas phase has only recently been advanced. Infrared (IR) spectra [3] which are attributed to $Me_2Si=CH_2$ have been recorded at low temperature. For structural information, a very recent electron diffraction (ED) study [4] has reported two bond lengths, Si=C and Si-C, of $Me_2Si=CH_2$. The heat of formation and the Si-C π bonded strength have been estimated from the proton affinity data of ion cyclotron reasonace (ICR) spectroscopy [5].

Several ab initio theoretical studies [6] are available, but so far they have been limited to the parent compound $H_2Si=CH_2$, indicating that $H_2Si=CH_2$ is less stable or comparable in energy to $HSi-CH_3$ [6g,6h,6j]. Considering the fact that most experiments involved $Me_2Si=CH_2$, we have carried out the first ab initio MO study for this dimethyl compound and have found that $Me_2Si=CH_2$ is substantially more stable than the corresponding silylene $MeSi-CH_2Me$. We also report theoretical predictions on the structure and properties of this molecule, which should be useful for further experimental considerations.

Table I. Energies (kcal/mol) of Isomers II
and III, Relative to I.

Method	II	III
RHF	16.0	58.7
GVB(6/pp)	18.0	62.4
RHF + CI(S+D)[a]	20.5	70.8
RHF + CI(S+D+QC)[a]	21.8	73.1

[a]S+D = all single and double excitations,
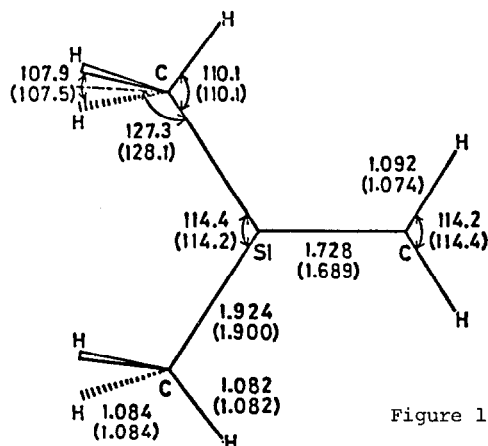QC = correction for quadruple excitations.

Figure 1

All calculations were carried out with the split-valence 4-31G basis set [7] by means of the closed-shell Hartree-Fock (RHF) and generalized valence bond (GVB) methods [8]. In GVB calculations, all (six) valence electron pairs but the CH bonds in the two methyl groups were allowed to split (correlate) into nonorthogonal, singly occupied, singlet coupled orbitals, this being denoted as GVB(6/pp). Geometries were fully optimized with the RHF and GVB energy gradient methods [9]. Energies were also calculated with the configuration interaction (CI) method [10] including all the single and double excitations relative to the RHF reference configuration, except that the core orbitals were frozen. In addition, the contribution of unlinked quadruple excitations to the correlation energy was estimated with Davidson's method [11].
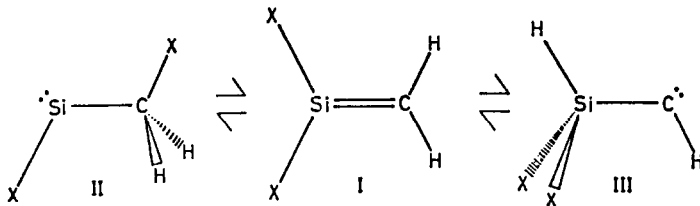
We first examine the thermodynamic stability of the three isomers $X_2Si=CH_2$(I), $X\ddot{S}i-CH_2X$(II) and $X_2HSi-\ddot{C}H$(III) in the singlet state at their respectively RHF-optimized geometries. The results for X = Me are shown in Table I. As in X = H, dimethylsilylcarbene (III) is most unstable. For X = Me, 1,1-dimethylsilaethylene (I) is more stable than methylethylsilylene (II), by 22 kcal/mol in our best calculation. (The use of Huzinaga-Dunning basis set reduces the value to some extent [12]). This is in a clear contrast to the results obtained previously [6g,6h,6j] for X = H, where silaethylene is less stable or comparable in energy to silylene. Based on the results we believe that 1,1-dimethylsilaethylene is a thermodynamically stable molecule. It is interesting to point out that the preference of I has been further enhanced by X = F [12]. With a proper choice of substituents it might be possible to isolate a relatively stable compound with a silicon-carbon double bond.

We now turn to the structure of $Me_2Si=CH_2$. In Figure 1 are shown the equilibrium geometries in Å and degrees predicted by GVB and RHF in parentheses for the singlet ground state. This

Table II. Selected Values of Predicted Vibrational Frequencies ν_i (cm^{-1}) and Dipole Moment Derivatives $|\partial\mu/\partial Q_i|$ (D$\cdot$Å$^{-1}\cdot$amu$^{-1/2}$) for $Me_2Si{=}CH_2$.

	assignment		ν_i	$|\partial\mu/\partial Q_i|$		assignment		ν_i	$|\partial\mu/\partial Q_i|$
A_1	$SiMe_2$	bend	190	0.2	B_1	CSiMe	bend	230	1.0
	$SiMe_2$	sym-str	560	0.5		$SiMe_2$	anti-str	660	2.7
	Si=C	str	1000	2.8		CH_2	rock	750	3.9
						$SiMe_2$	rock	860	2.3
A_2	CH_2	torsion	570	0	B_2	MeSiC	wag	200	1.2
	torsion around Si=C		810	0		CH_2	wag	780	3.6
						$SiMe_2$	wag	850	0.7

planar ground state is found to lie 36 kcal/mol below the lowest triplet in the perpendicular, $SiMe_2$-flapped geometry (not shown here) [12]. The calculated Si=C lengths r_e in Figure 1 are nearly equal to our (1.729 Å with GVB and 1.686 Å with RHF [12]) and previous results [6d,df] for $H_2Si{=}CH_2$. The ED determined r_g, 1.83±0.04 Å [4] for $Me_2Si{=}CH_2$ is substantially longer than the calculated r_e and may be worth reexamining. The ED value, 1.91±0.02 Å, of the Si-C length is in good agreement with the calculated values in Figure 1. We also note that the Si-C length is virtually unchanged when X is changed to F [12].

The rotational barrier E_r around a double bond has been considered to be a measure of the π bond strength E_π [6]. Using the GVB optimized geometries and energies, we have obtained $E_r =$ 47 kcal/mol, which is almost the same to our (43 kcal/mol) and previous (46 kcal/mol) [6d] value for $H_2Si{=}CH_2$. These values are considerably larger than estimates of $E_\pi \simeq 34$ kcal/mol from an ICR study [5], 26 – 46 kcal/mol by Walsh [13], and 28±8 kcal/mol by Gusel'nikov and Nametkin [14]. Either of the above E_r or E_π is less than the corresponding value (the calculated $E_r =$ 64 – 66 kcal/mol [6d,12] and the experimental estimate $E_r =$ 65 kcal/mol) [15] for ethylene, indicating that the Si=C π bond is weaker than the C=C π bond.

We have calculated the vibrational frequencies and dipole moment derivatives in the RHF method. At this level of calculation, the calculated frequencies ν_{calc} are expected to be larger than the observed ω_{obs} by (12±3)% [16]. Therefore, as prediction we listed in Table II $\nu_{calc}/1.12$ for vibrations excluding CH_3 and CH_2 str and bend vibrations, which are over 1300 cm^{-1}, and CH_3 rot. We predict an intense Si=C stretching band at 1000 cm^{-1} which is in agreement with the preliminary assignment of the observed 1001 cm^{-1} band by Mal'tsev et al. [3b]. The corresponding frequencies for deuterated species would be 920 cm^{-1} for $Me_2Si{=}CD_2$, 980 cm^{-1} for $(CD_3)_2Si{=}CH_2$ and 890 cm^{-1} for $(CD_3)_2Si{=}CD_2$. We note, however, that the isomer II also has a moderately strong band of CH_3 rocking at the calculated and corrected frequency of 1000 cm^{-1} [12].

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