Double-bonded Divalent Silicon: *Ab-initio* Calculations on the Species HSiN, HNSi, HCSiH, and H_2CSi

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Summary *Ab-initio* calculations on the species HSiN, HNSi, HCSiH, and H_2CSi suggest that multiple bonded silicon is more likely to be found in a divalent than in a quadrivalent state.

The reluctance of silicon and other second-row elements to form stable multiple bonded species has provided much stimulation to synthetic investigations and to quantum mechanical calculations. Chemical trapping experiments have indicated that molecules with carbon to silicon double bonds are intermediates in various processes, in particular the pyrolysis of silacyclobutanes.[1] The compound Me_2Si=CHMe has been identified by i.r. matrix isolation techniques.[2]

Recent interest in interstellar molecules and, in particular, the detection of rotational lines from unstable species such as HNC prior to laboratory observation,[3] has suggested that multiple bonded silicon molecules might be observed by radio astronomy. Lovas[4] has attributed some interstellar lines to HSiN, but this species is unknown in the laboratory whereas its isomer, HNSi, has been observed by i.r. matrix isolation.[5]

In an attempt to calculate accurate geometries for HSiN and HNSi, as an aid to microwave identification we have obtained the surprising result that HNSi is by far the more stable of the two isomers. This is in contrast to the carbon analogue for which the most recent estimate is that HCN is more stable than HNC by 61 kJ mol^{-1}.[6]

The above result has been obtained at several levels of calculation from a minimal basis SCF to an extended basis SCF with polarization functions and with configuration interaction and there is no doubt as to its veracity. The energy difference, which is in the range 300—400 kJ mol^{-1}, is much too large to be altered in sign by a more extensive calculation. The full details of this calculation will be published elsewhere[7] and we quote here (Table 1) only a summary of the SCF extended basis results which include geometry optimization.

Table 1. Properties of HSiNN and HNSi predicted by extended basis SCF calculations.[a]

	Optimised distances/Å			Total energy /hartrees
	R(H–Si)	R(H–N)	R(Si–N)	
HNSi		0·985	1·525	−343·96330
HSiN	1·459		1·526	−343·82155

[a] Exothermicity, 372 kJ mol^{-1}.

An analysis of the electronic wave function by a Mulliken population analysis shows no surprises for HSiN and this molecule is completely analogous to the carbon analogue and can be represented by the valence structure H-Si≡N. The results for HNSi are however again unexpected. Calculations[8] on HNC show the carbon atom to be negatively charged, whereas in HNSi the silicon atom carries a net charge of +0·71 e. The total bond overlap population of the N–Si bond is also low, 1·01 compared with the 1·62 in HSiN. The most appropriate valence description seems to be a resonance between H–N=Si, $\overset{+}{H}\overset{-}{N}{=}Si$, and $H{-}\overset{-}{N}{-}\overset{+}{Si}$, the silicon atom in each case being divalent, *i.e.* no promotion of the 3*s* electrons. The greater stability of HNSi over HSiN appears to reside primarily in a more favourable electrostatic energy in that for the species NSi^- we calculate that 98% of the net charge resides on the nitrogen

Table 2. Properties of CH_2Si and HCSiH predicted by DZ-SCF calculations.[a]

	Optimised distances/Å			Angles/°		
	R(C-Si)	*R*(C-H)	*R*(Si-H)	HCH	HCSi	Total energy/hartree
CH_2Si	1·72	1·08	—	112·9	123·55	−327·83795
H-C-Si-H	1·587	1·060	1·453	—	—	−327·74024

[a] Exothermicity, 256 kJ mol^{-1}.

atom. Thus a proton will preferably attach to NSi at the nitrogen end.

As a further test of this tendency for the stability of divalent, double-bonded silicon we have calculated the geometries and energies of $CH_2{=}Si$ and $HC{\equiv}SiH$. The results of a double-zeta SCF calculation are shown in Table 2. These again contrast with those for carbon analogues[9] in that the divalent silicon compound, which has a closed-shell singlet ground state, is by far the more stable, the difference being too large to be reversed by more exact calculations. Our calculations show that $CH_2{=}Si$ is planar and that HC-SiH is linear.

Calculations on $CH_2{=}SiH_2$ using the same basis, with the optimized geometry previously determined by Schegal *et al.*[10] and on H_2, makes $CH_2{=}SiH_2$ more stable than $CH_2{=}Si$ plus H_2 by 73 kJ mol^{-1}. However, such calculations which are with a relatively small basis and which make no allowance for differences in correlation energy are not sufficiently accurate to establish that $CH_2{=}SiH_2$ is in fact the more stable form. The calculations we have made suggest that it is worth searching for molecules with unsaturated bonds to silicon in which silicon is behaving as a divalent species.

Added in proof. I. Dubois and H. Leclerq have reported the detection of CH_2Si in the flash discharge of alkylsilanes (21st Liege Astrophysical Symposium, 1977).

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