Ab initio Calculations on Tautomers of $CSiH^-$, $CSiH_2$, and $CSiH_3^+$. Examples of the Tendency of Silicon to avoid Formation of Multiple Bonds with Carbon

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Summary *Ab initio* calculations on the energy hypersurfaces for $CSiH^-$, $CSiH_2$, and $CSiH_3^+$ reveal one, two, and three minima, respectively, with structures in which all the hydrogens are bonded to carbon being the most stable on each surface

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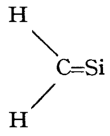
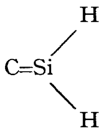
The absence of definitive experimental evidence on tautomers of CH_2Si and the instability of compounds containing silicon–carbon double bonds suggest that silicon is reluctant to form multiple bonds with carbon There has been considerable theoretical work on tautomers of $CSiH_4$ aimed particularly at their relative stabilities, profiles to interconversion, and establishing whether their ground states are singlets or triplets[1] Minimal basis set *ab initio* molecular orbitals give singlet methylsilylene to be of similar energy to silene, and improvement of the wavefunction to the double-zeta level results in a further relative stabilisation of the methylsilylene. This tendency for the hydrogen atoms to be bonded to the carbon atom leaving a formally electron-deficient silicon atom is shown even more dramatically in the more unsaturated CH_2Si system, where (**1**) is calculated to be considerably more stable than (**2**).[2,3]



(**1**)

$H{-}C{\equiv}Si{-}H$

(**2**)



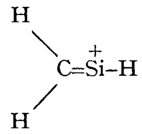
(**3**)

We now report that we have examined the profile to interconversion of (**1**), (**2**), and (**3**), both at the minimal STO-4G[4] and double-zeta[5] levels. Geometries at several points on the profiles to interconversion of (**1**) and (**2**), and (**2**) and (**3**) were optimised by fixing the migrating hydrogen at some point (*e.g.* a quarter of the distance between carbon and silicon) and optimising all other geometric parameters including the distance of the migrating hydrogen from the carbon–silicon internuclear axis. At both levels of calculation, silyne (**2**) collapses *without barrier* to the most stable tautomer, (**1**). Structure (**3**) is computed to be less stable than (**1**) by 375 and 389 kJ mol^{-1} at the STO-4G and double-zeta levels, respectively, but there is a barrier [91·2 kJ mol^{-1} above (**3**) at the double-zeta level] to migration of the first hydrogen from the silicon atom of (**3**).

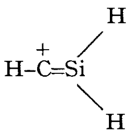
Silicenium ions, $XSiH_2^+$, have previously been studied both theoretically[6] and experimentally[7] but the unsaturated cations $XSiH^+$ have not been investigated. The results of our *ab initio* calculations on the tautomeric cations (**4**)—(**7**) are now reported in the Table. The most remarkable feature of these structures is that as the charge becomes more localised on silicon the structure becomes more stable, regardless of the valence of silicon. As on the CH_2Si surface, the most stable tautomer, (**4**), has all the hydrogens

$Me{-}Si^{+}$

(**4**)



(**5**)



(**6**)

$\overset{+}{C}{-}SiH_3$

(**7**)

$H{-}C{\equiv}Si^{-}$

(**8**)

$H{-}Si{\equiv}C^{-}$

(**9**)

attached to the carbon atom. This cation is more stable than the silicon analogue of the vinyl cation, (**5**), by 239 kJ mol^{-1}. The less stable tautomers, (**6**) and (**7**), lie 349 and 580 kJ mol^{-1}, respectively, above (**4**). These energy differences are not changed significantly by improving the basis set by inclusion of *d*-functions on silicon and carbon.

Structure (**5**) collapses *without barrier* into (**4**), while the profiles for interconversion of (**6**) into (**4**), and (**7**) into (**6**) have barriers of 124 and 53 kJ mol^{-1}, respectively, above the less stable tautomers in these equilibria (reaction profiles were optimised with the STO-4G basis set).

The energy surface for $CSiH^-$ also shows some unusual features. Deprotonation of $CSiH_2$ can, in principle, result in one of two anions, $H{-}C{\equiv}Si^-$ (**8**) or $H{-}Si{\equiv}C^-$ (**9**), but a search of energy surface at the double-zeta level showed only one minimum, corresponding to structure (**8**), and a maximum corresponding to structure (**9**).

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TABLE. Optimised geometries and energies for singlet states[a] from double-zeta calculations

	Point group	Optimised distance/Å			Optimised angle/°		Total energy /hartree
		C–Si	C–H	Si–H	HCSi	HSiC	
(**1**)[b]	C_{2v}	1·72	1·08	—	123·5	—	−327·83021
(**2**)[b,c]	$C_{\infty v}$	1·59	1·06	1·45	—	—	−327·73468
(**3**)	C_{2v}	1·78	—	1·47	—	120·0	−327·68208
(**4**)	C_{3v}	1·86	1·10	—	112·1	—	−328·18156
(**5**)[c,d]	C_{2v}[e]	1·68	1·08	1·43	116·4	180·0	−328·09056
(**6**)[d]	C_{2v}	1·73	1·07	1·47	180·0	115·2	−328·04860
(**7**)	C_{3v}	2·07	—	1·47	—	100·0	−327·96062
(**8**)	$C_{\infty v}$	1·65	1·08	—	180·0	—	−327·23451

[a] Preliminary calculations show the most stable triplets on the $CSiH^-$, $CSiH_2$, and $CSiH_3^+$ surfaces to be less stable than the most stable singlets. [b] Geometries taken from ref. 3. [c] Not at a minimum on the energy hypersurface. [d] At the STO-4G level, both ions were found to have C_{2v} symmetry. This symmetry was assumed in the double-zeta calculations. [e] Assumed.

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