On the Experimental–Theoretical Discrepancy regarding the Silicon–Carbon Double Bond Length

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Ab initio calculations show that the C=Si bond length of 1.764 Å in $(Me_3Si)_2Si=C(adamantyl)(OSiMe_3)$ is electronically elongated (mainly by $OSiMe_3$) and that the unperturbed *r*(C=Si) is *ca.* 1.70 Å, much shorter than the 1.832 Å measured by electron diffraction.

Silicon–carbon double bonds (silenes) are the subject of considerable recent experimental and theoretical interest.[1—4] However, there is still no agreement on the most fundamental property of this bond, *i.e.*, the C=Si bond length. Mahaffy *et al.* reported recently an electron diffraction study of $H_2C=SiMe_2$ (**1**) and obtained a value of 1.832 ± 0.005 Å for *r*(C=Si).[2] On the other hand, Schaefer *et al.* have carried out 'state of art' *ab initio* calculations (employing a polarized basis set and including correlation energy) for (**1**) and found a much shorter C=Si distance of 1.705 Å.[3] Brook *et al.* have succeeded in isolating the first solid stable silene, *i.e.*, $(Me_3Si)_2Si=C(OSiMe_3)(adamantyl)$ (**2**), and have carried out the crystal structure analysis which gives *r*(C=Si) of 1.764 Å, intermediate between the theoretical and the experimental value for (**1**).[4] Brook's value was not suitable for resolving the controversy[3] because (**2**) is heavily substituted and the effect of substituents on the C=Si distance is not known. However, such substituent effects can be studied reliably by computation techniques. In this communication we present evidence from *ab initio* calculations which strongly supports the conclusion of Schaefer *et al.* that the characteristic unperturbed C=Si bond length is *ca.* 1.70 Å.[3]

We have calculated† the optimized geometries of an extensive set of mono- and di-substituted silenes,[5] using the economic, yet reliable, 3-21G basis set.[6] Its reliability is demonstrated by the excellent agreement with the considerably more sophisticated calculations of Schaefer *et al.*: *e.g.*, in $H_2C=SiH_2$ *r*(C=Si) is 1.718 Å at 3-21G compared to 1.705 Å according to Schaefer *et al.*[3] A consistent picture regarding the effect of substituents on *r*(C=Si) emerges from the computational results.[5] The major factor which determines the C=Si distance is the substituent effect on the C=Si bond ionicity. This bond is highly polarized even in $H_2C=SiH_2$ (Si positively charged, C negatively charged). Substituents that decrease this polarization (inductive rather than conjugative effects are important[5]) and thus decrease the C=Si bond ionicity, cause elongation of the bond and *vice versa*.‡ For example, in $H_2Si=CH(OSiH_3)$ the electronegative oxygen decreases the bond polarity and *r*(C=Si) increases by 0.031 Å to 1.749 Å compared to $H_2C=SiH_2$. Conversely, in $H_2C=SiH(OSiH_3)$, *r*(C=Si) = 1.705 Å, 0.013 Å shorter than in $H_2C=SiH_2$.§ Similarly, in both $H_2Si=CHMe$ and $H_2C=SiHSiH_3$, *r*(C=Si) is 0.007 Å longer than in $H_2C=SiH_2$. Furthermore, the effect of substituents on the C=Si distance is additive; *e.g.*, the optimized 3-21G *r*(C=Si) in $H_3SiHSi=CH(OSiH_3)$ is the same as that obtained by adding the individual contributions of the substituents. On the basis of this additivity we estimate that in $(H_3Si)_2Si=CMe(OSiH_3)$, a close electronic model of (**2**), *r*(C=Si) = {1.718 [*r*(C=Si) in $H_2C=SiH_2$] + 2(1.725—1.718) + (1.725 − 1.718) + (1.749 − 1.718) Å; *i.e.*, changes in *r*(C=Si) due to substitution by two H_3Si, Me, and $OSiH_3$ respectively} = 1.770 Å. This distance is essentially identical to Brook's experimental value of 1.764 Å.[4] Although this close agreement may be somewhat fortuitous the general trend is not. The agreement between the calculated *r*(Si–Si) in H_3SiH-$Si=CH_2$ (2.36 Å) and in (**2**) (2.35 Å) lends further credibility to the calculations. We conclude that in (**2**), *r*(C=Si) is elongated relative to $H_2Si=CH_2$ by the electronic effects of the substituents (mainly by the $OSiMe_3$ group). Steric congestion in (**2**) is relieved by distortion of the bond angles and by a 16° twisting about the double bond.[4]¶

$H_2C=SiMe_2$
(**1**)

$(Me_3Si)_2Si=C(OSiMe_3)(adamantyl)$
(**2**)

The calculations therefore support strongly a *r*(C=Si) of 1.70 Å in unperturbed silenes [*e.g.*, $H_2Si=CH_2$ and (**1**)] and suggest a re-examination of the electron diffraction analysis by Mahaffy *et al.* which yielded a much longer bond of 1.83 Å.[2]

Added in proof: M. S. Gordon and C. George, *J. Am. Chem. Soc.*, 1984, **106**, 609, have reported recently similiar calculated *r*(C=Si) in $H_2C=SiH(OH)$ and $H_2Si=CH(OH)$ but the relevance of these results to the experimental–theoretical discrepancy was not pointed out.

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‡ Correlations between bond lengths and bond ionicities are well established. See: J. E. Huheey, 'Inorganic Chemistry, Principles of Structure and Reactivity,' 3rd edn., Harper and Row, New York, 1983, pp. 260—262.

§ Similar changes, although smaller, were reported for $H_2C=SiHF$ and $FHC=SiH_2$ by M. S. Gordon, *J. Am. Chem. Soc.*, 1982, **104**, 4352.

¶ A 16° twisting causes elongation of *r*(C=Si) in $H_2C=SiH_2$ by *ca.* 0.015 Å