

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 (Me₃Si)₂Si=C(adamantyl)(OSiMe₃) is electronically elongated (mainly by OSiMe₃) and that the unperturbed $r(\text{C}=\text{Si})$ is ca. 1.70 Å, much shorter than the 1.832 Å measured by electron diffraction.

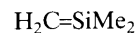
Silicon–carbon double bonds (silenes) are the subject of considerable recent experimental and theoretical interest.^{1–4} However, there is still no agreement on the most fundamental property of this bond, *i.e.*, the C=Si bond length. Mahaffy *et al.* reported recently an electron diffraction study of H₂C=SiMe₂ (1) and obtained a value of 1.832 ± 0.005 Å for $r(\text{C}=\text{Si})$.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.*, (Me₃Si)₂Si=C(OSiMe₃)(adamantyl) (2), and have carried out the crystal structure analysis which gives $r(\text{C}=\text{Si})$ of 1.764 Å, intermediate between the theoretical and the experimental value for (1).⁴ Brook's value was not suitable for resolving the controversy³ 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 H₂C=SiH₂ $r(\text{C}=\text{Si})$ 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 $r(\text{C}=\text{Si})$ 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 H₂C=SiH₂ (Si positively charged, C negatively charged). Substituents that decrease this polarization (inductive rather than conjugative effects are important⁵) and thus decrease the C=Si bond ionicity, cause elongation of the bond and *vice versa*.[‡] For example, in H₂Si=CH(OSiH₃) the electronegative oxygen decreases the bond polarity and $r(\text{C}=\text{Si})$ increases by 0.031 Å to 1.749 Å compared to H₂C=SiH₂. Conversely, in H₂C=SiH(OSiH₃), $r(\text{C}=\text{Si}) = 1.705$ Å, 0.013 Å shorter than in H₂C=SiH₂.[§] Similarly, in both H₂Si=CHMe and H₂C=SiHSiH₃, $r(\text{C}=\text{Si})$ is 0.007 Å longer than in H₂C=SiH₂. Furthermore, the effect of substituents on the C=Si distance is additive; *e.g.*, the optimized 3-21G $r(\text{C}=\text{Si})$ in H₃SiHSi=CH(OSiH₃) is the same

[†] A modified version of the Gaussian 80 series of programs was used: J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, *Quantum Chemistry Program Exchange*, 1980, **13**, 406.

[‡] 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 H₂C=SiHF and FHC=SiH₂ by M. S. Gordon, *J. Am. Chem. Soc.*, 1982, **104**, 4352.



(1)



(2)

as that obtained by adding the individual contributions of the substituents. On the basis of this additivity we estimate that in (H₃Si)₂Si=CMe(OSiH₃), a close electronic model of (2), $r(\text{C}=\text{Si}) = \{1.718 [r(\text{C}=\text{Si}) \text{ in } \text{H}_2\text{C}=\text{SiH}_2] + 2(1.725 - 1.718) + (1.725 - 1.718) + (1.749 - 1.718) \text{ Å}; \text{ i.e., changes in } r(\text{C}=\text{Si}) \text{ due to substitution by two H}_3\text{Si, Me, and OSiH}_3 \text{ respectively} \} = 1.770 \text{ Å}$. 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 $r(\text{Si}-\text{Si})$ in H₃SiH-Si=CH₂ (2.36 Å) and in (2) (2.35 Å) lends further credibility to the calculations. We conclude that in (2), $r(\text{C}=\text{Si})$ is elongated relative to H₂Si=CH₂ by the electronic effects of the substituents (mainly by the OSiMe₃ group). Steric congestion in (2) is relieved by distortion of the bond angles and by a 16° twisting about the double bond.[¶]

The calculations therefore support strongly a $r(\text{C}=\text{Si})$ of 1.70 Å in unperturbed silenes [*e.g.*, H₂Si=CH₂ 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 similar calculated $r(\text{C}=\text{Si})$ in H₂C=SiH(OH) and H₂Si=CH(OH) but the relevance of these results to the experimental–theoretical discrepancy was not pointed out.

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[¶] A 16° twisting causes elongation of $r(\text{C}=\text{Si})$ in H₂C=SiH₂ by ca. 0.015 Å