

# 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<sub>3</sub>Si)<sub>2</sub>Si=C(adamantyl)(OSiMe<sub>3</sub>) is electronically elongated (mainly by OSiMe<sub>3</sub>) and that the unperturbed *r*(C=Si) is ca. 1.70 Å, much shorter than the 1.832 Å measured by electron diffraction.

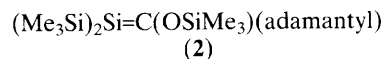
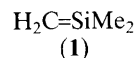
Silicon–carbon double bonds (silenes) are the subject of considerable recent experimental and theoretical interest.<sup>1–4</sup> However, there is still no agreement on the most fundamental property of this bond, *i.e.*, the C=Si bond length. Mahaffy *et al.* reported recently an electron diffraction study of H<sub>2</sub>C=SiMe<sub>2</sub> (1) and obtained a value of 1.832 ± 0.005 Å for *r*(C=Si).<sup>2</sup> 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.<sup>3</sup> Brook *et al.* have succeeded in isolating the first solid stable silene, *i.e.*, (Me<sub>3</sub>Si)<sub>2</sub>Si=C(OSiMe<sub>3</sub>)(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).<sup>4</sup> Brook's value was not suitable for resolving the controversy<sup>3</sup> 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.<sup>3</sup>

We have calculated† the optimized geometries of an extensive set of mono- and di-substituted silenes,<sup>5</sup> using the economic, yet reliable, 3-21G basis set.<sup>6</sup> Its reliability is demonstrated by the excellent agreement with the considerably more sophisticated calculations of Schaefer *et al.*: *e.g.*, in H<sub>2</sub>C=SiH<sub>2</sub> *r*(C=Si) is 1.718 Å at 3-21G compared to 1.705 Å according to Schaefer *et al.*<sup>3</sup> A consistent picture regarding the effect of substituents on *r*(C=Si) emerges from the computational results.<sup>5</sup> 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<sub>2</sub>C=SiH<sub>2</sub> (Si positively charged, C negatively charged). Substituents that decrease this polarization (inductive rather than conjugative effects are important<sup>5</sup>) and thus decrease the C=Si bond ionicity, cause elongation of the bond and *vice versa*.‡ For example, in H<sub>2</sub>Si=CH(OSiH<sub>3</sub>) the electronegative oxygen decreases the bond polarity and *r*(C=Si) increases by 0.031 Å to 1.749 Å compared to H<sub>2</sub>C=SiH<sub>2</sub>. Conversely, in H<sub>2</sub>C=SiH(OSiH<sub>3</sub>), *r*(C=Si) = 1.705 Å, 0.013 Å shorter than in H<sub>2</sub>C=SiH<sub>2</sub>.§ Similarly, in both H<sub>2</sub>Si=CHMe and H<sub>2</sub>C=SiHSiH<sub>3</sub>, *r*(C=Si) is 0.007 Å longer than in H<sub>2</sub>C=SiH<sub>2</sub>. Furthermore, the effect of substituents on the C=Si distance is additive; *e.g.*, the optimized 3-21G *r*(C=Si) in H<sub>3</sub>SiHSi=CH(OSiH<sub>3</sub>) 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 H<sub>2</sub>C=SiHF and FHC=SiH<sub>2</sub> by M. S. Gordon, *J. Am. Chem. Soc.*, 1982, **104**, 4352.



as that obtained by adding the individual contributions of the substituents. On the basis of this additivity we estimate that in (H<sub>3</sub>Si)<sub>2</sub>Si=CMe(OSiH<sub>3</sub>), a close electronic model of (2), *r*(C=Si) = {1.718 [*r*(C=Si) in H<sub>2</sub>C=SiH<sub>2</sub>] + 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<sub>3</sub>Si, Me, and OSiH<sub>3</sub> respectively} = 1.770 Å. This distance is essentially identical to Brook's experimental value of 1.764 Å.<sup>4</sup> Although this close agreement may be somewhat fortuitous the general trend is not. The agreement between the calculated *r*(Si–Si) in H<sub>3</sub>SiH–Si=CH<sub>2</sub> (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<sub>2</sub>Si=CH<sub>2</sub> by the electronic effects of the substituents (mainly by the OSiMe<sub>3</sub> group). Steric congestion in (2) is relieved by distortion of the bond angles and by a 16° twisting about the double bond.<sup>¶</sup>

The calculations therefore support strongly a *r*(C=Si) of 1.70 Å in unperturbed silenes [*e.g.*, H<sub>2</sub>Si=CH<sub>2</sub> 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.<sup>2</sup>

Added in proof: M. S. Gordon and C. George, *J. Am. Chem. Soc.*, 1984, **106**, 609, have reported recently similar calculated *r*(C=Si) in H<sub>2</sub>C=SiH(OH) and H<sub>2</sub>Si=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*(C=Si) in H<sub>2</sub>C=SiH<sub>2</sub> by ca. 0.015 Å