

A THEORETICAL STUDY OF MULTIPLE BONDING IN CARBON AND SILICON

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Summary

Multiple bonding in carbon and silicon is investigated by FSGO calculations on Si_2H_6 , $\text{SiH}_2=\text{SiH}_2$, $\text{SiH}\equiv\text{SiH}$, CH_3SiH_3 , $\text{CH}_2=\text{SiH}_2$ and $\text{CH}\equiv\text{SiH}$. Silicon is found to be reluctant to adopt trigonal coordination, preferring a tetrahedral environment in $\text{SiH}_2=\text{SiH}_2$ and in $\text{CH}_2=\text{SiH}_2$. $D_\pi(\text{Si}=\text{Si})$ and $D_\pi(\text{C}=\text{Si})$ are predicted to be about a half and a third, respectively, of $D_\pi(\text{C}=\text{C})$. Orbital density comparisons are made which suggest that despite silicon and carbon having equivalent valence configurations, silicon might be too electropositive to form stable unsaturated compounds.

Introduction

Of the Group IVB elements, carbon is atypical in being the only one capable of forming stable, multiply-bonded molecules. Despite having equivalent valence shell configurations, so that there are available orbitals which can participate in multiple bonds, silicon and its congeners seem reluctant to adopt trigonal (or digonal) coordination in their compounds. This phenomenon has not attracted much theoretical interest, although there have been some semi-empirical calculations on the carbon-silicon and silicon-silicon double bonds [1,2]. Evidence for the existence or otherwise of compounds in which silicon is apparently involved in an olefin-type linkage has been reviewed by several authors [3-5].

In the present study, the Floating Spherical Gaussian Orbital (FSGO) model of Frost [6] has been used to investigate the structures of CH_3SiH_3 , Si_2H_6 , $\text{CH}_2=\text{SiH}_2$, Si_2H_4 , $\text{CH}\equiv\text{SiH}$ and Si_2H_2 . The FSGO approach is the simplest of ab initio calculational schemes, and so it has been possible to carry out full parameter and geometry searches.

The FSGO model, in contrast to the Molecular Orbital (MO) method, presupposes that there can be a classical description for a particular molecular system. It is a localised orbital model which assigns each electron pair to a

floating spherical gaussian function,

$$\psi_i = \left[\frac{2\alpha_i}{\pi} \right]^{3/4} \exp[-\alpha_i(r - R_i)^2]$$

which can be identified with a lone pair, bond pair or atomic core orbital [6,7]. The position R_i and exponent α_i are usually fully optimised together with bond lengths and interbond angles so that the total molecular energy is minimised. The FSGO approach is well-suited for a seemingly initial survey of multiple bonding involving silicon by *ab initio* means. It is worth emphasising here that the basis functions used in the calculations consist only of the FSGO's, so that, for example, an MO-like population analysis cannot be made of the FSGO wavefunction. However, the model lends itself to alternative interpretations [8,9].

Calculations

In Fig. 1, the basic FSGO descriptions of AH_4 , A_2H_6 , A_2H_4 and A_2H_2 molecules are illustrated. In methane the FSGO basis consists of five functions, one on the carbon nucleus representing the core and four (one each) floating along the C-H bonds. Silane is described in an equivalent way, with the Si *KL* core consisting of two functions representing a 1s and a 2s orbital, respectively, situated on the Si nucleus, surrounded by six FSGO's displaced along the x , y and z axes suitably combined to produce lobe-type $2p_x$, $2p_y$ and $2p_z$ functions. This is not the conventional FSGO description of an *L* shell [18], but it is advantageous both conceptually and numerically (producing a better conditioned density matrix).

The FSGO descriptions of ethane, silylmethane and disilane are straightforward, with an FSGO situated along the AA' axis. For the multiply-bonded molecules, the usual FSGO approach is to fix two FSGO's above and below the molecular plane for double bonds and three FSGO's arranged in an equilateral

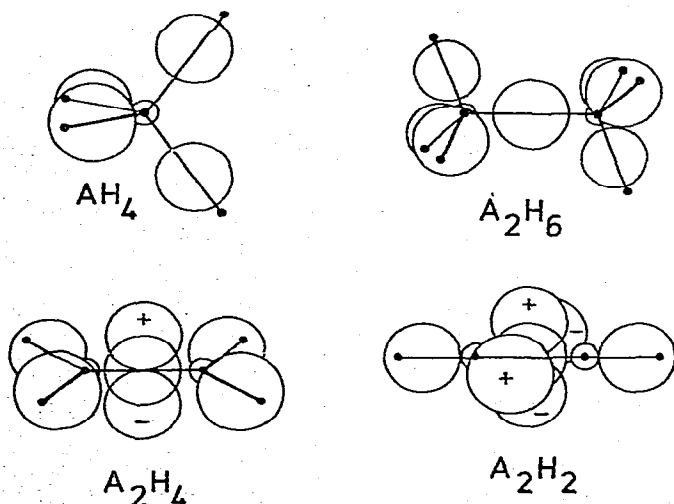


Fig. 1. FSGO descriptions of AH_4 , A_2H_6 , A_2H_4 and A_2H_2 systems. Each FSGO is represented by a circle.

fashion about the AA' axis for A₂H₂ systems [10]. This approach produces numerical problems for large molecules. The limiting case is therefore taken in which, for example, the two FSGO's in the double bond are replaced by an axially situated function (σ) together with the difference of two gaussians to produce a *p*-type lobe function (π). The σ and π orbitals have a common exponent. The triple bond is similarly represented (see Fig. 1).

Two further calculations were made for CH₂=SiH₂ and CH≡SiH, in which the positions of the σ and π orbitals in the multiple bonds were unconstrained with respect to each other. By analogy to MO theory, these are called "*d* _{π} " calculations, since it is possible to displace a π function (but not σ) by the addition of a suitable orbital of *d* symmetry. The significance of these calculations will be discussed later on. The σ and π orbitals still had a common exponent.

Results

The calculated structures are listed in Table 1. Frost's results for methane and ethane are included for purposes of comparison, whilst the results quoted for ethylene and acetylene represent "limiting" geometries, and are slightly different from the original FSGO calculations [10].

One test for any theoretical model must be the quality of its structural predictions. For the FSGO model, C—H distances are as usual slightly too long [7]. The environmental trend is accurately followed, as it is for the carbon—carbon bond lengths. Interbond angles are gratifyingly close to experiment.

TABLE 1
CALCULATED GEOMETRIES^a

Compound	Distance (Å)	Angle (°)
CH ₄ ^b	<i>r</i> _{CH} = 1.115 (1.094)	
SiH ₄	<i>r</i> _{SiH} = 1.462 (1.477)	
CH ₃ —CH ₃ ^{c,d}	<i>r</i> _{CH} = 1.120 (1.093), <i>r</i> _{CC} = 1.501 (1.534),	<HCH = 108.2 (109.1)
CH ₂ =CH ₂	<i>r</i> _{CH} = 1.101 (1.086), <i>r</i> _{CC} = 1.349 (1.338),	<HCH = 118.8 (117.3)
CH≡CH	<i>r</i> _{CH} = 1.077 (1.059), <i>r</i> _{CC} = 1.203 (1.205)	
SiH ₃ —SiH ₃ ^c	<i>r</i> _{SiH} = 1.466 (1.492), <i>r</i> _{SiSi} = 2.254 (2.331),	<HSiH = 108.7 (108.6)
SiH ₂ =SiH ₂	<i>r</i> _{SiH} = 1.451, <i>r</i> _{SiSi} = 1.988,	<HSiH = 111.9
SiH≡SiH	<i>r</i> _{SiH} = 1.440, <i>r</i> _{SiSi} = 1.778	
CH ₃ —SiH ₃ ^c	<i>r</i> _{CH} = 1.124 (1.093), <i>r</i> _{SiH} = 1.466 (1.485), <i>r</i> _{CSi} = 1.839 (1.867),	<HCH = 108.5 (107.8) <HSiH = 108.1 (108.3),
CH ₂ =SiH ₂ ^e	<i>r</i> _{CH} = 1.116 (1.112), <i>r</i> _{SiH} = 1.457 (1.455), <i>r</i> _{CSi} = 1.638 (1.666),	<HCH = 122.3 (122.0) <HSiH = 109.5 (109.4),
CH≡SiH ^e	<i>r</i> _{CH} = 1.085 (1.087), <i>r</i> _{SiH} = 1.444 (1.443), <i>r</i> _{CSi} = 1.503 (1.501)	

Average deviations: *r*_{CH} 2.1%, *r*_{SiH} 1.3%, *r*_{CC} 1.0%, *r*_{SiSi} 3.3%, *r*_{CSi} 1.5%, <HCH 0.9%, <HSiH 0.1%.

^a Where available, experimental results are in parentheses: CH₄, SiH₄, C₂H₆, C₂H₄, C₂H₂ ref. [12]; Si₂H₆ ref. [13]; CH₃SiH₃ ref. [14]. ^b Ref. [11]. ^c Staggered configurations. ^d Ref. [10]. ^e "*d* _{π} " calculations in parentheses.

TABLE 2
TOTAL MOLECULAR ENERGIES (a.u.)

Compound	Energy (a.u.)
CH ₄ ^a	-33.9921
C ₂ H ₆ ^{b,c}	-67.0048
C ₂ H ₄	-65.8360
C ₂ H ₂	-64.6831
SiH ₄	-251.2678
Si ₂ H ₆ ^c	-501.5516
Si ₂ H ₄	-500.4122
Si ₂ H ₂	-499.2694
CH ₃ SiH ₃ ^c	-284.2691
CH ₂ SiH ₂ ^d	-283.0754
CHSiH ^d	-281.8758

^a Ref. [11]. ^b Ref. [10]. ^c Staggered geometries. Calculated rotational barriers (kJ/mol): C₂H₆ 23.8 [10], CH₃SiH₃ 8.27, Si₂H₆ 3.34; experiment 12.6 [17], 7.1 [14] and 4.6 (estimate [16]). The eclipsed geometries were fully optimised. ^d "d_π" calculations: CH₂SiH₂ -283.0800, CHSiH -281.8762.

The structures found for the silanes reproduce satisfactorily the experimental results. The geometry found for Si₂H₄ is, however, unexpected. The ca. 112° result indicates a preference for the tetrahedral angle. The geometrical results found here do not coincide too well with those used by the CNDO calculations of Curtis [1]. For the mixed hydrides, the FSGO calculation on CH₃SiH₃ has produced an acceptable geometry. However, Damrauer and Williams [2] find a CNDO structure for CH₂=SiH₂ which is approximately 10% different from that given in Table 1. For this molecule, the tendency for the silicon centre to remain "tetrahedral" is repeated, whilst the methylene group takes on a trigonal angle. The "d_π" calculations produced only minor structural changes.

For each set of molecules A₂H_{2n} (n = 1,3), the calculations indicated a similar trend for A-H and A-A' distances. It is interesting to note that since the

TABLE 3
DIPOLE MOMENTS

Compound	Dipole moment (Debye)
(i) Molecules	
CH ₃ SiH ₃ ^a	0.54 D
CH ₂ SiH ₂ ^b	1.37 D
CHSiH ^b	2.83 D
(ii) C-Si bonds ^c	
C ⁻ -Si ⁺	0.95 D
C ⁻ =Si ⁺	2.91 D
C ⁻ ≡Si ⁺	4.23 D

^a Experiment 0.73 D [15]. ^b "d_π" calculations: CH₂SiH₂ 2.39 D, CHSiH 2.65 D. ^c Assuming μ(C⁻H⁺) = 0.4 D [15], μ(Si⁺H⁻) = 1.0 D [3].

TABLE 4
CALCULATED HEATS OF REACTION (kJ/mol⁻¹)

Reaction	ΔH
$C_2H_6 + SiH_4 \rightarrow CH_3SiH_3 + CH_4$	+30
$C_2H_4 + SiH_4 \rightarrow CH_2SiH_2 + CH_4$	+95
$C_2H_2 + SiH_4 \rightarrow CHSiH + CH_4$	+218
$Si_2H_6 + CH_4 \rightarrow CH_3SiH_3 + SiH_4$	+18
$Si_2H_4 + CH_4 \rightarrow CH_2SiH_2 + SiH_4$	+160
$Si_2H_2 + CH_4 \rightarrow CHSiH + SiH_4$	+310

FSGO basis cannot accommodate the concept of hybridisation, this device is therefore not required to account for these trends.

Table 2 lists the calculated total energies. In general, FSGO total energies are about 85% of the Hartree-Fock results (this is due to the single gaussian representation of the atomic core, which lacks a cusp at the nucleus). However, despite this deficiency in total energies, relative energies are often faithfully reproduced [7]. The rotational barriers for methylsilane and disilane are closer to experiment than the FSGO result for ethane [10].

The molecular dipole moments of the three mixed hydrides are given in Table 3. As observed by Bellama et al. [19], after resolution of standard values for the bond dipoles, the carbon-silicon single bond is found to have the expected C^-Si^+ direction, which is opposite to the overall molecular moment. The FSGO C-Si bond moment is slightly larger than other estimates [3,19]. In the unsaturated molecules, the polarity of the C-Si bond increases with bond order. This is in agreement with other calculations: Curtis found $\mu(C=Si^+)$ 2.99 D [1].

Thermodynamics

Tables 4-6 list respectively certain heats of reaction calculated from the total energies of Table 2, heats of formation derived using the heats of reactions given in Table 4, and bond energies obtained from the heats of formation. The heats of reaction in Table 4 indicate that carbon-silicon multiple bonding is thermodynamically less attractive than is multiple bonding between the same element. It is not possible to make a direct comparison in this way between the

TABLE 5
HEATS OF FORMATION (kJ/mole)

experimental ^a					
CH ₄	-75	SiH ₄	+34	C(g)	+717
C ₂ H ₆	-85	Si ₂ H ₆	+80	Si(g)	+456
C ₂ H ₄	+52	CH ₃ SiH ₃	-17 ^b	H(g)	+218
C ₂ H ₂	+227				
calculated					
Si ₂ H ₆	+145	CH ₃ SiH ₃	+54		
Si ₂ H ₄	+205	CH ₂ SiH ₂	+256		
Si ₂ H ₂	+353	CHSiH	+554		

^a Ref. [21]. ^b Ref. [20].

TABLE 6
BOND ENERGIES (kJ/mol⁻¹)

standard ^a					
C—H	413	Si—H	318	$D_{\pi}(\text{C}=\text{C})$	264
C—Si	305	Si—Si	226		
calculated					
Si—Si	167	C—Si	234	$D_{\pi}(\text{Si}=\text{Si})$	140
Si=Si	307	C=Si	327	$D_{\pi}(\text{C}=\text{Si})$	93
Si≡Si	359	C≡Si	324		

^a Ref. [21].

multiple bonds, because the bond dissociation energy $B(\text{C—H})$ is different from $B(\text{Si—H})$. However, heats of formation can be estimated by using the experimental values listed in Table 5 for the equations in Table 4. $\Delta H_f(\text{CH}_3\text{SiH}_3)$ has been taken from the most recent estimate [20] (which is ± 8 kJ mol⁻¹). In the second part of Table 5, it can be seen that the molecules become progressively more endothermic with unsaturation. Comparing the semi-empirical results for Si_2H_6 and CH_3SiH_3 listed here with the experimental values included in the first part of the Table shows that although there is a considerable discrepancy (which is to be expected for such an approximate model) the difference between the heats of formation is realistically estimated. The conclusion to be drawn here is that silicon olefins should be more stable than the mixed hydride analogues. This is in agreement with the results of Curtis [1].

The bond energies given in Table 6 have been derived assuming, for consistency, the experimental heats of formation of $\text{C}(\text{g})$, $\text{Si}(\text{g})$ and $\text{H}(\text{g})$ listed in Table 5 together with the standard values for $B(\text{C—H})$ and $B(\text{Si—H})$. As can be seen, this results in an apparent underestimation of 70 kJ mol⁻¹ for the Si—Si and C—Si bonds (cf. Table 5). However, the value for the Si=Si bond is in close agreement with a semi-empirical estimate of 318 kJ mol⁻¹ [21]. The π -bond energies, Table 6, decrease in the order $\text{C}=\text{C} > \text{Si}=\text{Si} > \text{C}=\text{Si}$. Walsh [22] has estimated $D_{\pi}(\text{C}=\text{Si})$ in the chemical intermediate $\text{Me}_2\text{Si}=\text{CH}_2$ to lie between 119 and 192 kJ mol⁻¹, a result which is not in conflict with the present value since it is conceivable that substitution would have stabilised the π -bond.

Discussion

To sum up, the results suggest that (i) silicon is reluctant to adopt trigonal coordination, (ii) the carbon—silicon bond becomes more polar with increasing bond order, (iii) unsaturated compounds involving silicon have a relatively high endothermicity, and (iv) the π -bond energy in these compounds is considerably lower than in the olefins. The " d_{π} " calculations serve to emphasise these points. The separation of σ and π bonds in $\text{CH}_2=\text{SiH}_2$ displaces the π -bond towards the carbon; this implies a tendency for there to be very low Si d -orbital participation in the polar π -bond. There is no stabilisation to be gained by the π -orbital enforcing trigonal coordination on the silylene grouping. In the linear $\text{CH}\equiv\text{SiH}$ molecule, the unconstrained π -bonds are slightly displaced towards the silicon, which is fixed in a digonal environment. d -orbital participation is therefore pos-

TABLE 7
ORBITAL DENSITIES

C—H		Si—H	
CH ₄	0.242	SiH ₄	0.150
C ₂ H ₆	0.242	Si ₂ H ₆	0.148
C ₂ H ₄	0.259	Si ₂ H ₄	0.149
C ₂ H ₂	0.279	Si ₂ H ₂	0.148
CH ₃ SiH ₃	0.230	CH ₃ SiH ₃	0.151
CH ₂ SiH ₂	0.238	CH ₂ SiH ₂	0.151
CHSiH	0.277	CHSiH	0.148

C—C		C—Si		Si—Si	
C ₂ H ₆	0.350	CH ₃ SiH ₃	0.193	Si ₂ H ₆	0.119
C ₂ H ₄	0.238	CH ₂ SiH ₂	0.153	Si ₂ H ₄	0.091
C ₂ H ₂	0.220	CHSiH	0.134	Si ₂ H ₂	0.083

sible when there is no other option. Reference to Table 6, however, shows that the C≡Si bond is relatively destabilised with respect to the other multiple bonds.

As mentioned in the Introduction, the FSGO model does not lend itself to an MO-type population analysis. However, since it is a localised orbital model, it is of interest to compare relative electron densities calculated from the norm of the wavefunction at the orbital centres (this is a justifiable procedure since although the FSGO's are mutually non-orthogonal, the overlap between the orbitals is of the order of 0.15). These are listed in Table 7 for the C—H, Si—H, C—C, Si—Si and C—Si bonding orbitals. The most striking difference between carbon and silicon in their respective bonds to hydrogen is that there is hardly any environmental change in the Si—H density. For the C—H orbital, the orbital density increases with decreasing bond length as the coordination changes from tetrahedral to digonal, as is to be expected. There is only a slight but irregular change in the Si—H orbital density. All AA' bonds show a decrease in orbital density with increasing bond order (note that this is a point density). It is of further interest that the AA' orbital density is always greater than the AH and A'H densities in the exothermic compounds.

It is apparent that the insensitivity of the Si—H orbital density to environment is due to its effective "control" by hydrogen and not silicon. This is probably a result of the electropositive nature of silicon with respect to hydrogen, i.e. $x_{\text{Si}} < x_{\text{H}}$. This is contrary to the situation in the hydrocarbons, when $x_{\text{C}} > x_{\text{H}}$, implying that carbon can make its own arrangements about the electronic distribution. When H is substituted by R in the Si—H bond, other interactions, involving for example a π -type inductive effect, etc., can influence the overall electron density distribution in the Si—R bond. Unfortunately, the effect of substitution is difficult to quantify, since the group electronegativity of a substituent depends largely on the particular system involved. The methyl group, for example, has a relatively low electronegativity when attached to a carboxo group [23], which bears some similarity to methyl substitution in CH₂=SiH₂ to produce CH₂=SiMe₂. This silicon analogue of isobutene has been postulated as an intermediate in several processes [5]. It is noteworthy that a large number of possible

substituents have a relatively high group electronegativity * [23] implying a tendency towards a diradical structure. This possibility has been suggested by Margrave et al. [24] in connexion with the dimerisation of SiF_2 at low temperatures. However, further polymerisation in this case cannot be excluded [5].

Conclusion

It is suggested therefore that although silicon has the equivalent valence shell configuration to carbon, it might be too electropositive to form multiple bonds with a high enough π -bond energy. The effect of substituents, which has been emphasised in this connexion, is being further investigated, together with the possible diradical nature of the $\text{C}=\text{Si}$ and $\text{Si}=\text{Si}$ bonds using spin-coupled wavefunctions.

References

- 1 M.D. Curtis, *J. Organomet. Chem.*, 60 (1973) 63.
- 2 D. Damrauer and D.R. Williams, *J. Organomet. Chem.*, 66 (1974) 241.
- 3 C. Eaborn, *Organosilicon Compounds*, Butterworths, London (1960).
- 4 C.J. Attridge, *Org. Chem. Rev. A*, 5 (1970) 323.
- 5 L.E. Gusel'nikov, N.S. Nametkin and V.M. Vdovin, *Account. Chem. Res.*, 8 (1975) 18.
- 6 A.A. Frost, *J. Chem. Phys.*, 47 (1967) 3707, 3714.
- 7 P.H. Blustin and J.W. Linnett, *J. Chem. Soc. Faraday Trans. II*, 70 (1974) 274.
- 8 P.H. Blustin and J.W. Linnett, *J. Chem. Soc. Faraday Trans. II*, 70 (1974) 826.
- 9 P.H. Blustin, *Chem. Phys. Lett.*, (1975), in press.
- 10 A.A. Frost and R.A. Rouse, *J. Am. Chem. Soc.*, 90 (1968) 1965.
- 11 A.A. Frost, *J. Phys. Chem.*, 72 (1968) 1289.
- 12 *Chem. Soc. Spec. Publ.*, 11 (1958) and Supplement.
- 13 B. Beagley, A.R. Conrad, J.M. Freeman, J.J. Monaghan, B.G. Norton and G.C. Holywell, *J. Mol. Struct.*, 11 (1972) 371.
- 14 R.W. Kilb and L. Pierce, *J. Chem. Phys.*, 27 (1957) 108.
- 15 G.J. Moody and J.D.R. Thomas, *Dipole Moments in Inorganic Chemistry*, E. Arnold, London, 1971.
- 16 R.A. Scott and H.A. Scheraga, *J. Chem. Phys.*, 42 (1965) 2209.
- 17 S. Weiss and G.E. Leroi, *J. Chem. Phys.*, 48 (1968) 962.
- 18 S.Y. Chu and A.A. Frost, *J. Chem. Phys.*, 54 (1971) 760.
- 19 J.M. Bellama, R.S. Evans and J.E. Huheey, *J. Am. Chem. Soc.*, 95 (1973) 7242.
- 20 D. Quane, *J. Phys. Chem.*, 75 (1971) 2480.
- 21 D.A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, Cambridge University Press, 1968.
- 22 R. Walsh, *J. Organomet. Chem.*, 38 (1972) 245.
- 23 J. Hinze, M.A. Whitehead and H.H. Jaffe, *J. Am. Chem. Soc.*, 85 (1963) 148.
- 24 J.L. Margrave and P.W. Wilson, *Account. Chem. Res.*, 4 (1971) 145.

* This statement leads to the facile conclusion that stabilisation of multiply-bonded silicon will not be easy to achieve!