

## $p_x-p_x$ BONDING IN SILICON COMPOUNDS. EHMO AND CNDO CALCULATIONS\*

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(Received February 8th, 1973)

### SUMMARY

Extended Hückel (EHMO) calculations on the molecule  $H_2CSiH_2$  (silaethylene) and  $H_2SiSiH_2$  (disilaethylene) have been performed and the results subjected to a Mulliken population analysis to elucidate the factors responsible for the instability of such molecules. These calculations indicate that the C=Si  $\pi$ -bond is exceedingly polar, and that energy mismatching of carbon and silicon  $p$ -orbitals is in large part responsible for the weakness of the  $\pi$ -bond. The relatively high overlap population of the Si=Si  $\pi$ -bond suggests that compounds containing such bonds might be amenable to isolation. These conclusions were reinforced by calculating barriers to rotation about the  $\pi$ -bond via EHMO and CNDO methods; the barrier increases in the order C=Si < Si=Si < C=C. In contrast to  $C_2H_4$  and  $Si_2H_4$  in which the triplet state of the 90°-twisted molecule has lowest energy, the singlet state of twisted  $H_2CSiH_2$  is lowest and corresponds to the configuration,  $H_2C^--Si^+H_2$ . Although Si  $d$ -orbitals strengthen  $\pi$ -bonds by the formation of  $p-d$  hybrids, inclusion of  $d$ -orbitals in the basis set decreases the rotational barrier by providing greatly increased bonding capabilities in the excited states.

### INTRODUCTION

Recently the question of  $p_x-p_x$  bonding involving silicon was reviewed<sup>1</sup>. The two most quoted reasons for the lack of multiple bonding involving Si and other heavy atoms are a lack of good  $p_x-p_x$  overlap and "inner shell" repulsions.

Twenty years ago, Mulliken<sup>2</sup> pointed out that  $np_x-np_x$  ( $n > 2$ ) overlaps are in some cases greater than  $2p_x-2p_x$  overlaps at bonding distances. Mulliken claimed, however, that one should properly compare overlap integrals at constant  $\xi$  where

$$\xi = R/(r_a+r_b) \quad (1)$$

( $R$  = bond distance,  $r_i = n_i^2 a_0 / Z_{eff}$ ; i.e.,  $r_i$  is the maximum in the radial probability curve.) Thus,  $\xi = 1.0$  corresponds to a bond length,  $R$ , at which the radial maxima of orbitals A and B coincide. At  $\xi = 1.0$ , the C-C  $\pi$ -overlaps were found to be greater

\* Presented in part at the 3rd. International Organosilicon Symposium, Madison, Wisc., 1972.

than Si-Si  $\pi$ -overlaps (0.29 and 0.22, respectively)<sup>2</sup>. However, when the  $\sigma$ -overlaps were compared at  $\xi = 1.0$ , the third-row overlaps were found to be greater than the corresponding second-row overlaps; and Mulliken concluded that third-row elements form relatively stronger  $\sigma$ -bonds (as compared to  $\pi$ -bonds) than second-row elements. The lack of  $\pi$ -bonding in compounds of heavy elements was thus attributed to the relatively stronger  $\sigma$ -bonds available upon polymerization.

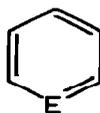
Typical values of  $\xi$  at the observed bonding distances range from 0.7 (H-H) to 1.77 (F-F). That is, molecules adopt that bonding distance which corresponds to the lowest energy irrespective of whether or not the radial maxima are superimposed. In addition, arguments based solely on overlap are not sufficient to gauge the strength of a covalent interaction especially in heteroatomic bonds. The relative energies of the orbitals also influence the strength of the covalent interaction. This is widely recognized<sup>3</sup> and is the basis of the Mulliken-Wolfsberg-Helmholtz (MWH) approximation of off-diagonal elements,  $H_{ij}$ :

$$H_{ij} = 0.5 K S_{ij} (H_{ii} + H_{jj}) . \quad (2)$$

It is thus necessary to make some estimate of the  $H_{ij}$ -elements involved in the  $\pi$ -bond rather than simply comparing overlap integrals.

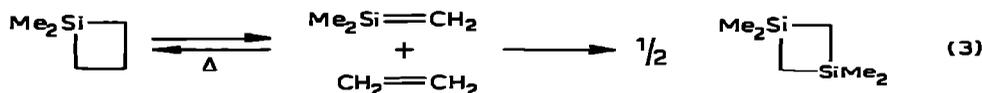
Mulliken<sup>2</sup> also discussed the role of "inner shell" repulsions some time ago. Pitzer<sup>4</sup>, who is responsible for the concept, based his arguments on pictorial representations of the overlap. Mulliken, by calculation of the relevant integrals, showed that inner shell-inner shell overlaps were negligible ( $< 10^{-3}$ ); but inner shell-valence shell overlaps could be of greater importance. Here, the relevant overlaps had values up to 0.1; but contrary to Pitzer's suggestion, these inner shell-valence shell repulsions were no larger for third-row than for second-row elements. Thus, these repulsions should not be responsible for the lack of  $\pi$ -bonding observed in heavy elements.

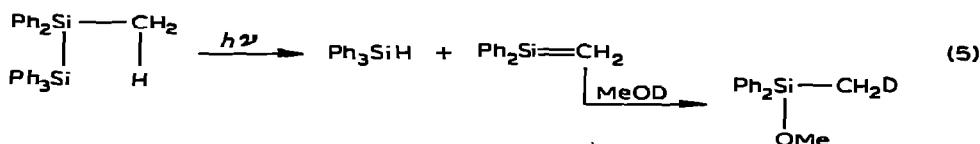
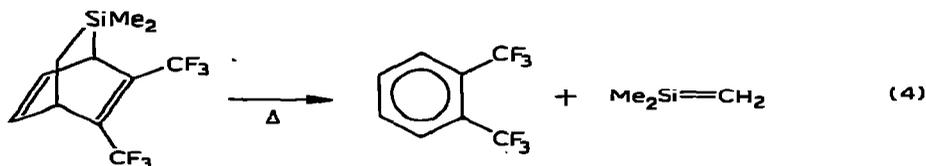
There is a renewed interest in the synthesis of compounds with multiple bonds to heavy elements. The recent isolation<sup>5</sup> of phospho-, arsa-, stibabenzene (I) with aromatic properties show that heavy atoms can indeed participate in multiple bonding.



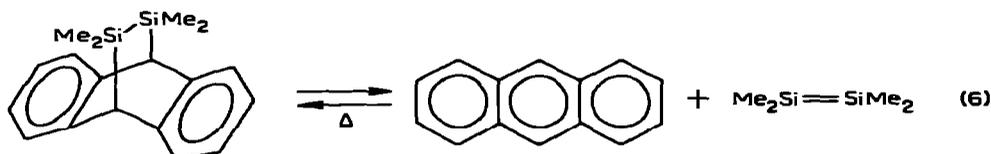
(I) E = P, As, Sb, Bi

Double bonds between carbon and silicon have recently been invoked as intermediates in the thermolysis of a silacyclobutane<sup>6</sup> and a silabicyclooctadiene<sup>7</sup>, and in the photolysis of a disilane<sup>8</sup>:





Similarly, Roark and Peddle<sup>9</sup> have reported evidence for a Si=Si double bond:



This molecular orbital study of C=Si and Si=Si double bonds was undertaken to provide a theoretical framework for the interpretation of current experimental results and to aid in the design of new experiments. Hoffmann's EHMO<sup>3</sup> method has been used to calculate eigenvectors which were used as a basis for a Mulliken population analysis<sup>10</sup>. Mulliken<sup>10</sup> has argued that a high overlap population is indicative of a strong covalent interaction, and this criterion is applied to the C=Si and Si=Si bonds. The use of neutral atom valence state ionization potentials (VSIP) for the diagonal elements,  $H_{ii}$ , led to large charge separations in  $H_2CSiH_2$ . The CNDO method<sup>11,12</sup>, which explicitly accounts for coulombic interactions, was used to calculate a more reasonable charge distribution. The CNDO method, because of its neglect of differential overlap, cannot be used for a population analysis, so the EHMO and CNDO methods are complimentary in this sense.

#### PARAMETERS

In both the EHMO and CNDO methods, the necessary input parameters are values for the diagonal elements,  $H_{ii}$ , Slater exponents, atomic coordinates, and a formula for generating the off-diagonal elements,  $H_{ij}$ . The Slater exponents are those of Clementi and Raimondi<sup>13</sup>. In the EHMO method, the  $H_{ii}$  were the VSIP of neutral atoms<sup>14</sup>, and the  $H_{ij}$  were generated by the MWH formula with  $K=1.75$ . A value of  $-5.50$  eV for the VSIP of the silicon  $d$ -orbitals has been found to give  $d$ -orbital populations comparable to those found in *ab initio* calculations<sup>15,16,17,18</sup>. The parameters used in the EHMO calculations are summarized in Table 1.

The bond distances used in both the EHMO and CNDO calculations are C=C 1.34, C-H 1.10, C-Si 1.90, Si=Si 2.20, Si-H 1.46. All bond angles were set at  $120^\circ$ . The CNDO<sup>19</sup> method and parameters used in this study have been described previously<sup>11</sup>.

TABLE 1

## EHMO PARAMETERS

	$\zeta^a$	$-H_{ii}(eV)$		$\zeta$	$-H_{ii}(eV)$
H1s	1.200	13.60	Si3s	1.634	14.82
C2s	1.625	21.34	Si3p	1.428	7.75
C2p	1.625	11.27	Si3d	1.000	5.50

<sup>a</sup> Orbital exponent.

## RESULTS

A summary\* of the overlap integrals involving the  $\pi$ -orbitals is given in Table 2. Noteworthy are the large values associated with the  $3d_x$  orbitals, and the relatively lower value for C-Si  $\pi$ -overlap. Fig. 1 schematically shows the form of the molecular orbitals and their relative energies as calculated by the EHMO method. The numbers over each energy level represent the overlap populations between the central atoms for each MO (see below).

TABLE 2

## OVERLAP INTEGRALS

	S		S
$2p_x-2p_x$	0.270	$3p_x-3p_x$	0.228
$2p_x-3p_x$	0.182	$3p_x-3d_x$	0.448
$2p_x-3d_x$	0.362	$3d_x-3d_x$	0.303

The ordering of the energy levels is  $(\sigma_s)^2 (\sigma_s^*)^2 (\pi_{||})^2 (\pi_{||}^*)^2 (\sigma_p)^2 (\pi)^2$ . In the  $D_{2h}$  point group, these are the  $1a_g, b_{3u}, b_{2u}, b_{1g}, 2a_g$  and  $b_{1u}$  orbitals; while the symbols appropriate to the  $C_{2v}$  point group are  $1a_1, 2a_1, 1b_2, 2b_2, 3a_1$  and  $b_1$  orbitals, respectively. The  $\sigma_s$  and  $\sigma_p$  levels involve both E-E and E-H bonding (E=C, Si), whereas the  $\sigma_s^*, \pi_{||}$ , and  $\pi_{||}^*$  are primarily E-H bonding. The ordering of the EHMO levels for  $C_2H_4$  is consistent with that deduced from the photoelectron spectrum<sup>20</sup>. The ordering of the CNDO levels for  $CH_2SiH_2$  and  $Si_2H_4$  agrees with the EHMO order, but the CNDO results place the  $\pi_{||}^*(b_{1g})$  level higher than the  $\pi(b_{1u})$  level in  $C_2H_4$  (see Tables 3 and 4).

Assuming Koopman's theorem applies, an estimate of the ionization potentials may be made by "scaling" the calculated value to a known value. (This method assumes that the calculations are capable of predicting trends in molecular properties.) The "scaled" potentials are shown in Table 5.

## A. Overlap populations

Figure 1 gives the overlap populations<sup>10</sup> for each MO, calculated with VSIP ( $3d$ ) = -5.50 eV. Positive numbers indicate bonding behavior for that MO, while

\* A complete set of overlap integrals, eigenvectors, and eigenvalues is available from the author upon request.

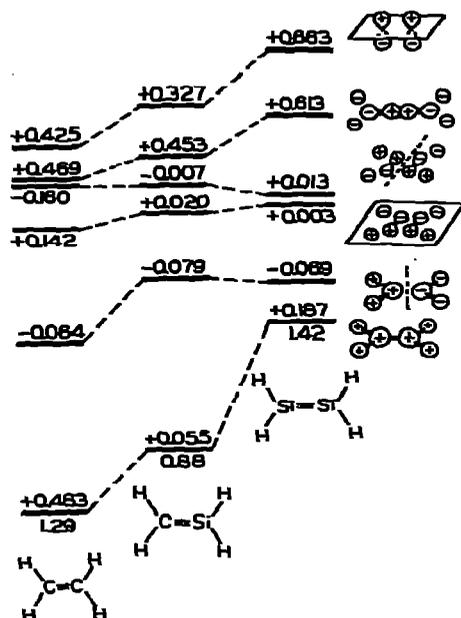


Fig. 1. Relative energies and X-Y overlap populations for  $H_2XYH_2$  molecules ( $X, Y = C, Si$ ).

TABLE 3

**EHMO EIGENVALUES AND TOTAL ELECTRONIC ENERGIES OF  $H_2XYH_2$  IN PLANAR AND TWISTED GEOMETRIES\***

<i>X</i>	<i>Y</i>	$\sigma_s$	$\sigma_s^*$	$\pi_{  }$	$\pi_{  }^*$	$\sigma_p$	$\pi$	$E_T$	
<i>(i) sp</i> basis set; planar geometry									
C	C	-26.82	-20.45	-16.29	-14.53	-14.42	-13.07	-211.16	
C	Si	-24.10	-18.00	-15.58	-14.24	-13.22	-11.50	-193.26	
Si	Si	-19.25	-17.42	-14.41	-14.18	-11.61	- 8.83	-171.39	
<i>(ii) spd</i> basis set; planar geometry									
C	Si	-24.16	-18.00	-15.58	-14.35	-13.29	-11.67	-194.10	
Si	Si	-19.29	-17.42	-14.49	-14.28	-11.81	- 9.12	-172.81	
<i>X</i>	<i>Y</i>	$\sigma_s$	$\sigma_s^*$	$\pi_x$	$\pi_y$	$\sigma_p$	$p_x$	$p_y$	$E_T$
<i>(iii) sp</i> basis set; twisted 90°									
C	C	-26.83	-20.53	-15.72	-15.72	-14.42	-10.60	-10.60	-207.64
C	Si	-24.10	-18.00	-15.55	-14.33	-13.21	-11.23	- 7.49	-192.85
Si	Si	-19.25	-17.42	-14.30	-14.30	-11.60	- 7.73	- 7.73	-169.22
<i>(iv) spd</i> basis set; twisted 90°									
C	Si	-24.16	-18.00	-15.55	-14.41	-13.27	-11.59	- 7.59	-193.98
Si	Si	-19.29	-17.43	-14.39	-14.39	-11.78	- 8.75	- 8.75	-172.04

\* All energies in eV; see Fig. 1 and text for descriptions of the molecular orbitals.

TABLE 4

CNDO ONE ELECTRON ENERGY LEVELS FOR PLANAR (SINGLET)  $H_2XYH_2$ 

X	Y	$\sigma_s$	$\sigma_p^*$	$\pi_{  }$	$\pi_{\perp}^*$	$\sigma_p$	$\pi$	LUMO <sup>a</sup>
C	C	-39.11	-27.40	-25.22	-15.87	-19.03	-16.04	+5.33 <sup>b</sup>
C	Si	-30.86	-20.17	-20.07	-16.21	-15.06	-11.95	+0.18 <sup>c</sup>
Si	Si	-23.04	-19.14	-16.83	-15.94	-14.49	-12.02	-2.64 <sup>d</sup>

<sup>a</sup> Lowest unoccupied level into which an electron, originally in the HOMO, is placed to generate the electron configuration used in the calculation of the planar triplet energies. CNDO incorrectly places the  $\pi_{\perp}^*$  level of  $C_2H_4$  higher than the  $\pi$ -level (see text).

<sup>b</sup> A  $\pi^*$  MO; the triplet state configuration is thus ...  $(\pi_{\perp}^*)^1 (\pi^*)^1$ . This configuration arises from the incorrect placement of the  $\pi_{\perp}^*$  level.

<sup>c</sup> A  $\sigma_p^*$ -MO; triplet configuration: ...  $(\pi)^1 (\sigma_p^*)^1$ .

<sup>d</sup> A  $\pi_{||}(b_{2u})$ -type orbital with Si(3d)-Si(3d)-H(1s) bonding; triplet configuration: ...  $(\pi)^1 (\pi_{||-d})^1$ .

TABLE 5

## ESTIMATED IONIZATION POTENTIALS

	$C_2H_4$	$CH_2SiH_2$	$Si_2H_4$
EHMO	(10.5)	9.11	6.56
CNDO	(10.5)	6.62	6.68
obs.	10.51		

negative numbers indicate anti-bonding behavior. For example, in ethylene the  $1a_g(\sigma_s)$  and  $2a_g(\sigma_p)$  are strongly C-C bonding, the  $b_{2u}(\pi_{||})$  less so; while the  $b_{3u}(\sigma_p^*)$  and  $b_{1g}(\pi_{\perp}^*)$  are slightly C-C anti-bonding (but strongly C-H bonding). The  $\pi$ -bond ( $b_{1u}$ ) is also strongly bonding, and the total C-C overlap population is 1.29 (summed over all occupied MO's).

The picture is much the same for disilaethylene,  $Si_2H_4$ , except that the  $1a_g(\sigma_s)$  MO is somewhat less and the  $2a_g(\sigma_p)$  level somewhat more Si-Si bonding than the corresponding C-C values in  $C_2H_4$ . Of special interest is the very high overlap population in the  $\pi(b_{1u})$  MO. This overlap population may be broken down into  $p$ - $p$ ,  $p$ - $d$ , and  $d$ - $d$  contributions as follows:

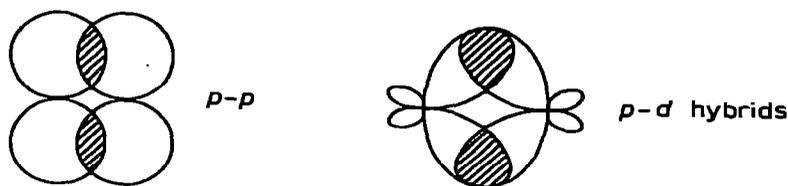
$$\begin{array}{ccc} p-p & p-d & d-d \\ 0.277 & +0.348 & +0.038 = 0.663 \end{array}$$

The  $p$ - $d$  contribution is seen to outweigh the  $p$ - $p$  contribution when the  $d$ -orbital energy is set at  $-5.50$  eV. This is primarily a consequence of the large ( $p$ - $d$ )  $\pi$ -overlap integral\* since the wavefunction itself is composed mainly of  $3p$ -orbitals:

$$\pi(b_{1u}) = 0.551(3p_x^A + 3p_x^B) - 0.176(3d_x^A - 3d_x^B)$$

With no  $d$ -orbitals in the basis set, the  $\pi$ -overlap population is 0.372, and the wavefunction is  $\pi(b_{1u}) = 0.638(3p_x^A + 3p_x^B)$ . Thus, the  $\pi$ -bond overlap population is quite

\* For the MO,  $\Psi = C_A \phi_A^A + C_B \phi_B^B$ , the overlap population between atoms A and B is  $\rho_{AB} = 4C_A C_B S_{AB}$ .



sensitive to the admixture of  $d$ -orbitals (to form  $p-d$  hybrids) since the  $(p-d)\pi$ -overlap integrals are so large (see Table 2).

Conversely, the overlap populations in the  $\sigma$ -framework have a much lower dependence on  $d$ -orbital parameterization. This can be thought of as an MO description of the higher polarizability of the  $\pi$ -bond compared to the  $\sigma$ -bonds. The  $d$ -orbitals are acting as polarization functions for the  $s$ - and  $p$ -orbitals<sup>21,22</sup>.

The results for silaethylene present a different picture, however. The  $\sigma_s(1a_1)$  level is essentially C-H bonding, while the  $\sigma_s^*(2a_1)$  is primarily Si-H bonding. Similarly the  $\pi_{||}(1b_2)$  is C(2p)-H bonding, and the  $\pi_{||}^*(2b_2)$  is Si(3p)-H bonding. The first MO to give substantial C-Si bonding is the  $\sigma_p(3a_1)$  level which is composed primarily of C and Si  $p$ -orbitals:

$$\begin{aligned} \sigma_p(3a_1) = & -0.144 C(2s) - 0.632 C(2p) - 0.105 Si(3s) \\ & + 0.314 Si(3p) - 0.067 Si(z^2) - 0.065 (x^2 - y^2) \\ & + 0.192 (H_1 + H_2)_C + 0.230 (H_3 + H_4)_{Si} \end{aligned}$$

The C-Si  $\pi$ -bond ( $b_1$ ) overlap population is 0.327 and is composed of  $p-p$  and  $p-d$  contributions:

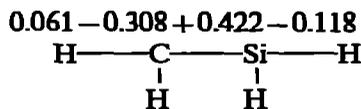
$$\begin{array}{ll} 2p-3p & 2p-3d \\ 0.130 + & 0.197 = 0.327 \end{array}$$

With no  $d$ -orbitals, the  $p-p$  overlap population is 0.158. The corresponding wave functions are:

$$\begin{aligned} \pi(b_1) = & 0.878 C(2p) + 0.203 Si(3p) - 0.155 Si(xz) & (\text{VSIP } (3d) = -5.50) \\ \pi(b_1) = & 0.931 C(2p) + 0.233 Si(3p) & (\text{no } d\text{-orbitals}) \end{aligned}$$

Not only is the  $\pi$ -bond overlap population smaller than those in  $C_2H_4$  or  $Si_2H_4$ , the electron distribution is exceedingly asymmetric being localized primarily in the C(2p)-orbital. The calculated charges in the  $\pi$ -bond alone are C(-0.71), Si(+0.71), and C(-0.81), Si(+0.81) with and without  $d$ -orbitals, respectively. The total charge summed over all MO's was calculated to be C(-1.1) and Si(+1.6) ( $d$ -orbitals included). These results suggest that the C=Si double bond approximates a carbanion-siliconium ion pair,  $H_2C^- - Si^+H_2$ , rather than a diradical as is often suggested<sup>1</sup>.

Since the EHMO method does not include coulomb interactions, the charge separation is grossly overestimated. The charges calculated by CNDO, while lower, still indicate an exceedingly polar bond:



The calculated  $\pi$ -bond polarity is C(0.264) Si(-0.264). For comparison, the CNDO  $\pi$ -bond polarity of  $\text{H}_2\text{CO}$  is C(0.158) O(-0.158). For  $\text{C}_2\text{H}_4$  and  $\text{Si}_2\text{H}_4$ , the CNDO charges are C(-0.029) H(0.0145) and Si(0.161) H(-0.0805), respectively. The dipole moment calculated for  $\text{H}_2\text{CSiH}_2$  by the CNDO method is 2.99D. The strongest experimental evidence for the highly polar nature of the C=Si double bond is the extremely high intensity of the band at  $1407\text{ cm}^{-1}$  ascribed to the C=Si double bond stretch in matrix isolated  $\text{Me}_2\text{Si}=\text{CH}_2$ <sup>23</sup>.

### B. Internal rotation barriers

The barrier to rotating one end of the  $\text{H}_2\text{XYH}_2$  molecule  $90^\circ$  with respect to the other end should be a measure of the strength of the  $\pi$ -bond since, to a first approximation, the  $\sigma$ -bonds remain unchanged on rotation about their axes. Furthermore, the net X-Y bonding of the  $\pi_{\parallel}$  and  $\pi_{\perp}^*$  combination is minimal. The correlations between the MO's of the  $D_{2h}$  (planar) and  $D_{2d}$  (twisted) geometries for  $\text{E}_2\text{H}_4$  are shown in Fig. 2. In Table 3 the total electronic energies as calculated by the EHMO method are tabulated. The energy difference between the planar and twisted geometries gives the EHMO rotation barriers which are collected in Table 6. Also given is the loss in total X-Y overlap population ( $\Delta\rho$ ) upon twisting the molecules.

Calculations with both basis sets show the ordering of  $\pi$ -bond strengths as

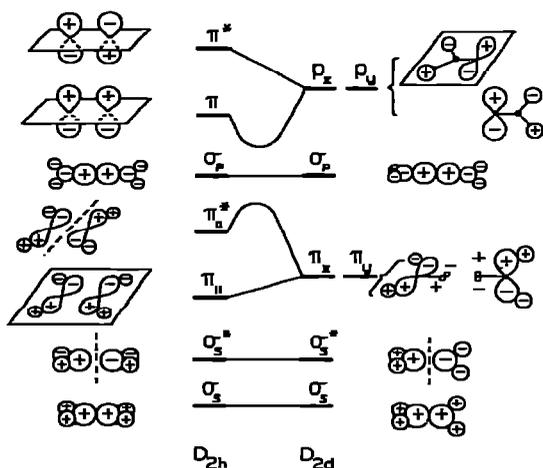


Fig. 2. Correlation of molecular orbitals of planar ( $D_{2h}$ ) and  $90^\circ$ -twisted ( $D_{2d}$ )  $\text{E}_2\text{H}_4$  (E = C, Si).

TABLE 6

EHMO ROTATION BARRIERS (kcal/mole) AND CHANGE IN OVERLAP POPULATION OF  $\text{H}_2\text{XYH}_2$

X	Y	$\Delta E(sp^d)$	$\Delta E(sp)$	$\Delta\rho(sp^d)$	$\Delta\rho(sp)$
C	C		81.21		0.312
C	Si	2.63	9.54	0.001	0.109
Si	Si	17.64	50.01	0.025	0.306

$C=Si < Si=Si < C=C$  in agreement with conclusions based on the population analyses. At first glance, it would appear that the  $sp$ -basis set gives a stronger  $\pi$ -bond than the  $spd$ -basis set in contradiction to the population analysis results. However, inclusion of the  $d$ -orbitals gives rise to greatly increased bonding capabilities in the excited states such as represented by the twisted geometry. This is dramatically illustrated by the changes in the overlap population upon twisting the molecule (Table 6). For example, the C-Si overlap populations in the " $p_C$ " MO (see below) of twisted  $H_2CSiH_2$  are 0.260 and 0.010 in the  $spd$ - and  $sp$ -basis sets, respectively. Of the 0.260, 0.259 is made up of  $C(2p_x)$ -Si( $xy$ ) overlap population, and the corresponding wavefunctions are:

$$p_C(sp d) = 0.883 C(2p_x) + 0.089 Si(3p_x) - 0.203 Si(xz) \dots$$

$$p_C(sp) = 0.986 C(2p_x) + 0.013 Si(3p_x) \dots$$

(terms involving H-atoms omitted)

An inspection of Table 3 also shows the stabilizing effect of  $d$ -orbitals on the twisted geometry. The energy of the  $p_x$ - $p_y$  pair of  $H_2SiSiH_2$  is lowered by almost 1 eV upon inclusion of the  $d$ -orbitals. For comparison, the  $d$ -orbital stabilization of the  $\pi$ -bond in the planar form is 0.3 eV, and the  $\sigma$ -bond stabilization is typically 0.1 eV. These results suggest that the Si  $d$ -orbitals are important not only in the excited electronic states of the equilibrium geometry, but also play an important role in lowest electronic states of "excited" or non-equilibrium geometries. In the particular case at hand, inclusion of  $d$ -orbitals has the effect of strengthening the  $\pi$ -bond to silicon, but also provides much lower energy pathways for its disruption.

There is, of course, a marked qualitative difference in the behavior of  $H_2CSiH_2$  upon twisting as compared to  $E_2H_4$  ( $E=C, Si$ ). The degeneracy of the  $\pi_x$ ,  $\pi_y$  and  $p_x$ ,  $p_y$  pairs (see Fig. 2) is lifted since the two ends of the molecule are no longer identical. In silaethylene, the  $\pi_x$  orbital is essentially  $C(2p)$ -H bonding (" $\pi_C$ ") and the  $\pi_y$  is  $Si(3p)$ -H bonding (" $\pi_{Si}$ "). Similarly, the  $p_x$  and  $p_y$  molecular orbitals are split into " $p_C$ " and " $p_{Si}$ " orbitals:

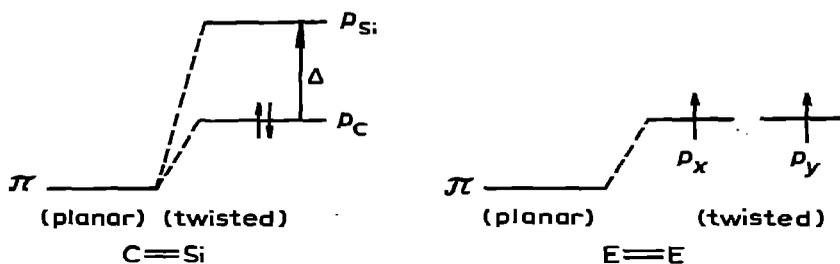


Fig. 3. Behavior of  $\pi$ -bond upon twisting.

The  $(2e)^2 (\equiv (p_x)^1 (p_y)^1)$  configuration of the twisted  $(D_{2d})E_2H_4$  gives rise to both triplet and singlet states:

$$(2e)^2 \rightarrow {}^3A_2 + {}^1A_1 + {}^1B_1 + {}^1B_2$$

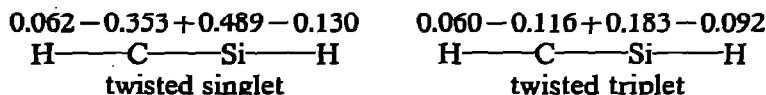
The  ${}^3A_2$  is expected to be the lowest energy state. Whether a singlet or triplet state is

lower in twisted  $H_2SCiH_2$ , depends on the separation,  $\Delta$  (Fig. 3), between the  $p_C$  and  $p_{Si}$  orbitals. The calculated EHMO separation is about 4 eV which is greater than the usual electron pairing energies. The EHMO thus predicts a singlet state for twisted silaethylene, and triplet states for  $D_{2d} E_2H_4$ .

These conclusions are substantiated by CNDO calculations on singlet and triplet species. For completeness, the triplet state energies of the planar species were also calculated. In the planar triplets, one electron each is placed in the HOMO and LUMO calculated for the planar singlets (see Table 4). The results are displayed in Table 7.

The interpretation of these results may not be unambiguous since the unrestricted<sup>12</sup> manner with which CNDO calculates open-shell energies leads to wavefunctions which are not eigenfunctions of the spin operator,  $S^2$ . In particular, the singlet functions for twisted  $E_2H_4$  are mixtures of functions corresponding to the three singlet states from the  $(2e)^2$  configuration, the  $M_s = 0$  component of the triplet state, and doubly excited states<sup>24</sup>. Nevertheless, the calculations show the triplet state of twisted  $Si_2H_4$  is the lowest energy excited state as is found for  $C_2H_4$ <sup>25</sup>.

Conversely, the singlet state (twisted) corresponding to  $H_2C^- - Si^+H_2$  is calculated to be the lowest energy excited state of silaethylene. This result is consistent with the suggestion that the  $\pi$ -bond in planar  $H_2CSiH_2$  is exceedingly polar; and upon twisting, the  $\pi$ -electrons remain essentially localized in the  $C(2p)$  orbital. In the triplet state of twisted  $H_2CSiH_2$ , one electron each is placed in the  $C(2p)$  and  $Si(3p)$  orbitals giving a lower dipole moment (Table 7) and less charge separation:



As was found with the EHMO method, the CNDO rotational barriers are  $C=Si < Si=Si < C=C$ , the values being 9, 34, and 111 kcal/mole, respectively (for the difference between ground state and lowest state of twisted molecule). For comparison,

TABLE 7

ELECTRONIC<sup>a</sup> AND TOTAL<sup>b</sup> CNDO ENERGIES FOR  $H_2XYH_2$  IN SINGLET AND TRIPLET STATES AND PLANAR AND TWISTED GEOMETRIES

Planar geometry					Twisted geometry				
X	Y	$E_e^a$	$E_T^b$	$\mu(D)^c$	X	Y	$E_e$	$E_T$	$\mu(D)$
<i>(i) Singlets</i>									
C	C	-994.44	-464.32		C	C	-987.88	-458.17	
C	Si	-799.70	-380.78	2.99	C	Si	-799.10	-380.37	3.19
Si	Si	-669.37	-308.81		Si	Si	-667.65	-307.29	
<i>(ii) Triplets</i>									
C	C	-984.21	-454.08		C	C	-989.20	-459.49	
C	Si	-797.16	-378.22	1.80	C	Si	-796.84	-378.12	1.80
Si	Si	-667.84	-307.24		Si	Si	-667.71	-307.35	

<sup>a</sup>Electronic energy. <sup>b</sup>Total energy =  $E_e - \sum_{A < B} Z_A Z_B / R_{AB}$ . All energies in eV. (c) Calculated dipole moment, see ref. 11, 12 for details.

Herzberg<sup>25</sup> gives the triplet and singlet states of  $C_2H_4$  in the  $D_{2d}$  conformation at < 82 and 115 kcal/mole, respectively, above the ground state. The "thermodynamic" strength of the  $C=C$   $\pi$ -bond is about 60 kcal/mole. Walsh<sup>26</sup>, using the kinetic data of Flowers and Gusel'nikov<sup>6</sup>, has estimated the  $C=Si$   $\pi$ -bond strength to lie between the limits,  $28 < D_\pi < 46$  kcal/mole. The much lower values calculated in this work probably arise from neglect of the coulombic terms in EHMO and undue involvement of  $d$ -orbitals in the CNDO method.

There are no reported physical properties of compounds of the type  $R_2Si=SiR_2$ , but Dyatkina *et al.*<sup>27</sup> have estimated the Hückel parameter,  $\beta_{SiSi}^\pi$ , to be about  $-1.0$  eV. They find that this value gives a reasonable band structure in solid silicon. The difference between the EHMO energies of the  $\pi$ -bond and the  $p$ -orbital is approximately equal to  $\beta^\pi$ . In the  $sp$ -basis set  $\beta^\pi \approx -1.1$  eV, while with the  $spd$ -basis set the "apparent"  $\beta^\pi = -1.4$  eV for the  $Si=Si$   $\pi$ -bond. The corresponding value for  $C=C$  is  $-1.80$  eV, compared with Dyatkina's<sup>27</sup> value of  $-1.7$  eV.

### C. Reactivity

1,1-Dimethyl-1-silaethylene,  $Me_2Si=CH_2$ , is known to dimerize to the 1,3-disilacyclobutane very readily. Barton<sup>23</sup> observed that the IR band ascribed to the  $C=Si$  stretch rapidly disappeared when the matrix-isolated  $Me_2Si=CH_2$  was allowed to warm. Flowers and Gusel'nikov<sup>6</sup> estimated the activation energy for the dimerization of  $Me_2Si=CH_2$  to be about 11 kcal/mole (*cf.* 37.7 kcal/mole for the dimerization of  $C_2H_4$ ).

The high polarity calculated for the  $C=Si$   $\pi$ -bond should facilitate head-to-tail dimerization. From a molecular orbital standpoint, the LUMO and HOMO of  $H_2CSiH_2$  are shown schematically in Fig. 4. The relative sizes of the atomic orbitals represent the contribution of that atomic orbital to the MO. Thus, in the  $\pi$ -bond, the electrons are strongly localized on carbon, but the reverse is true in the  $\pi^*$ -LUMO. In a head-to-tail dimerization, there is a net positive overlap (bonding) between the HOMO and LUMO—a situation that lowers the orbital symmetry restriction to dimerization<sup>28</sup>.

Woodward and Hoffmann<sup>29</sup> have cautioned that heteroatoms must be replaced by their isoelectronic carbon groupings when deciding if a reaction is

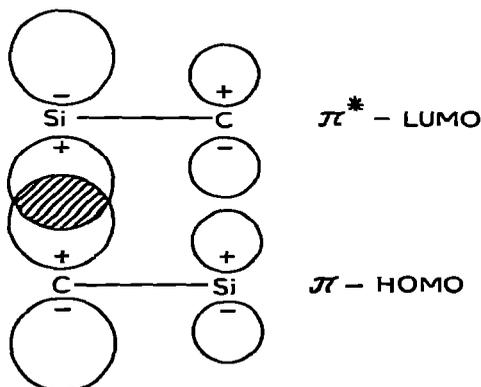


Fig. 4. Orientation of HOMO and LUMO in head-to-tail dimerization of  $C=Si$ .

allowed or forbidden. However, the symmetry restriction, while still present, will be decreased the greater the extent of electronic distortion introduced by the heteroatom. This conclusion follows irrespective of the overall strength of the  $\pi$ -bond. Thus,  $\text{H}_2\text{C}=\text{S}$  has a half-life of only about 6 min. at  $10^{-5}$  mm<sup>30</sup> even though the C=S bond strength is about 124 kcal/mole<sup>31</sup> (cf.  $D(\text{C}=\text{C})$  146 kcal/mole).

The general compression of the virtual levels upon inclusion of the  $d$ -orbitals is another effect which mitigates the symmetry barriers to reaction. In particular, a decrease in the  $\pi$ - $\pi^*$  separation,  $\Delta$ , should lower the activation energy for dimerization. The  $\pi$ - $\pi^*$  separation calculated for  $\text{H}_2\text{CSiH}_2$  is 4.48 and 4.30 eV in the  $sp$ - and  $spd$ -basis sets, respectively. The effect is much more pronounced in  $\text{Si}_2\text{H}_4$  (Fig. 5).

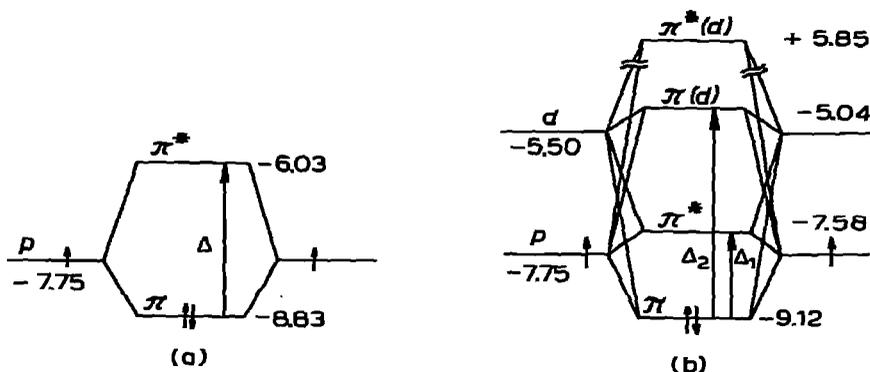


Fig. 5. EHMO energies of the  $\pi$ -levels of  $\text{Si}_2\text{H}_4$  without (a) and with (b)  $d$ -orbitals.

Without  $d$ -orbitals,  $\Delta = 2.80$  eV, but with  $d$ -orbitals,  $\Delta_1(\pi-\pi^*)$  is only 1.54 eV. In addition, a second  $\pi$ -level,  $\pi(d)$ , lies only 4 eV above the  $\pi(p)$  level. The presence of an additional empty  $\pi$ -level would also help stabilize the transition state associated with dimerization.

## CONCLUSIONS

The calculations on  $\text{H}_2\text{CSiH}_2$  are in accord with what little is known about this type of molecule. The C=Si  $\pi$ -bond is expected to be exceedingly polar and reactive, behaving like a carbanion-siliconium ion combination. The Si=Si  $\pi$ -interaction is calculated to be more substantial than the C=Si interaction; but the presence of low-lying excited states, coupled with the inherently weaker bond, bestow a kinetic lability on the molecule. The diradical,  $\text{H}_2\dot{\text{S}}\text{i}-\text{SiH}_2$ , is calculated to be only 1.5 eV less stable than the  $\pi$ -bonded form,  $\text{H}_2\text{Si}=\text{SiH}_2$ . Nevertheless, a suitably substituted derivative, e.g., tetra-*t*-butyldisilaethylene, might be amenable to isolation provided a low temperature synthesis can be devised. Such experimental aspects are currently under investigation in our laboratories.

## ACKNOWLEDGEMENTS

The author thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The University of Michigan Computing Center generously provided computer time.

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