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Investigation of the Electronic Structures of Vinyl Silicon Compounds by the Free Electron Method

D. R. Armstrong and P. G. Perkins

University of Newcastle upon Tyne

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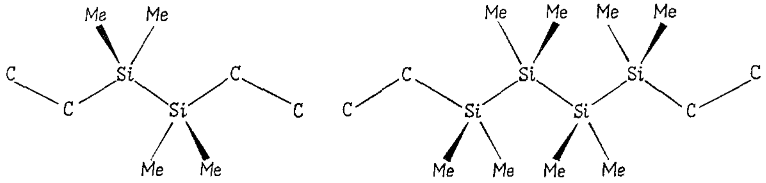
The two compounds, $Me_4Si_2\ (C_2H_3)_2$ and $Me_8Si_2\ (C_2H_3)_2$ have been studied by the antisymmetrized free electron molecular orbital method. Electron delocalisation over the whole chain *via* the silicon atoms occurs and a satisfactory account of the electronic spectra may be obtained.

$Me_4Si_2\ (C_2H_3)_2$ und $Me_8Si_4\ (C_2H_3)_2$ wurden nach der MO-Methode des freien Elektronengases behandelt. Delokalisierung der Elektronen über die Si-Atome der Kette wird festgestellt. Die berechneten Spektren sind zufriedenstellend.

On a étudié par la méthode des orbitales moléculaires d'électrons libres avec antisymétrisation les composés $Me_4Si_2(C_2H_3)_2$ et $Me_8Si_2(C_2H_3)_2$. Il se produit une délocalisation électronique le long de toute la chaîne par l'intermédiaire des atomes de silicium, et l'on peut rendre compte d'une manière satisfaisante des spectres électroniques.

1. Introduction and Method

Recently [*1*] the free electron model has been shown to be useful for calculating the positions of spectral bands in vinylboranes where electron delocalisation occurs between the empty boron p_π orbital and the vinyl groups. In the two methyl vinyl silanes, $Me_4Si_2\ (C_2H_3)_2$ and $Me_8Si_4\ (C_2H_3)_2$, the first intense electronic transition bands have been reported by Gilman [*3*], and are at 225 mμ ($\varepsilon_{\max} = 7900$) and 243 mμ ($\varepsilon_{\max} = 14000$) respectively. The marked difference in position of these relative to ethylene was ascribed to electron delocalisation between the vinyl groups *via* the intervening silicon atoms. Such an effect must arise by $p_\pi - d_\pi$ and $d_\pi - d_\pi$ bonding in which the empty $3d$ orbitals of the silicons participate.



I *II*

Fig. 1. Methylvinylsilanes

The situation here is not as well-defined as with vinylboranes because, whereas the latter possess a horizontal plane of symmetry which confers σ–π separability, in the silane case each silicon atom is in an approximately tetrahedral configuration (Fig. 1) which allows mixing between all three $3p$ orbitals and also three of the $3d$ set. In view of this, π overlap along the chain can only be effective if the d-orbitals do not participate in bonding to any extent with the carbon atoms of the methyl group: assuming this condition the $2p_\pi - 3d_\pi$ and $3d_\pi - 3d_\pi$ overlap should be quite strong.

The molecular chain of these systems may be regarded as a linear potential well inside which the π electrons are free to move restricted only by *a)* the height of the end walls and *b)* the central potential barrier imposed by the silicon atoms. This barrier extends from the mid-point of one C–Si bond to an equivalent point on the other; the overall length of the well is thus the total length of the chain plus one bond length (1.46 Å) at each end [*1*]. Other bond lengths necessary to the calculation were taken from ref. [*8*] and are:

$$\mathrm{C{=}C}: 1.35\ \text{Å};\quad \mathrm{Si{-}Si}: 2.30\ \text{Å};\quad \mathrm{Si{-}C}: 1.86\ \text{Å}\,.$$

The length of the potential wells are thus 11.64 and 16.24 Å.

The height of the central potential barrier should be equal to the difference in valence state ionisation potential of an electron in a carbon $2p_\pi$ orbital:

$$\mathrm{C}\,tri\,tri\,tri\,p_\pi \rightarrow \mathrm{C}^+tri\,tri\,tri\,,\quad I = 11.16\ \text{eV}\quad [4]$$

and an electron in a silicon $3d_\pi$ orbital,

$$\mathrm{Si}^-te\,te\,te\,te\,d_\pi \rightarrow \mathrm{Si}\,te\,te\,te\,te\,.$$

The only figure available in the literature for silicon relates to the process

$$\mathrm{Si}^-te\,te\,te\,te^2 \rightarrow \mathrm{Si}\,te\,te\,te\,te\,,\quad I = 2.78\ \text{eV}\quad [4]$$

and if this is employed the barrier height is 8.38 eV.

It is however possible to obtain a reasonable estimate of the energy of the process $\mathrm{Si}^-te\,te\,te\,te^2 \rightarrow \mathrm{Si}^-te\,te\,te\,te\,d_\pi$ because it will be close to that required for excitation of an electron from a $3p$ to a $3d$ orbital of the silicon negative ion. We cannot obtain this quantity directly for Si^-, but for the series of isoelectronic entities, P, S^+, Cl^{++}, the $3p - 3d$ separation energies are listed [*5*]:

$$\begin{aligned}
&\mathrm{P}: && {}^4S_{3/2} \rightarrow {}^2F_{5/2}\ E = 8.726\ \text{eV}\\
&\mathrm{S}^+: && {}^4S_{3/2} \rightarrow {}^4F_{3/2}\ E = 13.658\ \text{eV}\\
&\mathrm{Cl}^{++}: && {}^4S_{3/2} \rightarrow {}^4F_{3/2}\ E = 18.164\ \text{eV}\,.
\end{aligned}$$

From these figures, coupled with the appropriate ionisation data [*4*], the d-ionisation potentials for the above are found to be 3.390, 10.673, 22.799 eV, respectively. Hence the corresponding quantity for Si^- may be readily obtained by extrapolation using the expression

$$I = A\,Z^{*2} + B\,Z^* + C$$

in which Z^* for the members of the series (non-Slater [2]) are taken as 1.5 (Si^-), 2.5 (P), 3.5 (S^+), 4.5 (Cl^{++}). This leads finally to a value of 0.950 eV for the d-ionisation potential of Si^- and of 10.21 eV for the height of the C–Si barrier.

The solution to the barrier problem which incorporates finite boundary walls (providing for ionisation of the molecule) have been given before [*1*]. For compatibility with the magnitude of the barrier (10.21 eV) the end wall height was taken as 25 eV and for comparison, a second calculation was performed in which the above two parameters were given the values 8.38 and 30 eV respectively.

The core eigenenergies were calculated using a procedure written for the Newcastle University KDF 9 computer and finally the energies of the electronic eigenstates of the molecule obtained from the expression [7]

$$E\,{}^{1,3}\Psi_{i,a} - E\,{}^{1}\Psi_0 = I_a + \sum_j (2\,J_{ja} - K_{ja}) - I_i - \sum_j (2\,J_{ij} - K_{ij}) - \\ - (J_{ja} - K_{ia}) \pm K_{ia}\,.$$

The integrals J_{ij}, K_{ij} may be computed by OLSEWSKI's method [6]. Finally, the electronic configurations were allowed to interact under C_{2h} symmetry (Fig. 1) (c. f. *trans*-butadiene) and the A_g and B_u states separated. Intensities were not calculated as the one-dimensional free electron model can make no allowance for transitions polarized at right angles to the chain. However, qualitatively we should expect 0 → 0 transitions to ${}^1B_u$ states (V_{23}, V_{14}) to be strongly allowed (polarized along the chain) whereas those to ${}^1A_g$ states (V_{13}, V_{24}) will be forbidden or at least only weakly allowed by chain twisting.

2. Result and Discussion

The results of the calculations are collected in Tab. 1 and 2.

Superimposition of a central barrier on a linear well attenuates the symmetric energy levels mainly and causes their convergence towards the next higher antisymmetric one (Tab. 1). For the disilane the two lowest core energies are equal but the second pair are separated slightly (0.05 — 0.14 eV). For the tetrasilane the longer barrier brings about a merging of both pairs of levels. We therefore expect very similar energies for all four bands, the differences being dictated by the magnitude of the coulomb and exchange terms.

Tab. 2 lists the final energies for both calculations after electron interaction was included, and are relative to zero ground state energy. They predict that, for the disilane, strong bands should occur at 216 — 225 mμ and at 198 — 203 mμ. The former peak has been observed. There may be further weak absorption at longer wavelengths although the bands at 235 mμ and 225 mμ may merge. Each

Table 1. *Core energies* (eV)

Comp.	E_1	E_2	E_3	E_4	Δ (1.3)	Δ (1.4)	Δ (2.3)	Δ (2.4)
		Barrier = 8.38 eV			End walls = 30 eV			
I	1.633		6.135	6.272	4.503	4.639	4.503	6.639
II	1.633		6.204		4.571			
		Barrier = 10.21 eV			End walls = 25 eV			
I	1.660		6.354	6.408	4.694	4.748	4.694	4.748
II	1.660		6.381		4.721			

I — Tetramethyldivinyldisilane.
II — Octamethyldivinyltetrasilane.

Table 2. *Electronic state energies of vinylsilanes in* eV (*in* mμ)*

Comp.	State	V_{13} (A_g)	V_{14} (B_u)	V_{23} (B_u)	V_{24} (A_g)	T_{13}	T_{14}	T_{23}	T_{24}
		Barrier = 8.38 eV			End walls = 30 eV				
I	a	5.188	5.794	5.414	5.216	5.158	5.717	4.527	5.076
	b	5.271 (235)	6.115 (203)	5.520 (225)	5.772 (215)	4.943 (251)	6.044 (205)	4.626 (268)	5.717 (217)
II	a	5.062	5.339	5.224	4.985	5.040	5.344	4.588	4.884
	b	5.375 (231)	5.612 (221)	5.241 (237)	5.017 (247)	5.364 (231)	5.549 (223)	4.613 (269)	4.790 (259)
		Barrier = 10.21 eV			End walls = 25 eV				
I	a	5.433	5.903	5.659	5.325	5.163	5.521	4.711	5.061
	b	5.926 (209)	6.248 (198)	5.730 (216)	5.456 (227)	5.708 (217)	5.883 (211)	4.765 (260)	4.932 (251)
II	a	5.212	5.549	5.374	5.135	5.190	5.494	4.738	5.034
	b	5.521 (225)	5.759 (215)	5.388 (230)	5.161 (240)	5.511 (225)	5.696 (218)	4.760 (260)	4.937 (251)

* Relative to $^1\Gamma_1$ ground state of zero energy.
a — Before configuration interaction.
b — After configuration interaction.

absorption band of the tetrasilane should be shifted bathochromically with respect to those above with intense absorption manifest 215 – 221 mμ and 230 – 237 mμ with possible further weak absorption near 247 mμ. The first intense band measured differs from the one observed by 6 – 13 mμ ($\sim$ 0.15 eV). Hence the results are quite good for such a simple model.

The observed intensities of the strong bands in the tetra- and disilanes are in the approximate ratio 2:1. It seems therefore that in the former the two ^1B_u states overlap in energy but not in the latter. In agreement with this, all four calculated ^1A_g, ^1B_u states of the tetrasilane are close-lying whereas for the other compound the two ^1B_u states are separated by 22 mμ (eV). Small red shifts only are expected on going from disilane to tetrasilane. This is because on free electron theory the wave function decays exponentially in the barrier region and lengthening the path of delocalisation by inserting two more silicon atoms does not have nearly such a marked effect as if it were carbon atoms which were interposed. For the same reason, the π electron densities on the two inner silicon atoms in the tetrasilane will be very small indeed as also will be the silicon-silicon $d_\pi - d_\pi$ bond order between them. This pair of atoms should therefore be the most vulnerable to coordination with ligands.

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Prof. Dr. P. G. PERKINS
Dept. of Inorganic Chemistry, University
Newcastle on Tyne (Great Britain)