

QUANTUM CHEMICAL CALCULATIONS OF SATURATED, UNSATURATED, AND AROMATIC COMPOUNDS OF SILICON II*. VINYL COMPOUNDS

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SUMMARY

Quantum chemical calculations have been carried out for vinyl derivatives of silicon. σ systems were treated according to a modified Del Re method; π systems were studied by a one-electronic LCAO-MO method improved by the ω technique. Results obtained for trimethylvinylsilane are compared with those obtained by variance analysis for the analogous carbon, germanium and tin derivatives. These show good agreement with the experimental data for the vinyl compounds.

INTRODUCTION

There exists a formal relationship between the compounds of silicon formed with saturated radicals and the analogous carbon compounds¹. The difference between these two types of compounds is the higher $+I$ effect due to the lower electronegativity of silicon. The difference is much greater in the case of unsaturated derivatives. In vinyl and phenyl compounds, silicon exerts a $-M$ effect as well; in allyl and benzyl compounds also a hyperconjugative interaction together with weak $d-\pi$ bonding is possible. These effects are due to the delocalization caused by the overlap of d and p orbitals. In this paper the quantum chemical calculations of π -bond systems emerging as a consequence of delocalization will be discussed.

RESULTS AND DISCUSSION

Method used for the calculations

Utilizing the simplified assumptions of Hückel, the LCAO-MO method for one electron was chosen. However, when writing the energy matrix proper to the π -systems, the necessary energy terms (coulomb, and exchange integrals) were not adopted on the basis of empirical parameters given in the literature (no such parameters are available for bonds with silicon) or according to empirical equations, but were calculated with the help of the Tables of Integrals² from known bond lengths, and ionization energies.

* For Part I see ref. 1.

In effect it was an effective Hamiltonian with which we operated if Hückel parameters were selected ideally

$$\alpha_i = \int \varphi_i \cdot H_{\text{eff}} \cdot \varphi_i \cdot d\tau,$$

respectively

$$\beta_{ij} = \int \varphi_i \cdot H_{\text{eff}} \cdot \varphi_j \cdot d\tau,$$

which takes into account electron interaction as well as nuclear attraction potentials, yielding figures in better agreement with the experimental data. On the basis of experimental data, the α -coulomb integral of a carbon atom in benzene can be approximately calculated, as well as the β -exchange integral of the carbon-carbon bond in the ring. The parameter h of the coulomb integral of the i^{th} atom can be given by:

$$h_i = \frac{\alpha_i - \alpha}{\beta}$$

and the parameter k of the exchange integral for the bond between atoms i and j , as:

$$k_{ij} = \frac{\beta_{ij}}{\beta}$$

With the help of the Tables of Integrals the coulomb and exchange integrals without electron interactions, (H_i and H_{ij} respectively,) can be calculated. Let the values obtained for the carbon atom of benzene ring be designated by H_C (the coulomb integral) and H_{CC} (the exchange integral) respectively. It seems justified to assume that the same ratios prevail between integrals irrespective of electron interactions as between the integrals (which account also for electron interactions, to a certain measure) expressed by the H_{eff} operators:

$$h_i = \frac{H_i - H_C}{H_{CC}} = \frac{\alpha_i - \alpha}{\beta},$$

respectively

$$k_{ij} = \frac{H_{ij}}{H_{CC}} = \frac{\beta_{ij}}{\beta}.$$

In this way, in the zeroth approximation we used the h and k parameters obtained with the help of the Tables of Integrals. Starting from the zeroth approximation, the results were corrected by the ω -technique, the amelioration thus achieved is due to taking (empirically) into account the electron interactions³.

In order to determine the quantum-chemical integrals between $2p\pi_r - 2p\pi_j$ and $2p\pi_r - 3d\pi_j$ (i and j being contiguous atoms) the eigen-value had to be determined on the basis of Hamilton operators [atomic orbital eigen-functions (φ_i) according to Slater were adopted]. To solve eigen-value problems, three fundamental integral values must be known. The overlap integral has the form:

$$S_{ij} = \int \varphi_i \cdot \varphi_j \cdot d\tau$$

The exchange integral is:

$$\beta_{ij} = \int \varphi_i \cdot H \cdot \varphi_j \cdot d\tau = \int \varphi_j \cdot H \cdot \varphi_i \cdot d\tau = E_j \cdot S_{ij} + \int \varphi_i \cdot \frac{Z_i^*}{r_i} \cdot \varphi_j \cdot d\tau = E_j \cdot S_{ij} + A_i$$

where E_j = ionization energy assigned to the φ_j atomic orbital, Z_i^* = the effective nuclear charge of the atom i , r_i = distance between the i^{th} nucleus and the electron, Z_i^*/r_i = the potential field of the i^{th} atom, and A_i = the reduced exchange integral.

The coulomb integral is:

$$\alpha_i = \int \varphi_i \cdot H \cdot \varphi_i \cdot d\tau = E_i + \int \varphi_i \cdot \frac{Z_j^*}{r_j} \cdot \varphi_i \cdot d\tau = E_i + C_j$$

where C_j = reduced coulomb integral.

According to Halmann and Hartmann⁴, it is easier to calculate the integrals, applying the hyperbolic co-ordination system rather than the polar coordinates. The new variables are (R is the bond length)

$$\begin{aligned} r_i + r_j &= R \cdot \xi & r_i - r_j &= R \cdot \eta \\ p &= \frac{1}{2}(\mu_i + \mu_j) \cdot \frac{R}{a_H} & (a_H &= 0.52917 \text{ \AA}) \\ t &= \frac{\mu_i - \mu_j}{\mu_i + \mu_j} & \mu_i &= \frac{Z_i^*}{n_i^*} \end{aligned}$$

where n_i^* is the effective principal quantum number of the i^{th} atom.

According to Slater, the analytic expressions of the atomic orbital eigenfunctions which determine φ_i and φ_j , respectively, are as follows:

$$\begin{aligned} \varphi(2p\pi) &= \left(\frac{3}{4} \frac{\mu^5}{\pi} \right)^{\frac{1}{2}} \cdot r \cdot e^{-\mu \cdot r} \cdot \sin \vartheta \cdot \cos \varphi \\ \varphi(3d_{-x}) &= \frac{\sqrt{2}\mu^{\frac{3}{2}}}{\sqrt{3\pi}} \cdot r^2 \cdot e^{-\mu \cdot r} \cdot \sin \vartheta \cdot \cos \vartheta \cdot \cos \varphi \end{aligned}$$

For partial integrals the definitions are

$$A_n(\alpha) = \int_1^{\infty} x^n \cdot e^{-\alpha \cdot x} \cdot dx \quad \text{and} \quad B_n(\alpha) = \int_{-1}^{+1} x^n \cdot e^{-\alpha \cdot x} \cdot dx$$

where α is a parameter fixed on the basis of the effective nuclear charge, and bond length (with variables $x = \xi$ and η , respectively). According to these equations and definitions the values of the fundamental integrals are given as follows.

$2p\pi_i - 2p\pi_j$ bond

Overlap integral.

$t \neq 0$

$$S = \frac{p^5}{2^5} \cdot (1 - t^2)^{\frac{3}{2}} \cdot [A_4 \cdot (B_0 - B_2) + A_2 \cdot (B_4 - B_0) + A_0 \cdot (B_2 - B_4)]$$

$$t = 0$$

$$S = \frac{p^5}{120} \cdot (5A_4 - 6A_2 + A_0)$$

Reduced exchange integral.

$$t \neq 0$$

$$A_i = \frac{p^6}{8R^2} \cdot (1-t)^{\frac{3}{2}} \cdot (1+t)^{\frac{3}{2}} \cdot [(A_3 - A_1) \cdot (B_0 - B_2) + (A_2 - A_0) \cdot (B_3 - B_1)]$$

$$A_j = \frac{p^6}{8R^2} \cdot (1+t)^{\frac{3}{2}} \cdot (1-t)^{\frac{3}{2}} \cdot [(A_3 - A_1) \cdot (B_0 - B_2) + (A_2 - A_0) \cdot (B_1 - B_3)]$$

$$t = 0$$

$$A = \frac{p^6}{6R^2} \cdot (A_3 - A_1)$$

In the case of both, the partial integrals $A_n: \alpha = p$, and $B_n: \alpha = p \cdot t$.

Reduced coulomb integrals.

$$t \neq 0: C_j = \frac{p^6}{8R^2} \cdot (1+t)^5 \cdot (1-t) \cdot [(A_3 - A_1) \cdot (B_0 - B_2) + (A_2 - A_0) \cdot (B_1 - B_3)]$$

$$C_i = \frac{p^6}{8R^2} \cdot (1+t) \cdot (1-t)^5 \cdot [(A_3 - A_1) \cdot (B_0 - B_2) + (A_2 - A_0) \cdot (B_1 - B_3)]$$

$$\alpha = p \cdot (1-t) \quad (\text{equally for } A_n \text{ or } B_n)$$

$$t = 0$$

$$C_i = C_j = \frac{p^6}{8R^2} \cdot [(A_3 - A_1) \cdot (B_0 - B_2) + (A_2 - A_0) \cdot (B_1 - B_3)]$$

$$\alpha = p$$

$2p\pi_i - 3d\pi_j$ bond

Overlap integral.

$$t \neq 0$$

$$S = \frac{p^6}{32\sqrt{6}} \cdot (1+t)^{\frac{3}{2}} \cdot (1-t)^{\frac{3}{2}} \cdot [A_5 \cdot (B_3 - B_1) + A_4 \cdot (B_0 - B_2) + A_3 \cdot (B_1 - B_5) + A_2 \cdot (B_4 - B_0) + A_1 \cdot (B_5 - B_3) + A_0 \cdot (B_2 - B_4)]$$

Reduced exchange integrals.

$$t \neq 0$$

$$A_i = \frac{p^7}{8\sqrt{6} \cdot R^2} \cdot (1-t^2)^{\frac{3}{2}} \cdot [(A_4 - A_0) \cdot (B_3 - B_1) + (A_3 - A_1) \cdot (B_0 - B_4)]$$

$$A_j = \frac{3p^7}{16\sqrt{6} \cdot R^2} \cdot (1+t)^{\frac{5}{2}} \cdot (1-t)^{\frac{5}{2}} \cdot [(A_4 + A_0 - 2A_2) \cdot (B_3 - B_1) + (A_3 - A_1) \cdot (B_0 + B_4 - 2B_2)]$$

In the case of A_m , $\alpha = p$; in that of B_m , $\alpha = p \cdot t$.

Reduced coulomb integrals.

$t \neq 0$

$$C_j = \frac{3p^6}{16R^2} \cdot (1+t)^5 \cdot (1-t) \cdot [(A_3 - A_1) \cdot (B_0 - B_2) + (A_2 - A_0) \cdot (B_1 - B_3)]$$

$\alpha = (1+t) \cdot p$

$$C_i = \frac{p^8}{48R^2} \cdot (1-t)^7 \cdot (1+t) \cdot [(A_5 - A_1) \cdot (B_2 - B_4) + (A_4 - A_2) \cdot (B_1 - B_5) + (A_4 - A_0) \cdot (B_1 - B_3) + (A_3 - A_1) \cdot (B_0 - B_4)]$$

$\alpha = (1-t)p$

The value of the integrals is a function of bond length and effective nuclear charge as shown by the above expressions. For Slater type functions the effective charge can be calculated according to Slater's rule⁵.

The effective nuclear charge of $3d$ electrons, is equal to zero according to Slater's rule, but it is used as a variation parameter. We have also calculated the effective nuclear charges and variation parameters, from the ionization potentials belonging to the individual atomic ground states as follows:

$$E_0 = -\frac{1}{2} \left(\frac{Z^*}{n^*} \right)^2$$

where E_0 = ionization potential in atomic units. Thus real variation parameters for the carbon and silicone atoms were obtained and thereby basic tendencies were obtainable for bond structure of organosilicon compounds.

According to Slater's rules, the effective nuclear charge for the $2p\pi$ orbital of the carbon atom is 3.25, whereas the effective nuclear charge calculated from the ionization energy of the $2p\pi$ orbital of carbon is 1.64. We calculated the quantum

TABLE I

RESULTS OF QUANTUM CHEMICAL CALCULATIONS DEALING WITH ETHYLENE (a.e. = atomic units)

E_0	1.64063 a.e.	0.41014 a.e.	11.16 eV
Z^*	3.25	1.64	
S	0.27126	0.62626	
α	2.00158 a.e.	0.88360 a.e.	7.5 eV
β	0.57784 a.e.	0.45597 a.e.	3.0 eV
I	2.58 a.e.	1.34 a.e.	10.5 eV
A	1.42 a.e.	0.42 a.e.	4.5 eV
ΔE	1.16 a.e.	0.92 a.e.	6.0 eV
α/β	3.4638	1.8962	2.5
Δ	± 0.27 a.e.	± 0.13 a.e.	

chemical integrals of ethylene defined above on the basis of each of these effective nuclear charges, and thus the molecular ionization energy I , the electron affinity A , the atomic ionization energy E_0 , the excitation energy ΔE , deducible from them

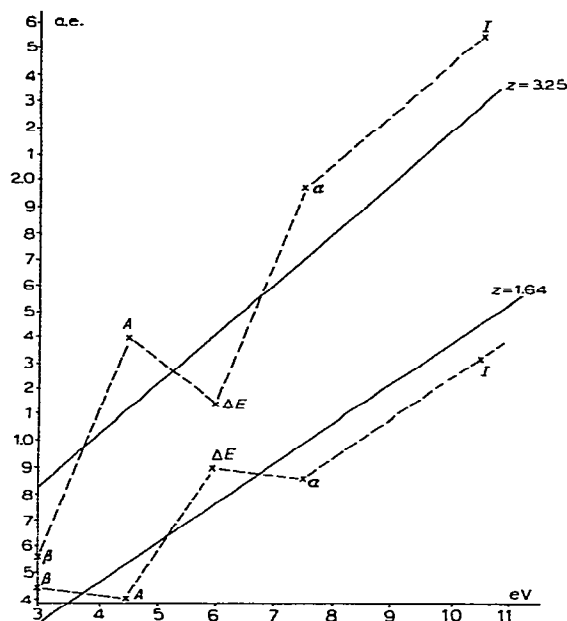


Fig. 1. Connection between calculated and experimental figures of the energy of ethylene.

(Table 1). In Fig. 1 the energy figures β , A , ΔE , α , and I obtained with the two methods are plotted as functions of experimental data. The upper straight line shows the correlation between the values calculated from Slater's effective nuclear charges and the values determined experimentally. According to Fig. 1 the deviation of energy values from the regression line is smaller when these are calculated on the basis of ionization energy. Figures in the last line in Table 1 show average deviations of energy values from this straight line. The lines ascend, in both the cases but the deviations differ in sign.

Though from ionization energies smaller figures are calculated than from Slater's effective nuclear charges, these smaller figures are still far higher than energies found experimentally. Thus it seems logical to define coulomb and exchange integrals by the parameters h and k previously mentioned. By the parameter-method absolute values are obtained for partial charges and π -bond orders, and relative values for the energy of molecular orbitals.

Vinyl derivatives

The modified method of Del Re was used to calculate the data for the σ systems, *i.e.* partial charges and dipole moments (the vinyl compounds of carbon and silicon). Quantum chemical calculations for the π systems of these compounds were carried out according to the LCAO-MO method modified by the one-electron ω technique. In Fig. 2 the partial charge distribution of the σ system of tert-butyl-ethylene is shown, and, in parantheses, the π partial charges respectively pertaining to

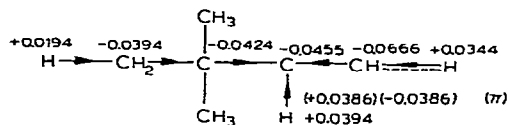


Fig. 2. Charge distribution of tert-butylethylene.

the α and β carbon atoms of the vinyl group. The σ dipole moment is 0.1299 D, in its calculation regular tetrahedric form, respectively bond angles of 120° which correspond to sp^2 hybridization, were assumed. The values for bond lengths being 1.54 Å for C-C, 1.353 Å for C=C, and 1.09 Å for C-H.

The σ dipole moment vector forms an angle of $70^\circ 30'$ with the bond axis of the vinyl group which corresponds to the vector direction of the π dipole moment. Thus the vector quantity and direction of the π dipole moment can be calculated taking 0.319 D as the value⁶ of the measured resultant dipole moment. It was found to be 0.234 D, and due to the $+I$ effect of the tert-butyl group it is directed from the α towards the β carbon atom of the vinyl group. It thus follows that 0.0386 is the partial charge of π . Since β carbon is more negative than α carbon, (according to Markownikow's rule) an addition reaction of hydrogen halides to tert-butylethylene occurs; and as σ and π dipole moments operate in the same direction their resultant vector will be greater than that of silicon derivatives.

For the π system of the analogous trimethylvinylsilane, tri-centric molecular orbitals were postulated. The integral values originally given in atomic units were recalculated to parameter-form, for which the α coulomb integral of the carbon in benzene, and the β exchange integral between the carbon atoms in the ring, were selected.

In the case of the ω technique, the value of ω was taken to be 1.4. Table 2

TABLE 2

INTEGRAL VALUES FOR TRIMETHYLVINYLSILANE. ORIGINAL FIGURES, AND THOSE OBTAINED BY ITERATION

	h_{Si}	$h_{C(1)}$	$h_{C(2)}$	k_{SiC}	k_{CC}
0	-1.8152	0	0	0.3374	1.032
∞	-1.8343	-0.0012	0.0203	0.3374	1.032

shows the coulomb and exchange integrals at the start and after successive approximations. Table 3 lists eigen-values E_1 , E_2 and E_3 , linear coefficients c_1 , c_2 , and c_3 , and the value for the $\pi-\pi^*$ transition. In Fig. 3 the first picture is that of the σ charge

TABLE 3

SYSTEM OF LINEAR COEFFICIENTS FOR TRIMETHYLVINYLSILANE

	c_1	c_2	c_3
$E_1 = \alpha + 1.0616\beta$	0.0825	0.7077	0.7017
$E_2 = \alpha - 0.9593\beta$	0.2565	0.6653	-0.7012
$E_3 = \alpha - 1.9177\beta$	0.9630	-0.2380	0.1268
$\pi-\pi^*$ transition		2.0209 β	

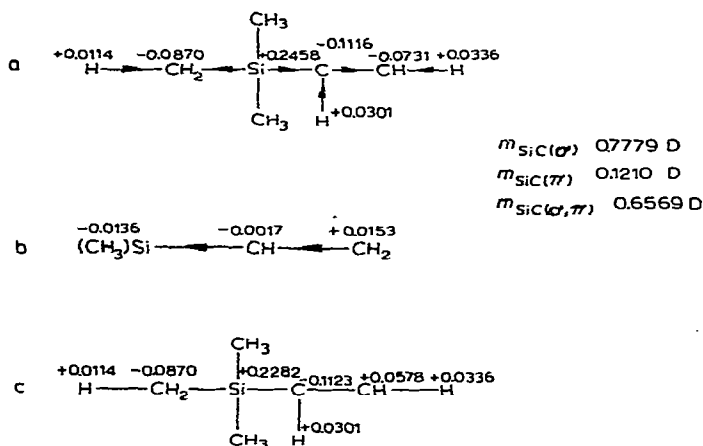


Fig. 3. Charge distribution of trimethylvinylsilane.

distribution of the molecule, the second is that of the π charge distribution, the last symbol stands for the resultant charges. It shows that σ and π charge shifts are in opposite directions therefore the overall partial charge of the silicon atom is smaller than that in tetramethylsilane or tetraethylsilane¹. Consequently, σ and π dipole moments pertaining to the carbon-silicon bond (designated as $m_{\text{SiC}(\sigma)}$ and $m_{\text{SiC}(\pi)}$) are also oppositely directed. In the calculation of dipole moments, regular tetrahedrons, and angles of 120° (corresponding to sp^2 hybridization) were assumed, and bond lengths known from the literature⁷ were used 1.347 Å for C=C; 1.09 Å for C-H; 1.853 Å for Si-C(vinyl); 1.888 Å for Si-C(methyl).

The calculated resultant dipole moment was 0.08 D which is in an acceptable approximation to the experimentally ascertained⁶ value of 0.229 D. The hydrogen atoms of the vinyl group are more positive than those of the methyl group, as supported by the values for the proton signals (3.73 for a hydrogen on the α -carbon, 4.12 for one on the β -carbon, and 9.83 for one in a methyl group). The positive partial charge of the hydrogen atoms in vinyl group is smaller than that in an analogous tert-butylethylene; which is also due to the $+I$ effect being higher in silicon than in carbon atom.

If the methyl groups of trimethylvinylsilane are substituted by hydrogen, there occurs a small change in the σ distribution (Fig. 4). Disregarding the σ - π

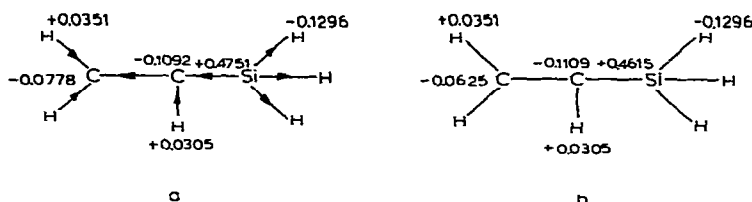


Fig. 4. σ (a) and σ,π (b) charge distribution of vinylsilane.

interaction, for the π system of this compound same results were applied as those for trimethylvinylsilane. Owing to the electrophilic character of the three hydrogen atoms bonded to silicon, the partial charge of the hydrogen atoms of the vinyl group increases slightly.

In trimethylvinylsilane the $\pi-\pi^*$ electron transition is smaller (2.0648β) than in ethylene, and this corresponds to the bathochromic shift (λ_{\max} 178, and 165 nm, respectively) as evident from the ultraviolet spectra. The bathochromic shift increases further in the vinyl derivatives of germanium and tin¹. Quantum chemical calculations with variance analysis were carried out in order to explain this observed shift.

In tert-butylethylene the electron repelling effect of the tertiary butyl group causes the exchange integral of the carbon-carbon bond in the vinyl group to decrease which explains the bathochromic shift with respect to ethylene. Thus if for one carbon atom of the vinyl group, $\alpha + h_1 \cdot \beta$ and for the other $\alpha + h_2 \cdot \beta$ and the exchange integral is $k \cdot \beta$, then the excitation energy for a $\pi-\pi^*$ transition is given by:

$$\Delta m = [(h_1 - h_2)^2 + 4k^2 \cdot \beta]^{\frac{1}{2}}$$

$\pi-\pi^*$ transition is a function of variation parameters h_1 , h_2 , and k . Thus according to the exponential equation:

$$k \cdot \beta = -B \cdot e^{-(b \cdot R/a_H)}$$

neglecting $(h_1 - h_2)^2$ being a very small digit, the parameter k for vinyl compounds is smaller⁸ than for ethylene. B and b , are material constants. The vinyl compounds have greater bond lengths and lower bond orders. A change of the value of k in this direction reduces Δm (λ_{\max} for ethylene is 178 nm).

Concerning the vinyl compounds of Group IV elements (taking into account the tendency of the changes in dipole moment also) a reasonable explanation of the shift in UV absorption maxima is possible assuming that silicon (and also germanium and tin) shows $-M$ effects. In quantum chemical calculations, choosing β for the exchange integral of the C=C bond, α for the coulomb integral of carbon atoms, $\alpha_i = \alpha + h \cdot \beta$ for the coulomb integral of the hetero-atom, and $k \cdot \beta$ for the integral of the exchange between hetero-atom and the carbon atom, the energies of the molecular orbitals are found as the solutions of the determinant of the third order matrix that can be thus constructed. Fig. 5 shows $\Delta m = E_2 - E_1$ energies corresponding to the

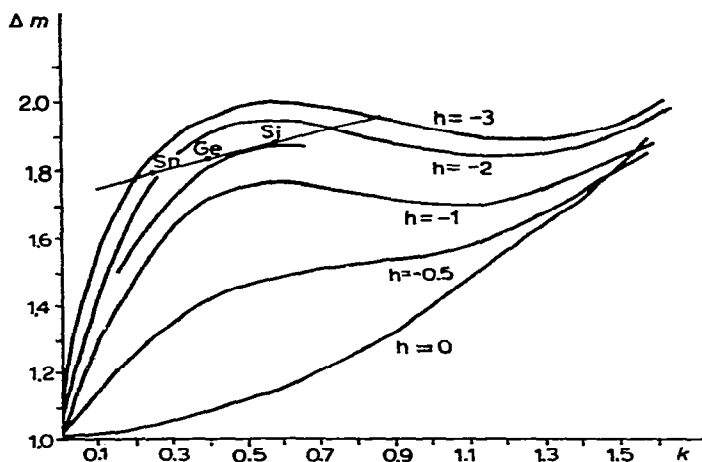


Fig. 5. Transition energies, as functions of h and k variable parameters, of the vinyl derivatives of Group IV elements.

various π - π^* transitions according to the variations of parameters k and h . With the help of the variation parameters a set of third order parabolic curves are obtained for Δm . On the basis of ionization energies and approximate values of exchange integrals, the value of parameter h for silicon germanium, and tin is -1.5 and -3 , parameter k varies between 0.8 and 0.2 . If these two parameters are diminished from silicon towards tin, the several approximate Δm values will be found along a straight line drawn across the set of curves. The energy needed for transition grows less as values of k and h decrease. This is in accordance with the fact that the bathochromic shift found experimentally¹ is not very significant.

The delocalization energy of trimethylvinylsilane is 0.0584β . The π -bond order of carbon-silicon bond is 0.1067 . The bond order (0.9932) of the vinyl group is smaller than that of ethylene, pointing to a shift of the electron pair in the direction of the silicon atom. Therefore the Raman frequency (1595 cm^{-1}) assigned to the C=C group is also lower, than that for ethylene, or tert-butylethylene (1648 cm^{-1})⁹.

Quantum chemical calculations by Matteson¹⁰ dealing with vinylboric acid esters have lead to similar results. Matteson found the boron-carbon bond to be partially of a double-bond type (π bond order 0.268) since the π electron pair will be co-ordinated to the unoccupied p -orbitals of boron. The π bond order of the vinyl group is 0.962 . It reveals the relationship between silicon and boron.

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