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QUANTUM CHEMICAL CALCULATIONS OF SATURATED, UNSATURATED, AND AROMATIC COMPOUNDS OF SILICON IV*. ALLYL AND BENZYL DERIVATIVES

J. NAGY AND J. RÉFFY
Department of Inorganic Chemistry, University of Technical Sciences, Budapest (Hungary)

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SUMMARY

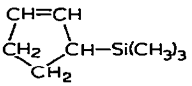
Quantum-chemical calculations showed that in compounds containing an allylsilicon group, besides the hyperconjugation effect of the CH_2 group, the bond between the *d* orbital of silicon and the carbon atom in β position relative to it has a π bond order of about 8%, and the long bond of about 5%. A similar long bond is formed also in the case of trimethylbenzylsilane.

RESULTS AND DISCUSSION

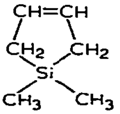
The ultraviolet absorption maximum of trimethylallylsilane appears at longer wavelengths, than that of trimethylvinylsilane[1]. (The situation is similar with the analogous germanium compounds.) The bathochromic effect of the allyl derivative (I) is due to an expansion of the conjugated system, as compared to the vinyl derivative.

$CH_2{=}CH{-}CH_2{-}Si(CH_3)_3$

(I)



(II)



(III)

The increased conjugation may be due to the hyperconjugative effect of the methylene group. The absorption maximum appears at a still longer wavelength for the cyclic derivative, 3-(trimethylsilyl)cyclopentene (II), containing an allylic double bond[2,3]. On the other hand, for the compound (III) where silicon atom becomes a part of the five-membered ring, the maximum absorption appears at a position closer to that of ethylene. Thus the bathochromic shift of allylsilane cannot be explained by the hyperconjugation effect alone. It seems more probable that the vacant *d* orbital of the silicon atom is capable to form with the *p* orbital of the carbon atom in position β with respect to the silicon atom a so called long bond (d–π bond), provided the steric

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* For part III see ref. 5.

arrangement of the compound makes it possible. The formation of the so called long bond further increases the conjugation. In trimethylallylsilane, the overlapping of *d* orbital of the silicon atom, and thus, the magnitude of the long bond, will vary with the angle of rotation about the rotational axis between the carbon atoms in α and β positions. In the compound (II) this axis is fixed, the long bond is greater than in (I) the conjugation of the molecule is stronger, thus its spectrum exhibits a bathochromic shift. The overlap mentioned above cannot occur in compound (III), and thus the absorption maximum considerably regresses. For a more exact study of the phenomena, calculations were made concerning the σ-system of trimethylallylsilane and its three possible π-systems employing the methods described earlier[1]. The conceivable π-systems are shown in Fig. 1. The energy of the molecular orbitals was calculated,

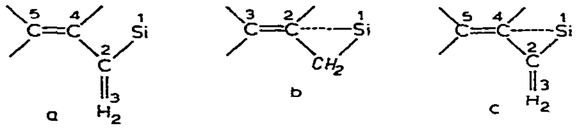


Fig. 1. Numbering of the assumed π-systems of trimethylallylsilane: a. hyperconjugation; b. long bond; c. hyperconjugation + long bond.

assuming in the first case hyperconjugation effect, in the second the formation of long bond, and in the third the simultaneous presence of both the hyperconjugation effect as well as the long bond.

Integral values used in the calculations are: $\alpha_{Si}=\alpha-1.8152\ \beta$, $\beta_{SiC}=0.3374\ \beta$, $\alpha_{H_2}=\alpha-0.5\ \beta$, $\beta_{C=H_2}=3.06\ \beta$. Exchange integral between the carbon atom of the methylene group and the one adjacent to it is: 0.8 β, and that corresponding to the long bond is less than β_{SiC} (since the bond distance is 2.78 Å instead of 1.54 Å, the $3d$ orbital of silicon and the $2p\pi$ orbital of carbon include an angle, and the rotation of the silicon atom about the axis diminishes the possibility of favourable overlaps). The calculated value of the latter integral is 0.1283 β.

The plot of the wave number (of the UV maxima) of related compounds against the calculated Δm transition (π–π^* transition) must give a linear correlation. If the corresponding values for ethylene, trimethylvinylsilane and trimethylallylsilane are plotted (assuming both hyperconjugation and long bond for trimethylallylsilane) the three points must lie on a straight line (Fig. 2). If, however, the exclusive presence of

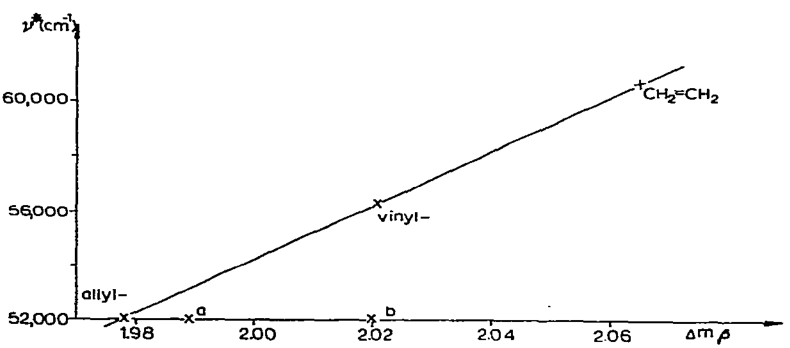


Fig. 2. Wave number of the absorption maxima of ethylene, vinyl- and allylsilane, and correlation between the energies of transition.

hyperconjugation, or alternatively, of the long bond is assumed (points marked by a and b, respectively, on the diagram), the point representing trimethylallylsilane is at a considerable distance from the straight line. The energies of the molecular orbitals are summarized in Table 1.

TABLE 1

ENERGIES OF THE MOLECULAR ORBITALS OF TRIMETHYLVINYLSILANE (I) AND 3-(TRIMETHYLSILYL)CYCLOPENTENE (II)

	(I)	(II)
E_1	$\alpha+2.9717\beta$	$\alpha+2.1762\beta$
E_2	$\alpha+0.9755\beta$	$\alpha+0.9107\beta$
E_3	$\alpha-1.0019\beta$	$\alpha-0.9530\beta$
E_4	$\alpha-1.8174\beta$	$\alpha-1.8520\beta$
E_5	$\alpha-3.4432\beta$	$\alpha-2.5967\beta$
Δm	1.9774β	1.8637β

Thus the most probable representation of the bond system of trimethylallylsilane will be the one calculated with the assumption of the simultaneous presence of both the long bond and hyperconjugation. The σ-,π- and the summarized (σ,π) charge distribution of the molecule is shown in Fig. 3. The silicon atom has a small partial negative π charge, the carbon atom in β position to the silicon atom a partial positive π charge, while the γ carbon atom has a partial negative charge. The result is in good agreement with the theory on the decomposition mechanism of allylsilanes[4], where the γ carbon atom first takes up a proton during acid decomposition, and the β

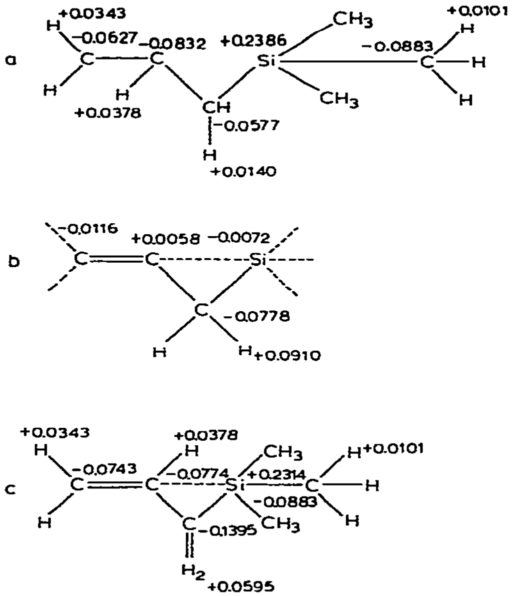


Fig. 3. Charge distribution of trimethylallylsilane: a. σ-charges; b. π-charges; c. resultant charges.

carbon atom of the cation thus formed binds the acid anion by addition. Knowing the partial charges, σ and π the resulting dipole moment have been calculated (bond distances used: Si–C 1.87 Å; C=C 1.353 Å; C–C 1.54 Å; C–H 1.09 Å). The values being 0.253 D for the σ-system and 0.293 D for the π-system. The two dipole moment vectors include an angle of 70°, and their resultant vector is 0.448 D which is in good agreement with the value 0.58 D, (the dipole moment measured[1]).

Similarly, a structure consistent with the hyperconjugation effect of the CH group and the presence of the long bond may be assumed for the cyclic compound (II). The values of the integrals differ at two sites, as compared to those for trimethylallylsilane. In the C–H hyperconjugation group the exchange integral is 2.16 β. Owing to the C–C bonding axis, being fixed in the ring, overlap resulting in the long bond has twice the probability as in the case of trimethylallylsilane, and thus the corresponding exchange integral is 0.2566 β. Thus the transition Δm calculated with above values, indicates a bathochromic shift as compared to compound (I) (Table 1). In spite of no experimental spectroscopic data being available for compound (II), this tendency can be established on the basis of the spectra of analogous germanium compounds. Fig. 4 summarizes results calculated for the charge distribution of the molecule.

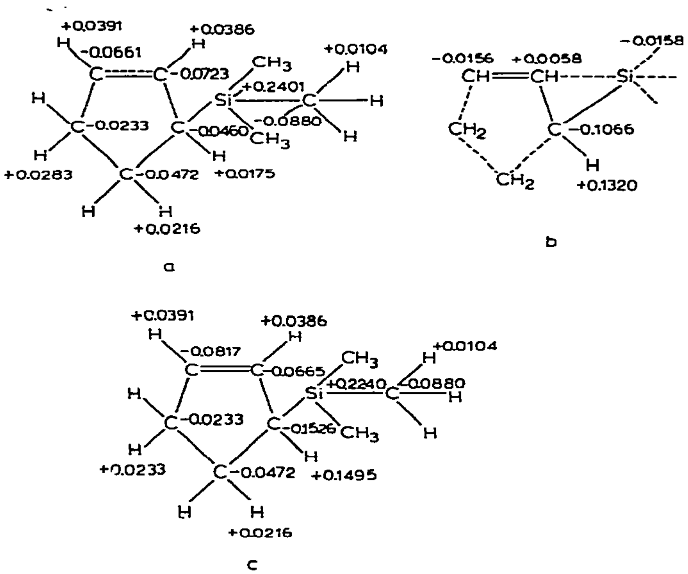


Fig. 4. Charge distribution of 3-(trimethylsilyl)cyclopentene: a. σ-charges; b. π-charges; c. resultant charges.

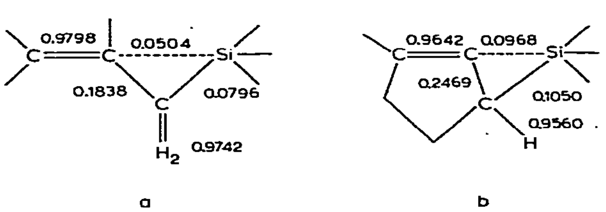


Fig. 5. π-Bond orders: a. trimethylallylsilane; b. 3-(trimethylsilyl)cyclopentene.

According to Fig. 5, showing the π bond orders of compound (I), the π bond between the carbon atom of the methylene group and the silicon atom is about 8% and the π bond order of the long bond is 5%. The double-bond character of the bond between the carbon atoms in β and γ positions with respect to the silicon atom diminishes only slightly, as compared to that in ethylene. The other molecule diagram of Fig. 5 also shows the π bond orders of compound (II). The π bond order of the bond between silicon and the carbon atom in α position and that of the long bond are higher in this molecule than in (I).

In trimethylbenzylsilane the CH_2 group exerts a hyperconjugating effect in the direction of the phenyl ring and the silicon atom, thus the 3*d* orbital of silicon is also capable to form *d*–π linkage, *i.e.* the long bond. The nine centered matrix of the π-system is built up from the same integral elements as in the case of phenylsilane and allylsilane. The energies of the molecular orbitals are listed in Table 2.

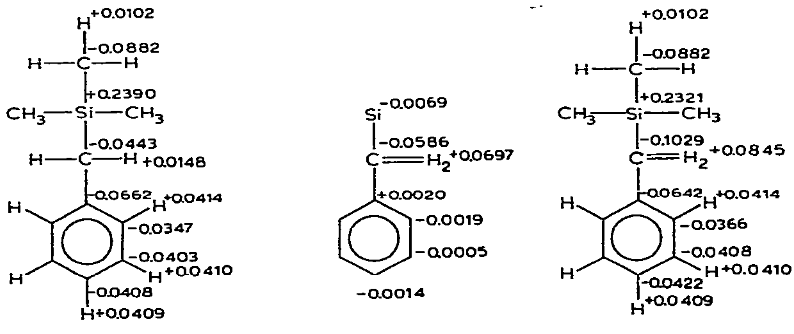
TABLE 2

ENERGIES OF THE MOLECULAR ORBITALS OF TRIMETHYLBENZYLSILANE

$E_1=\alpha+2.9949\beta$	$E_4=\alpha+0.9633\beta$	$E_7=\alpha-1.7927\beta$
$E_2=\alpha+1.9517\beta$	$E_5=\alpha-0.9787\beta$	$E_8=\alpha-2.0044\beta$
$E_3=\alpha+0.9988\beta$	$E_6=\alpha-1.0012\beta$	$E_9=\alpha-3.4479\beta$
$\Delta m=1.9420\beta$		

The calculated σ-,π-and resultant charge distribution of the molecule is summarized in Fig. 6. The π partial charges of the ring are in accordance with the experimental results obtained by Benkeser and Brumfield[6]. These authors obtained a mixture of *ortho*- (80 per cent) and *para*-nitro (20 per cent) derivatives on nitrating trimethylbenzylsilane with $Cu(NO_3)_2$ in acetic anhydride, indicating the $-CH_2Si(CH_3)_3$ group to be *ortho-para* directing in electrophilic substitutions. The free valence decreases in the order *ortho*, *para*, *meta*. (In Fig. 7, numbers marking the arrows indicate the free valences.)

The σ dipole moment calculated on the basis of the charge distribution in



a b c

Fig. 6. Charge distribution of trimethylbenzylsilane: a. σ-charges; b. π-charges; c. resultant charges.

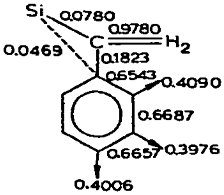


Fig. 7. π-Bond orders of trimethylbenzylsilane and its free valences.

trimethylbenzylsilane is 0.212 D, the π dipole moment 0.289 D, the two dipole moments include an angle of 66°46′, and the value of the resultant dipole moment is 0.420 D, which is in good agreement with the experimental value of 0.55 D (ref. 1).

The Si–C bonds with the adjacent carbon atom and that in β-position have a similar π bond order (Fig. 7) as the corresponding bonds of trimethylallylsilane. Results indicate the *d*–π linkage (long bond) formation in the benzyl derivative also.

For a quantitative study of the structure of silicon organic compounds we intend to continue our calculations using SCF-LCAO-MO method.

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