# THE ROLE OF d-ORBITALS IN VINYL, PHENYL, ALLYL AND BENZYL DERIVATIVES OF SILICON, GERMANIUM AND TIN II

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Earlier, PPP calculations have led us to the conclusion that in vinyl and phenyl derivatives of fourth main group elements a $(p-d)\pi$ interaction — starting from silicon compounds — formed between the $d$ orbitals of the heteroatom and the $p\pi$ orbitals of carbon atoms in $\alpha$ position [1]. Consideration of the interaction with the carbon atoms in $\beta$ position lessens the agreement between calculated and experimental results, and the $\beta$-interaction is less important with increasing size of the heteroatom. In allyl and benzyl derivatives a link of $(p-d)\sigma$ character is formed between the $d$ orbitals in $\alpha$, $\beta$, $\gamma$ positions. The higher the atomic number of the heteroatom, the more distant the still effective interactions (even $\gamma$-interaction in tin compounds). Electronic transition energies calculated taking into account the mentioned effects, are in accordance with the data of the ultraviolet spectra.

The PPP calculations prove the $d$ orbitals to be important for the examination of excited states. On the other hand, comparison between calculated and experimental dipole moments gives information on the role of $d$ orbitals in ground state.

To obtain this information the knowledge of $\sigma$ dipole moment, to be calculated by the Del Re method [2], is necessary. Earlier we modified the Del Re parameters of C—C and C—H bonds, and evaluated new parameters for Si—C bond [3]. Parameters for germanium compounds have been chosen on the basis of compounds with known dipole moment [4] presented in Table 1. Several different experimental dipole moment values found for a given compound caused a difficulty.

For calculating the $\sigma$ systems of molecules containing germanium, the following parameters had to be established: Coulomb parameter ($\delta^0_{\mathrm{Ge}}$), inductive parameters of Ge—C bond ($\gamma_{\mathrm{Ge(C)}}$ and $\gamma_{\mathrm{C(Ge)}}$), inductive parameters of Ge—Cl bond ($\gamma_{\mathrm{Ge(Cl)}}$ and $\gamma_{\mathrm{Cl(Ge)}}$), resonance integral parameters of Ge—C and Ge—Cl bonds ($\varepsilon_{\mathrm{GeC}}$ and $\varepsilon_{\mathrm{GeCl}}$, respectively).

The Coulomb parameter was chosen by considering the trends in the change of NMR $\tau$ signs (hydrogen chemical shifts) of the molecules $C(CH_3)_4$, $Si(CH_3)_4$, $Ge(CH_3)_4$ and in the electronegativity values of carbon, silicon and

Table 1

*Dipole moments of compounds used for the evaluation of Del Re parameters belonging to the Ge—C and Ge—Cl bonds*

| Compound | Experimental | Calculated |
|---|---|---|
| | dipole moment [D] | |
| $CH_3GeCl_3$ | 2.70; 2.63 | 2.67 |
| $(CH_3)_2GeCl_2$ | 3.14; 3.11 | 3.20 |
| $(CH_3)_3GeCl$ | 2.89; 2.78 | 2.83 |
| $(CH_3CH_2)_2GeCl$ | 3.19 | 3.22 |
| $(CH_3)_3GeCHClCH_3$ | 2.34 | 2.22 |
| $CH_3CH_2GeCl_3$ | 2.28; 2.87 | 2.66 |

germanium. The chemical shifts indicate higher electron density around the proton in tetramethylgermanium than in the analogous silicon and carbon compounds. This hints to a lower electronegativity of germanium than are those of carbon and silicon. It can be observed that the proton chemical shifts of tetramethylgermanium and tetramethylsilicon differ only slightly, indicating a slight electronegativity difference between germanium and silicon. The conclusions drawn from the NMR spectra are in accordance with the electronegativity values established by PAULING; according to the SANDERSON scale, however, the electronegativity of germanium is higher than that of silicon. For the determination of Coulomb parameter values the following equation was suggested by DEL RE:

$$\delta_A^0 = \frac{k(\chi_A - \chi_H)}{\chi_H}$$

where $\chi_A$ and $\chi_H$ are the electronegativities of atoms A and hydrogen, respectively; $k$ is a proportionality factor.

Since the Coulomb parameters of carbon and silicon are known, that of germanium can be calculated from the PAULING electronegativity values ($\delta_{\mathrm{Ge}}^0 = -0.15$).

Based on analogies between properties of fourth group elements, it can be assumed that $\gamma_{\mathrm{Ge(C)}} = \gamma_{\mathrm{Si(C)}}$ and $\gamma_{\mathrm{C(Ge)}} = \gamma_{\mathrm{C(Si)}}$. For the determination of the two additional inductive parameters, first the relative magnitudes of the dipole moments of compounds have been calculated in the series $(CH_3)_nGeCl_{4-n}$ ($n = 1, 2, 3$). Taking the measured dipole moment $\mu_1$ of the compound for $n = 1$ as reference:

$$\mu_1 : \mu_2 : \mu_3 = 1 : 1.17 : 1.06 \ .$$

The resultant dipole moment of each compound varies linearily with the variation of one of the inductive parameters. For various values of the resonance integral parameters ($\varepsilon_{GeC}$ and $\varepsilon_{GeCl}$) the ratios of dipole moments are constant, although their absolute values may deviate from the experimental data. For this reason in choosing the inductive parameters the dipole moments may be calculated with any $\varepsilon$ value. Systematically varying $\gamma_{Cl(Ge)}$ and $\gamma_{Ge(Cl)}$, inductive parameters, where calculated and measured dipole moment ratios agreed, have been accepted (Fig. 1).

Lack of a pair of parameters meeting this condition, is a hint to erroneous choice of the other parameters ($\delta^0_{Ge}$, $\gamma_{Ge(C)}$, $\gamma_{C(Ge)}$), hence this method is suitable for checking these parameters.

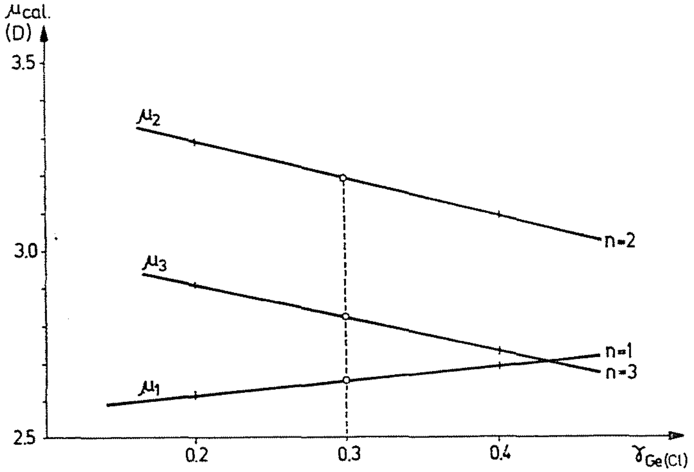

*Fig. 1.* $\gamma_{Ge(Cl)}$ dependence of the calculated dipole moments of compounds $(CH_3)_nGeCl_{4-n}$ for $\gamma_{Cl(Ge)}$ 0,1. The dotted vertical line corresponds to experimental dipole moment ratios

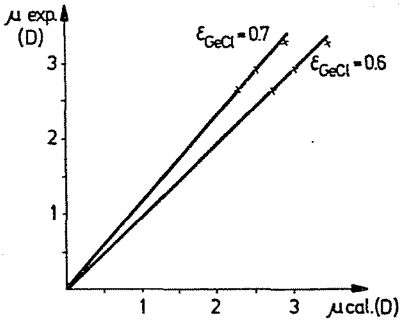

*Fig. 2.* Correlation between experimental and calculated dipole moments for compounds $(CH_3)_nGeCl_{4-n}$ in case of various $\varepsilon_{GeCl}$ parameters

Among the resonance integral parameters, $\varepsilon_{GeC}$ was determined by using the experimental dipole moment of molecule $(CH_3)_3GeCHClCH_3$, since the calculation of the dipole moment for this compound did not require the knowledge of $\varepsilon_{GeCl}$. Thereafter $\varepsilon_{GeCl}$ was varied (Fig. 2), that value was adopted where the absolute values of calculated and experimental dipole moments agreed. The DEL RE parameters evaluated for germanium compounds and used for silicon compounds have been compiled in Table 2. The data in Table 1 prove that dipole moments of the model compounds — calculated with the DEL RE parameters adopted for bonds containing germanium — practically coincide with the experimental dipole moments.

**Table 2**

*Del Re parameters*

| A—B bond | $\delta^0_A$ | $\delta^0_B$ | $\gamma_{A(B)}$ | $\gamma_{B(A)}$ | $\varepsilon_{AB}$ |
|---|---|---|---|---|---|
| C—H | $sp^3$: 0.07<br>$sp^2$: 0.12 | 0 | −0.2 | 0.4 | 1 |
| C—Si | $sp^3$: 0.07<br>$sp^2$: 0.12 | −0.1 | 0.4 | 0.2 | 0.9 |
| Si—Cl | −0.1 | 0.35 | 0.15 | 0.3 | 0.65 |
| C—Ge | $sp^3$: 0.07<br>$sp^2$: 0.12 | −0.15 | 0.4 | 0.2 | 0.7 |
| Ge—Cl | −0.15 | 0.35 | 0.1 | 0.3 | 0.6 |
| C—Cl | $sp^3$: 0.07<br>$sp^2$: 0.12 | 0.35 | 0.2 | 0.4 | 0.65 |

**Table 3**

*Calculated σ and π dipole moments and experimental dipole moments of the vinyl, phenyl, allyl and benzyl derivatives of silicon and germanium (in Debye)*

| Compound | | $\mu_\sigma$ | $\mu_{\pi,1}$ | $\mu_{\pi,2}$ | $\mu_{\pi,3}$ | $\mu_{\pi,4}$ | $\mu_{exp}$ |
|---|---|---|---|---|---|---|---|
| Vinyl | Si | 0.19 | — | 0.36 | 0.79 | — | 0.23 |
| | Ge | 0.33 | — | 0.26 | 0.57 | — | 0.32 |
| Phenyl | Si | 0.33 | 0.24 | 0.38 | 0.93 | — | 0.25 |
| | Ge | 0.49 | 0.25 | 0.27 | 0.65 | — | 0.38 |
| Allyl | Si | 0.16 | 0.14 | 0.34 | 0.48 | — | 0.58 |
| | Ge | 0.11 | 0.14 | 0.33 | 0.39 | 0.36 | 0.62 |
| Benzyl | Si | 0.20 | 0.14 | 0.36 | 0.41 | — | 0.55 |
| | Ge | 0.24 | 0.14 | 0.33 | 0.37 | 0.37 | 0.64 |

For the vinyl, phenyl, allyl and benzyl derivatives of silicon and germanium the vectorial sum of $\sigma$ and $\pi$ dipole moments obtained by the DEL RE and the PPP methods, respectively, has been calculated assuming various interactions, and investigated which kind of effects taken into consideration gave the best agreement with the experimental dipole moments. The calculated $\sigma$ and $\pi$ dipole moments as well as the experimental dipole moments [5, 6] for trimethylvinylsilane, trimethylphenylsilane, trimethylallylsilane, trimethylbenzylsilane and the corresponding germanium derivatives are presented in Table 3. In the PPP calculations the $\pi$ dipole moments were determined with various interactions taken into account such as: 1. hyperconjugative effect of methyl groups $\mu_{\pi,1}$, 2. $\alpha$-interaction between the $d$ orbital of hetero atom and the $p$ orbital of carbon atom in $\alpha$ position $\mu_{\pi,2}$, 3. $\alpha$- and $\beta$-interaction $\mu_{\pi,3}$, 4. $\alpha$-, $\beta$- and $\gamma$-interaction $\mu_{\pi,4}$.

**Table 4**

*Calculated dipole moments of the vinyl, phenyl, allyl and benzyl derivatives of silicon and germanium differences between the calculated and experimental dipole moments*
*(in Debye)*

| Compound | | $\mu_1$ | $\mu_2$ | $\mu_3$ | $\mu_4$ | $\Delta\mu_1$ | $\Delta\mu_2$ | $\Delta\mu_3$ | $\Delta\mu_4$ |
|---|---|---|---|---|---|---|---|---|---|
| Vinyl | Si | — | 0.18 | 0.60 | — | — | $-0.05^{\circ}$ | $+0.37^{*}$ | — |
| | Ge | — | 0.07 | 0.24 | — | — | $-0.025$ | $-0.08^{*\circ}$ | |
| Phenyl | Si | 0.09 | 0.05 | 0.60 | — | $-0.16^{\circ}$ | $-0.20^{*\circ}$ | $+0.35$ | — |
| | Ge | 0.24 | 0.22 | 0.16 | — | $-0.14^{\circ}$ | $-0.16^{*\circ}$ | $-0.22$ | — |
| Allyl | Si | 0.13 | 0.27 | 0.40 | — | $-0.45$ | $-0.31$ | $-0.18^{*\circ}$ | — |
| | Ge | 0.10 | 0.26 | 0.32 | 0.29 | $-0.48$ | $-0.36$ | $-0.30^{*\circ}$ | $-0.33$ |
| Benzyl | Si | 0.19 | 0.31 | 0.36 | — | $-0.36$ | $-0.23$ | $-0.19^{*\circ}$ | — |
| | Ge | 0.22 | 0.31 | 0.35 | 0.35 | $-0.42$ | $-0.33$ | $-0.29^{\circ}$ | $-0.29^{*\circ}$ |

In Table 4 the resultant calculated dipole moments and the differences between the calculated and experimental dipole moments are seen. In this table the calculations showing the best agreement with the experimental ultraviolet transitions have been marked by an asterisk, and small circles designate the best agreements between experimental and calculated dipole moments. Calculations yielding approximately identical $\Delta\mu$ values (differing by not more than 0.05 D) were considered as equivalent. A definite deviation between results of two different experimental methods is seen for a single compound out of eight. Hence extent and tendency of distant interactions are likely to be similar in excited and ground state, the role of hetero atom $d$ orbitals cannot be neglected even in the ground state of silicon and germanium compounds.

The C=C $\pi$ bond orders calculated by PPP method for vinyl and allyl derivatives in the case of calculations considered as best show a correlation with the infrared streching frequencies [7] of the double bond. The greatest deviation from the regression line is shown by the value corresponding to trimethylvinylgermanium (Table 5).

**Table 5**

*Stretching frequencies of the* C=C *double bond and* $\pi$ *bond orders calculated by PPP method*

| Compound | $\nu$[cm$^{-1}$] | $\pi$ bond order |
|---|---|---|
| $CH_2=CHC(CH_3)_3$ | 1645 | 0.9877 |
| $CH_2=CHSi(CH_3)_3$ | 1595 | 0.9653 |
| $CH_2=CHGe(CH_3)_3$ | 1590 | 0.9760 |
| $CH_2=CHCH_2C(CH_3)_3$ | 1650 | 0.9826 |
| $CH_2=CHCH_2Si(CH_3)_3$ | 1633 | 0.9749 |
| $CH_2=CHCH_2Ge(CH_3)_3$ | 1633 | 0.9776 |

## Summary

The $\sigma$ dipole moments for some vinyl, phenyl, allyl and benzyl derivatives of silicon and germanium were calculated using Del Re method. The Del Re parameters required for the calculations were evaluated for Ge—C and Ge—Cl bonds. The $\pi$ dipole moments of the compounds assuming various interactions were calculated by PPP method. The comparison between the experimental dipole moments and the vectorial sum of $\sigma$ and $\pi$ dipole moments proved the distant interactions to be significant; the role of *d* orbitals of silicon and germanium cannot be neglected either in the ground state of these compounds.

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