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

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Received June 26, 1975

The aim of our study has been to interpret the experimental ultraviolet spectrophotometric data of compounds of carbon, silicon, germanium and tin with organic unsaturated groups and investigate the role of the heteroatom d-orbitals.

Nowadays it is generally accepted and supported by experimental evidences that d-orbitals have an important role in the bond structure and the properties of phenyl, vinyl, benzyl and allyl derivatives of silicon. On the contrary, in the case of germanium and especially tin, the role of d-orbitals is very slight. This is confirmed for example by VAN DER BERGHE and VAN DER KELEN's investigation on Si^{29} and Sn^{119} NMR chemical shifts of methylhalogen derivatives of silicon and tin [1]. Only a very week backdonation is indicated by the experimental results for tin compounds. Even in these compounds, the d-orbitals are likely, however, to have a certain effect through the increase of orbital energies. This fact can be observed from photoelectron spectroscopic data. According to ab initio calculations with minimal basis set by HORN and MURREL [2], in vinyl and allylsilanes the d-orbitals have a large effect mostly on the virtual π^* orbitals, which are not substantial as for the ground state, but all the more important from the point of view of ultraviolet spectra. Thus although the $(d-p)\sigma$ and $(d-p)\pi$ interactions are not significant in the ground state of Ge and Sn compounds, they are supposed to have large effect on the ultraviolet spectra. This is confirmed by the fact that the ultraviolet spectrum of the trimethylphenyltin differs from that of benzene not only in the position of maxima, but in the shape of the curve, so it cannot be explained exclusively with shift upon inductive effect [3].

Results and discussion

To interpret the ultraviolet spectra quantumchemical calculations have been made by the PPP method, one of the most developed semiempiric π-electron methods [4, 5]. In calculations for investigating the role of d-orbitals in the usual way one d-orbital of the heteroatom was taken into consideration.

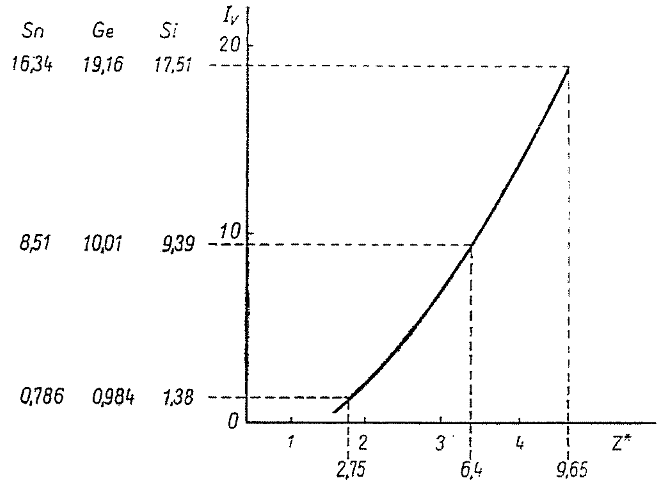


Fig. 1. Estimated ionization potentials of Ge and Sn d-orbitals

The most important part of the calculation is to choose the ionisation energies, the $\gamma(\mu - \mu)$ and $\gamma(\mu - \nu)$ one and two-center electronic repulsion integrals, resp., and the resonance integrals. For the latter a number of empiric equations are available, in this work the one and two center repulsion integrals were calculated according to formulae by Pariser [6] and by Mataga—Nishimoto [7], respectively, for the calculation of the resonance integrals the Helmholz—Wolfsberg equation [8] was used. It was very difficult, however, to estimate the value of valence state ionization energies for the d-orbitals of germanium and tin. The PPP method is generally applied for compounds of II^{nd} and III^{nd} row elements of known valence state ionization energies. Estimation started from the valence state ionization potentials of the s and p orbitals of silicon, germanium and tin, known from tables by Hinze and Jaffe [9] (Fig. 1). Levison and Perkins gave the value for 3d-orbital of silicon on the basis of spectrochemical data [10]. The ionization energy values belonging to different orbitals of silicon have been plotted versus the corresponding effective nuclear charges calculated according to the Burns' rules [11]. The function was supposed to be similar in shape for germanium and tin so the known values of s and p-orbitals of germanium and tin were taken at the corresponding points of silicon, resulting in a relative system of co-ordinates where the valence state ionization energies of d-orbitals of germanium and tin could be read off in knowledge of the effective nuclear charges. The values of electron affinity could be derived in the same way. The electron affinity varies like the ionisation energy, thus the one-center electron repulsion integrals was supposed not to change for germanium and tin compared with silicon. In lack of experimental data for bond distances those from similar compounds were adopted. The angles were taken as 120° for carbon atom in sp^2 hybrid state and tetrahedral elsewhere.

Investigating the phenyl derivatives of IV/1 group elements, the ultraviolet spectrum of tert.-buthylbenzene, a carbon derivative, is the simplest to explain. It has to be mentioned here that to interpret the spectra of phenyl compounds from among the vibration peaks not the 0—0 transitions but those of largest intensity were considered since in some compounds these were the only discernible transitions. Disregarding the hyperconjugation effect of methyl groups, the PPP calculation for tert.-buthylbenzene resulted in transitions characteristic of ultraviolet spectrum of benzene. With the inclusion of hyperconjugation and inductive effect of methyl groups, the slight bathochromic shift compared with benzene can be fairly reproduced. In the case of trimethylphenylsilane — omitting the d-orbital of the heteroatom from the π-system — the far hyperconjugation of methyl groups would result in a hypsochromic shift as compared with the tert.-buthylbenzene, but the experimental data indicate a bathochromic shift. Inclusion of d-orbital of silicon provides results agreeing with the spectrum. According to the calculations there is no considerable interaction between the silicon atom and the π-orbitals of the ring carbon atom in β-position. This is supported by the resulting excessive orbital energies and erroneous oscillator strengths. The greatest deviation between experimental and calculated values was observed for the p-band. In the case of phenyl derivatives of Ge and Sn the calculations give less reliable results because of the incertainty involved in the determination of parameters used for the calculation of molecules containing Ge and Sn and of the increase of correlation energy for elements with higher atomic numbers. Undoubtedly, however, the ultraviolet spectrum of trimethylphenylgermanium cannot be described with the hyperconjugative effect of the methyl groups alone or with an inductive effect, neglecting the d-orbitals. The 4d-orbital of germanium may have a significant role in excited state. Inclusion of the $5d$ orbital of tin also gives a better correlation with data of ultraviolet spectrum of trimethylphenyltin than if only the inductive and hyperconjugative effects were considered, neglecting the heteroatom or if a β-interaction between the d-orbital of tin and the ring carbon atom in β-position were taken into account. The results of the more important calculations for phenyl derivatives are summarized in Table 1. The values with an asterisk show the best calculated results.

Let us consider now the results obtained for the vinyl derivatives (Table 2). In the case of tert.-buthylethylene, similarly to tert.-buthylbenzene, the far hyperconjugative effect of the methyl groups results in a red shift compared with ethylene. In calculating without hyperconjugative effect, the absorption maximum characteristic of ethylene is recovered as it is seen in the table. In the case of trimethylvinylsilane a mere hyperconjugative

Table 1

Calculated and experimental ultraviolet transition energies of phenyl derivatives (in eV)

	Calculated						Experimental	
	Without heteroatom		Interaction in				ΔE	lg ε
			α-position		β-position			
	^1E	f	^1E	f	^1E	f		
C	*4.719	0.000	4.743	0.000				
	5.983	0.013	6.041	0.000	—		4.714	2.297
	6.793	0.214	6.866	1.173			5.949	3.929
	6.821	1.150	6.866	1.173				
Si	4.730	0.000	*4.668	0.027	4.810	0.002	4.687	2.358
	6.006	0.006	5.687	0.164	6.079	0.002	5.766	4.017
	6.816	1.213	6.397	0.499	6.665	1.161	6.595	
	6.838	1.158	6.429	0.415	6.667	1.160		
Ge	4.731	0.000	*4.693	0.001	4.787	0.001	4.798	2.297
	6.010	0.006	5.816	0.100	6.060	0.003	5.792	4.029
	6.820	1.213	6.440	0.543	6.660	1.046		
	6.838	1.158	6.535	0.486				
Sn	4.734	0.000	*4.707	0.001	4.803	0.001	4.793	2.778
	6.014	0.004	5.905	0.054	6.087	0.002	5.955	4.093
	6.826	1.199	6.557	0.773	6.841	0.338		
	6.846	1.161	6.673	0.751				

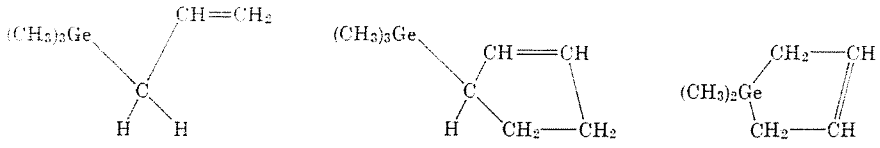
Table 2

Calculated and experimental ultraviolet transition energies of vinyl compounds (in eV)

	Calculated						Experimental ΔE
	Without heteroatom		Interaction in α-position		β-position		
	^1E	f	^1E	f	^1E	f	
C	*7.226	0.650	7.447	0.585	—		7.424 (ethylene)
Si	7.302	0.642	6.102	0.252	*6.932	0.318	6.964
			7.826	0.376	7.612	0.462	
Ge	7.304	0.644	6.262	0.224	*6.876	0.253	6.792
			7.755	0.395	7.569	0.479	
Sn	7.336	0.612	*6.530	0.265	7.298	0.167	6.635
			7.789	0.356	7.557	0.620	

effect results in higher transition energies than the experimental values, and assumption of $p\pi - d\pi$ interaction between the silicon atom and the α-carbon atom indicates absorption maximum at a much longer wavelength, even if the effect of methyl groups is included. Proper results are obtained by considering a $(p - d)\pi$ interaction between the d-orbital of the silicon atom and the β-carbon atom. This interaction is nearly as strong because of the large diameter of the *d*-orbital as the one between the silicon and α-carbon. The calculations by PPP method for trimethylvinylgermanium show similar effects as for the silicon derivative, that is, the ultraviolet spectrum can be explained by taking the $(p - d)\pi$ interaction between the d-orbital of germanium and the carbon atoms in α- and β-position into consideration. The calculated results of the tin derivative do not agree with experimental data assuming simultaneous α- and β-interaction, a mere α-interaction, however, provides fairly good transition energies.

The benzyl and allyl derivatives of IV/1 group elements exhibit many similarities. In both cases the ultraviolet spectra in going from carbon to tin show a bathochromic shift. Several kinds of effects may affect the bond structure of the molecules, thus according to MOLLERE and BOCK [12] hyperconjugative effect, inductive effect and $(p - d)\pi$ and $(p - d)\sigma$ interaction take place between the d-orbital of silicon atom and the α- and β-carbon atom, respectively. For the allylsilane three configurations have been considered, in two cases the silicon atom is in the plane of the ethylene nuclei either at far (trans) position or near to the double bond, and in the third case the silicon is rotated to its maximum displacement from the plane. This latter can be referred to as perpendicular configuration. According to MOLLERE and BOCK the total energy of the different configurations, calculated by CNDO/2 method, makes every configuration possible, but only the perpendicular position of silicon is favourable to the $(p - d)\sigma$ interaction. WEIDNER and SCHWEIG ascribe predominant role to the perpendicular configuration in the derivative not only of silicon, but of germanium and tin as well [13]. This is supported by ab initio calculations by HORN and MURREL [2] stating the approximately 13 kJ/mole energy difference between the perpendicular and parallel position to give a BOLTZMANN distribution of less than 1% in the parallel configuration at room temperature. Our previous calculations by HÜCKEL's method for germanium compounds containing a double bond in allyl position [14] have proved the importance of the β-interaction. Fig. 2 presents the ultraviolet absorption maxima of three germanium compounds. In the case of trimethylallylgermanium there is a possibility for perpendicular position of germanium, the increase of conjugation results in a red shift as compared to trimetylvinylgermanium. The rotation of compound II is hindered, therefore a larger bathochromatic shift is observed. In compound III the position of germanium is fixed in the plane, and there is no possibility



I 196 nm

II 204 nm

III 180 nm

Fig. 2. Ultraviolet absorption maxima of germanium compounds containing a C=C double bond in allyl position

for β-interaction, for this reason the spectrum shows a considerable hypsochromic shift. The results obtained by Hückel's LCAO method improved by ω-technique are in agreement with the effects mentioned.

Our PPP calculations for the allyl and benzyl derivatives of carbon provide appropriate ultraviolet transitions if the hyperconjugative effect of the CH_2 group is considered. Experimental and calculated data of the allyl compounds are seen in Table 3. In the case of silicon and germanium derivatives, calculation took interaction between the d-orbital of the heteroatom and the carbon atom in α-position besides hyperconjugation into account, and in some calculations in addition to these effects an interaction between the heteroatom and the β-carbon atom was supposed. Silicon and germanium were in perpendicular position. The results show the simultaneous presence of the three effects to be reckoned with, but in the case of the silicon derivatives free rotation sometimes removes the molecule from perpendicular configuration. The transition energies of trimethylallyltin calculated in similar manner are in disagreement with experimental data. In this case we attempted to take an interaction with the carbon atom in γ-position into consideration, and the results appear to be promising. The calculations for the benzyl derivatives (Table 4) indicate similar tendencies.

While calculation of ultraviolet transitions of the carbon, silicon and to some extent the germanium compounds seems to be feasible, the spectra of the tin compounds caused much trouble. It was difficult to interpret the contradiction that while according to numerous researchers and experimental evidences the d-orbital was loosing importance going toward tin, consequently the conjugation decreased, the spectrum generally showed a considerable bathochromic shift, usually an indication of increased conjugation. Omission of changes in the σ systems in the PPP method caused much difficulty. From carbon to tin the $+I$ effect of the heteroatom more and more increased, the electronegativity decreased, hence the heteroatom became ever more ionic. Consequently, the energy of the d-orbitals, that is the ionization energy increased, too. The valence state ionization energy of the d-orbital of tin is likely to exceed the corresponding value of silicon.

Table 3

Calculated and experimental ultraviolet transition energies of allyl derivatives (in eV)

	Calculated								Experimental ΔE
	Without heteroatom		α-position		Interaction in β-position		γ-position		
	^{1}E	f	^{1}E	f	^{1}E	f	^{1}E	f	
C	*7.029	0.553	—		—		—		
Si	7.029	0.553	6.428	0.035	*6.230	0.348	—		6.456
			7.108	0.536	7.529	0.238			
Ge	7.029	0.553	6.484	0.054	*6.313	0.287	5.922	0.210	6.325
			7.120	0.563	7.450	0.349	7.785	0.408	
Sn	7.029	0.553	6.743	0.130	6.439	0.409	*5.930	0.365	5.901
			7.151	0.487	7.683	0.246	7.865	0.302	

Table 4

Calculated and experimental ultraviolet transition energies of benzyl derivatives (in eV)

	Calculated								Experimental ΔE
	Without heteroatom		α-position		Interaction in β-position		γ-position		
	^{1}E	f	^{1}E	f	^{1}E	f	^{1}E	f	
C	*4.696	0.000							4.779
	5.940	0.031	—		—		—		5.876
	6.746	1.212							
	6.791	1.141							
Si	4.696	0.000	4.695	0.000	*4.648	0.001			4.635
	5.940	0.031	5.926	0.038	5.688	0.186			5.609
	6.746	1.212	6.369	0.053	6.392	0.431	—		
	6.791	1.141	6.610	0.147	6.468	0.543			
			6.770	1.166					
Ge	4.696	0.000	4.695	0.000	4.664	0.000	*4.583	0.002	4.604
	5.940	0.031	5.931	0.036	5.773	0.138	5.512	0.130	6.509
	6.746	1.212	6.488	0.110	6.458	0.571	6.231	0.429	
	6.791	1.141	6.709	0.465	6.563	0.615	6.421	0.371	
			6.778	1.111					
Sn	4.696	0.000	4.695	0.000	4.657	0.000	*4.568	0.002	4.544
	5.940	0.031	5.935	0.034	5.778	0.145	5.526	0.155	5.248
	6.746	1.212	6.682	0.702	6.533	0.859	6.310	0.559	
	6.791	1.141	6.770	1.002	6.622	0.840	6.472	0.556	

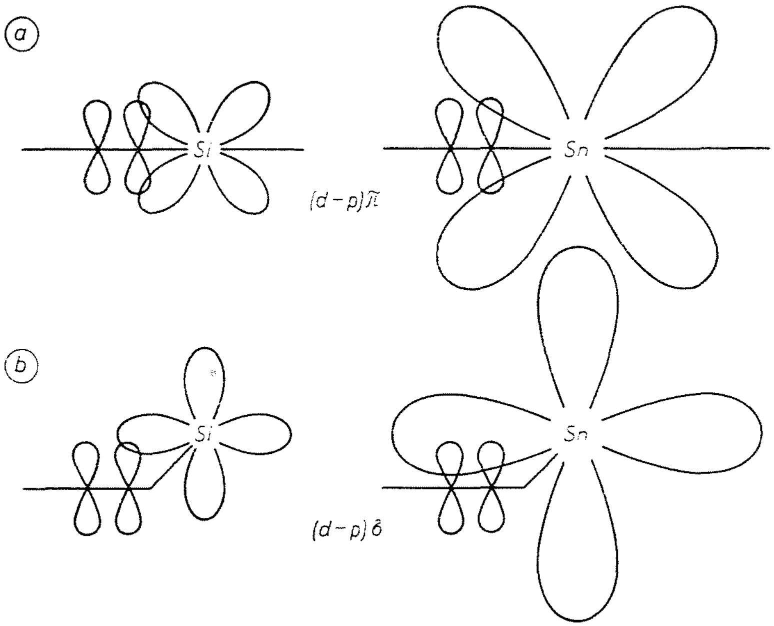


Fig. 3. Interactions with d-orbital of heteroatoms. *a)* vinyl and phenyl derivatives; *b)* allyl and benzyl derivatives

The situation may be similar for germanium, but our calculations showed this effect to be still rather insignificant, at least for the phenyl and vinyl derivatives. It is worth of study whether and to what extent the d-orbital of the heteroatom can overlap the pπ orbitals of the molecules (Fig. 3). In the case of the vinyl and phenyl derivatives the silicon atom is co-planar with the carbon atoms in α- and also in β-position, and a slight (d — p)π interaction is possible between the d-orbital of silicon atom and the pπ-orbital of the α-carbon atom. Toward tin, the d-orbitals become more and more diffuse and the figure exhibits slight overlap with the β-carbon atom considering their size. The size of orbitals is affected by the +I effect increasing toward the tin, to result in a positive charge on the tin atom. Thus the d-orbital of tin is contracted and the (d — p)π interaction is slightly increased. In the benzyl and allyl derivatives maximum overlap between the d-orbital of the heteroatom and the *p*-orbital of the carbon atom in β-position is in perpendicular configuration. This interaction is of (d — p)σ character, and increasing the size of the d-orbital it will be ever more significant. The +I effect here also results in pulling together the d-orbital and decreasing the (d — p)σ interaction.

As a consequence of the factors mentioned it can be stated as a rule that for the phenyl and vinyl derivatives consideration of the β-interaction impairs the results, to be precise, the greater the heteroatom, the more obvious is this effect. In allyl and benzyl derivatives consideration of the β-interaction improves the calculated values, moreover the greater the heteroatom, the farther interaction is advisably considered. Hence the tin compounds may be affected by γ-interaction. Consideration or neglect of the α-interaction can be included into this interpretation. The latter is equivalent to calculating without heteroatom. Since these calculations give unambiguously erroneous results, the conclusion can be drawn that the α-interaction has always to be taken into account. As a result of the effects mentioned a description can be given of the ultraviolet spectra of phenyl, vinyl, benzyl and allyl derivatives of the main group elements of the fourth column, practically in agreement with the experimental results. The theory does not contradict to the experimental facts, according to which the d-orbital in the germanium and tin compounds has a small influence on the bond structure of the molecules. That is to say, the investigations referred first of all to small molecules incessible to far interactions. As for the nearby adjacent atoms, the effect of the d-orbital is really slight.

Summary

Ultraviolet spectral data of vinyl, phenyl, allyl and benzyl derivatives of carbon, silicon, germanium and tin are compared with transition energies calculated by the PPP method. The role of d-orbitals are investigated. In the phenyl and vinyl derivatives α-interaction was found to have a dominant effect, in the case of the allyl and benzyl derivatives β- and γ-interactions can be effective first of all for tin atom.

References

1. Van der Berghe, E. V.—Van der Kelen, G. P.: J. Organomet. Chem. **59**, 175 (1973)
2. Horn, M.—Murrel. J. N.: J. Organomet. Chem. **70**, 51 (1974)
3. Nagy, J.—Réffy, J.—Kuszmann-Borbély, A.—Pálossy-Becker, K.: J. Organomet. Chem. **7**, 393 (1967)
4. Pariser, R.—Parr, R. G.: J. Chem. Phys. **21**, 466, 767 (1953)
5. Pople, J. A.: Trans. Farad. Soc. **49**, 1375 (1953)
6. Pariser, R.: J. Chem. Phys. **21**, 568 (1953)
7. Nishimoto, K.—Mataga, M.: Z. Physik. Chem. **12**, 335 (1957)
8. Wolsberg, M.—Helmholz, L.: J. Chem. Phys. **20**, 837 (1952)
9. Hinze, J.—Jaffe, H. H.: J. Am. Chem. Soc. **84**, 540 (1962)
10. Levison, K. A.—Perkins, P. G.: Theoret. Chim. Acta. **14**, 206 (1969)
11. Burns, G.: J. Chem. Phys. **41**, 1521 (1964)
12. Mollere, P.—Bock, H.—Becker, G.—Fritz, G.: J. Organomet. Chem. **46**, 89 (1972)
13. Weidner, U.—Schweig, A.: J. Organomet. Chem. **30**, 261 (1972)
14. Nagy, J.—Réffy, J.—Éliás, P.: Acta Chimica Acad. Sci. Hung. **63**, 403 (1970)

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