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BOND STRUCTURE IN THE ARYL DERIVATIVES OF THE ELEMENTS OF GROUP IV/1

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INTRODUCTION

On the basis of dipole moment measurements, Huang and Hui[1] concluded that d_π–p_π bonds form not only between carbon and silicon but also between carbon and tin. Thus conjugation includes silicon and tin atoms ($-M$ effect develops). Their conclusions were based on dipole moment data obtained on the *p*-substituted derivatives of tert-butylbenzene, trimethylphenylsilane and trimethylphenyltin. Bowden and Braude[2] recorded the ultravioletspectra of these compounds (in the case of the tin derivative, they investigated the triethyl compound instead of the trimethyl compound). Cowell and Weissman[3] investigated the conjugation between an aromatic ring and the silicon atom attached to it for the case of bis(2,2′-biphenylene)silane and its derivatives of anionic character containing one and two electrons. The ESR investigations confirm the conjugation between the two diphenyl rings and the silicon atom.

EXPERIMENTAL

Two series of compounds were prepared for the measurements: the series trimethylphenyl–E, and the series trimethylbenzyl–E where E is an element of Group IV/1 (carbon, silicon, germanium or tin).

The tert-butylbenzene, $C_6H_5C(CH_3)_3$, was prepared from benzyl chloride and tert-butyl chloride by a Friedel-Crafts reaction[4]. Trimethylphenylsilane, $C_6H_5Si(CH_3)_3$, and trimethylbenzylsilane, $C_6H_5CH_2Si(CH_3)_3$, were synthesized by Grignard's reaction from trimethylchlorosilane and bromobenzene or benzyl chloride, respectively[5]. Trimethylphenyltin, $C_6H_5Sn(CH_3)_3$, and trimethylbenzyltin, $C_6H_5CH_2Sn(CH_3)_3$, were obtained also by Grignard's reaction from trimethyltin chloride and bromobenzene or benzyl chloride, respectively[6]. Tetraphenylsilane, $(C_6H_5)_4Si$ was obtained from tetraethoxysilane and chlorobenzene by our previously reported method[7]. It was purified partly by distillation and partly by recrystallization from chlorobenzene.

The compounds synthesized were of normal purity as given in the literature. The purification was controlled using gas-chromatography.

The ultraviolet absorption spectra of the compounds were recorded and the positions of the absorption maxima were determined. The spectra were obtained by means of a Spectromom 201-Type ultraviolet spectrophotometer, using 10^{-2}–

10^{-5} *M* alcoholic solutions and quartz cuvettes of thickness 1 cm. To complete the work the dipole moments reviewed in the literature were re-examined and those of some compounds that were missing were determined by Onsager's method.

The results are given in Tables 1 and 2; the ultraviolet spectra of the compounds synthesized are shown in Figs. 1 and 2.

TABLE 1

THE ABSORPTION MAXIMA AND THE DIPOLE MOMENTS OF THE TRIMETHYLPHENYL–E COMPOUNDS

E	*λ(p-band) (nm)*	*ν**	*ε*	*λ(α-band) (nm)*	*ν**	*ε*	*μ*
C	208.4	47970	8500	257.6	38821	198	0.55
Si	211	47393	10600	264	37879	300	0.44
Ge	—	—	—	258.4	38700	198	0.38
Sn	209	47847	12400	252	39683	600	0.51
$(C_6H_5)_4Si$	211	47393	45000	264.6	37794	1800	—

TABLE 2

THE ABSORPTION MAXIMA AND DIPOLE MOMENTS OF THE TRIMETHYLBENZYL–E COMPOUNDS

E	*λ(p-band) (nm)*	*ν**	*ε*	*λ(α-band) (nm)*	*ν**	*ε*	*μ*
C	211	47393	4630	259.4	38551	164	—
Si	221	45249	8690	267.4	37397	430	0.55
Ge	225	44444	7200	269.4	37125	339	0.63
Sn	236	42373	5520	272.8	36657	494	0.91

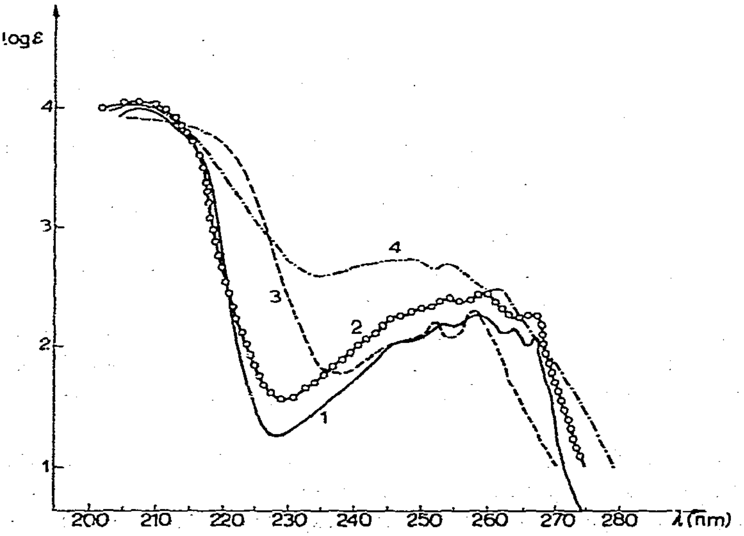

Fig. 1. The UV spectra of the $(CH_3)_3$–E–C_6H_5 series where E = C, Si, Ge, Sn. (1), tert-butylbenzene; (2), trimethylphenylsilane; (3), trimethylphenylgermanium; (4), trimethylphenyltin.

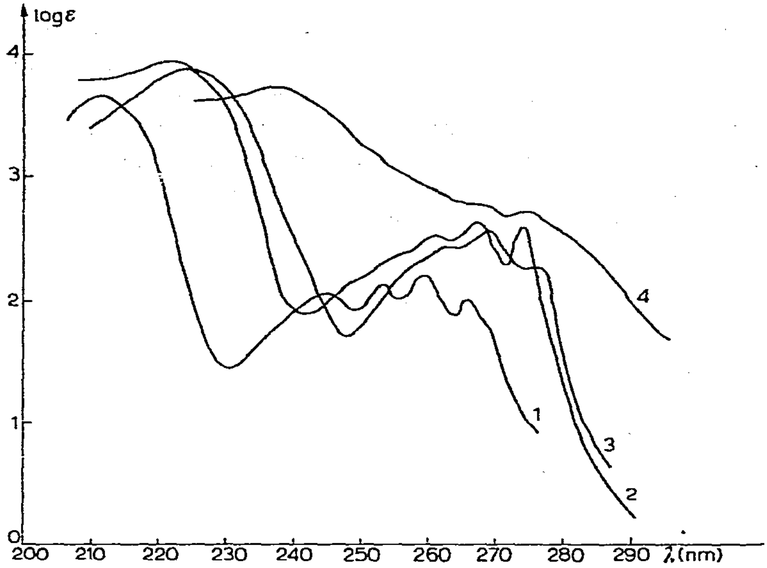

Fig. 2. The UV spectra of the $(CH_3)_3$-E-$CH_2C_6H_5$ series where E = C, Si, Ge, Sn. (1), neopentylbenzene; (2), trimethylbenzylsilane; (3), trimethylbenzylgermanium; (4), trimethylbenzyltin.

RESULTS AND DISCUSSION

LCAO–MO calculation for the phenyl-silicon group

In evaluating the ultraviolet spectra, the position of the most intense maximum of the α-band was first investigated; but the position of the maximum in the *p*-band is similar. The experimental data show that in the trimethylphenyl series the frequency of the absorption maximum reaches a minimum for the silicon compound and the value of the dipole moment is lowest for the silicon and germanium compounds. This phenomenon can be explained by assuming in these compounds (except the carbon analogue) *i.e.*, silicon, germanium and tin the formation of d_π–p_π bonds, this bond being strongest for silicon, *i.e.*, the conjugation is most pronounced (the strongest $-M$ effect), and the inductive effect $(+I)$ is greatest for tin. According to our investigations, an analogous change in the dipole moments can also be observed with the trimethylphenyl compounds. With the benzyl derivatives no mesomeric effects are possible, but inductive and hyperconjugation effects appear and, therefore, the wavelength of the absorption maximum and the value of the dipole moment show the same tendency to increase.

In the case of trimethylphenylsilane, the shift of the ultraviolet maximum has also been proved by quantum-chemical calculations. The experimental results showed that the spectrum of tetraphenylsilane shows a maximum absorption at the same wavelengths as that of trimethylphenylsilane. Therefore it can be supposed that probably the conjugation does not extend over all four phenyl groups, but that each phenyl group is in conjugative connection with a separate, vacant *d*-orbital; thus tetraphenylsilane can be divided into phenyl–silicon groups practically independent from one another. As the tetraphenylsilane molecule has more elements of symmetry and no methyl groups to cause hyperconjugation, it was easier to compute this model. Thus a one-electron molecular orbital LCAO-MO calculation was performed. Taking into account that, according to our supposition, the phenyl groups are independent of one another, it was sufficient to compute a single silicon–phenyl group and the group to be computed, therefore, consists of seven symmetry centres (Fig. 3). The coulomb integrals of all the carbon atoms belonging to the phenyl group chosen as being identical (α_0), and the coulomb integral of the silicon were calculated according to the following considerations.

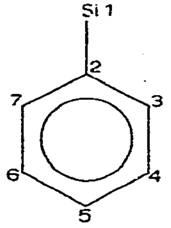

Fig. 3. The numbering of the phenyl–silicone group.

The ionisation energy of silicon is 8.16 eV, which is, in fact, the work function of the electron from the 3*p*-level. The promotion energy difference between the 3*p*- and 3*d*-levels amounts to 6.20 eV. The difference between these two values (1.96 eV) is approximately equal to the ionisation energy of the 3*d*-orbital. Since the coulomb integral of the carbon is approximately 6.80 eV, the resonance integral of the carbon–carbon bond in the case of benzene is 2.3–2.4 eV; on this basis the coulomb integral of silicon compared with that of the carbon atom in β-units is: $\alpha_{Si} = \alpha - 2\,\beta$.

The resonance integrals of the carbon–carbon bonds has also been taken as identical (β). The resonance integral of the silicon–carbon bond was computed by supposing the following proportionality:

$$\beta_{Si-C} = \frac{S_{Si-C}}{S_{C-C}}\beta$$

where S_{SiC} and S_{C-C} are the overlap integrals. The overlap integral of silicon was taken as 0.7 β using the integral table of the 3*d* and $2p_\pi$-orbitals, computed by us.

On the basis of the starting suppositions, the $C_6H_5Si\equiv$ group has C_{2v} symmetry; consequently, the two different eigen-values can be calculated from two matrix equations using the group theory. The approximation was improved using the ω-technique, when the coulomb integrals of the atoms were calculated on the basis of the formula:

$$\alpha_i = \alpha_0 + (1 - q_r)\omega\beta$$

where $\omega = 1.4$; α_0 is the value of the coulomb integral using a zero-order of approximation, and q_r is the partial charge share.

In Table 3 the coulomb integrals of the individual atoms selected at the start of the calculation, the values of the resonance integrals and the eigen-values obtained from them, the linear coefficients and the Δm-differences ($\pi \rightarrow \pi^*$ transition) are tabulated for the model having seven centres.

In Fig. 4 the most probable eigen-values of the molecular orbitals are separately

TABLE 3

DATA OF THE MOLECULAR ORBITAL CALCULATIONS FOR THE PHENYL–SILICON GROUP

No. of atoms	1	2	3	4	5	6	7
Coulomb integral	$\alpha-2\beta$	α	α	α	α	α	α
Resonance integral	$0.7\,\beta$	β	β	β	β	β	
Eigen-values	*Linear coefficients*						
$\varepsilon_1=\alpha+2.0216\,\beta$	0.0752	0.4320	0.4104	0.3976	0.3934	0.3976	0.4104
$\varepsilon_2=\alpha+1.0538\,\beta$	0.1319	0.5754	0.2570	−0.3046	−0.5780	−0.3046	0.2570
$\varepsilon_3=\alpha+\beta$	0.0000	0.0000	−0.5000	0.5000	0.0000	0.5000	−0.5000
$\varepsilon_4=\alpha-0.8618\,\beta$	0.3213	0.5224	−0.3376	−0.2315	0.5371	−0.2315	−0.3376
$\varepsilon_5=\alpha-\beta$	0.0000	0.0000	0.5000	−0.5000	0.0000	−0.5000	0.5000
$\varepsilon_6=\alpha-1.8211\,\beta$	0.5114	0.1294	−0.2980	0.4120	−0.4523	0.4120	−0.2980
$\varepsilon_7=\alpha-2.3920\,\beta$	0.7830	−0.4385	0.2504	−0.1604	0.1333	−0.1604	0.2504
Δm		$1.8618\,\beta$ ($\pi\rightarrow\pi^*$ transition)					

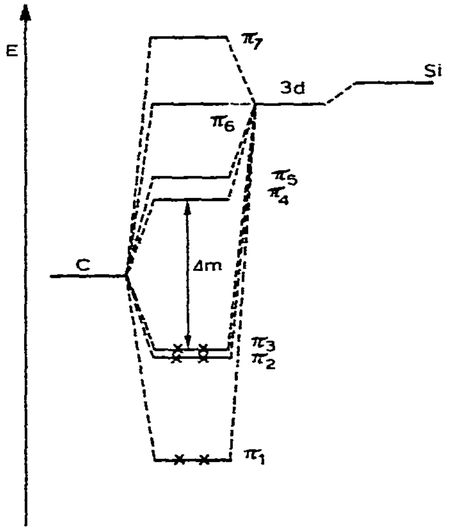

Fig. 4. Molecular orbital levels of the phenyl–silicon group.

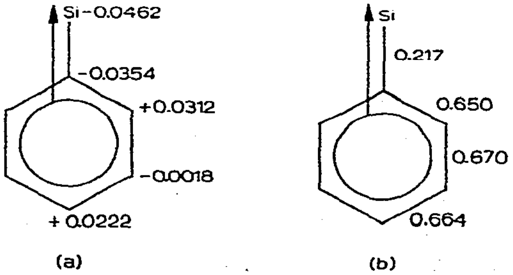

Fig. 5. (a), the partial charge share for phenyl–silicone group; (b), the π-bond orders for the phenyl–silicone group.

indicated and in Fig. 5 are shown the partial charge shares calculated by means of the linear coefficients and bond orders.

In Fig. 5b it can be seen that the bond order usually decreases in relation to that of benzene where the order of the π-bond is 0.667. This decrease is most pronounced between the second and the third carbon atoms. At the same time, the order of the d_π–p_π bond agrees approximately with the π-bond order computed by us for vinylsilanes (0.214).

In the case of tetraphenylsilane, the value of Δm is 1.8618 β, this being remarkably smaller than the value of 2 β for benzene. This proves that at trimethylphenylsilane the ultraviolet spectrum must show a bathochromic shift.

The effect of the elements of Group IV/1 on the ultraviolet spectrum of phenyl and benzyl derivatives

The evaluation of the experimental data shows that the compounds investigated are of four different types.

The situation is simplest in the case of the tert-butylbenzene, the molecular orbital levels of which (compared with those of benzene) are shown in β-units in Fig. 6. In this case an inductive (+*I*) effect appears. All the levels are shifted upwards by the +*I*-effect. The two degenerate *Π* and Δ benzene levels will split. One of the two double degenerate levels always remains unaltered while the other two are equally situated at a distance, Δ*x* from the $\alpha+\beta$ and $\alpha-\beta$ levels, respectively. Therefore, the difference, Δm, belonging to the transition between the last-occupied and the first-unoccupied molecular orbitals will be smaller than 2 β and this results in a limited bathochromic shift. At the same time, the +*I*-effect causes a considerable dipole moment.

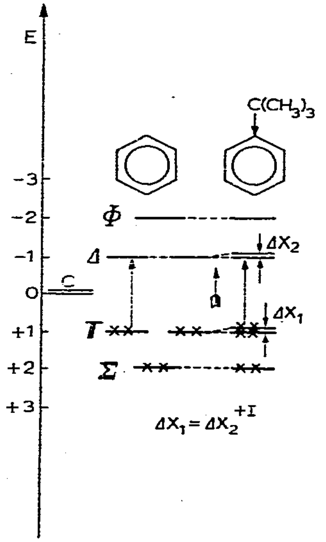

Fig. 6. Molecular orbital levels of tert-butylbenzene.

The other members of the trimethylphenyl–E group (where E = Si, Ge and

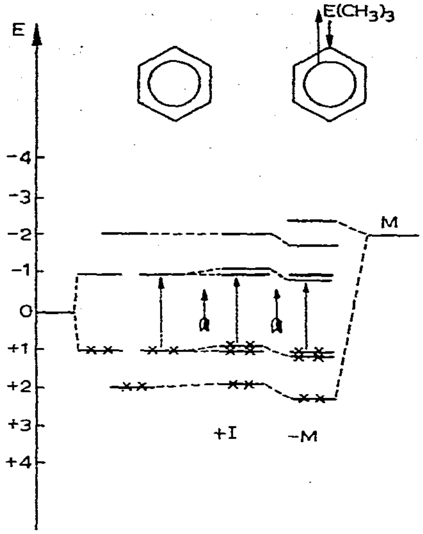

Fig. 7. Molecular orbital levels of the $(CH_3)_3$–E–C_6H_5 series, where E = Si, Ge, Sn.

Sn) belong to type II. The term-scale of molecules of this type is shown in Fig. 7.

Here, the degenerate levels of benzene will also split. Because of the +*I*-effect, two of them move upwards by a distance, Δx. At the same time, with molecules of this type the vacant *d*-orbitals of the E atom make possible the development of a mezomeric effect too. Because of the −*M* effect, the levels shift downwards, the upper of the originally degenerate levels shifting to a larger extent than the lower. Therefore, between the $\alpha+\beta$ and the $\alpha-\beta$ levels a new vacant energy level enters. As a result, with compounds containing silicon and germanium atoms a bathochromic shift appears, since with these compounds the −*M* effect is quite considerable. As is well known, the development of the mesomeric effect can be explained by the overlap of the nd_π-orbital of the E atom and the $2p_\pi$-orbital of the carbon atom, as shown in Fig. 8 for the case of the phenyl–silane bond. In the series silicon, germanium, tin, the +*I*-effect increases, and the −*M* effect decreases. Because of the two opposing effects, moving from silicon to tin, a hypsochromic effect develops, because the upper level (the level of the first unoccupied molecular orbital) shifts towards the $\alpha-\beta$ level and thus the energy required for the excitation must increase (264 nm → 252 nm). This has also been proved by quantum-chemical calculations.

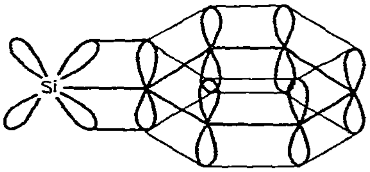

Fig. 8. The π-bond developing from the atomic orbitals of the phenyl–silicone group.

Calculations were started also for the seven-center model and the coulomb integrals of each carbon atom and the resonance integrals of the carbon–carbon bonds were regarded as being identical. In the matrix equations, for the coulomb and resonance integrals of the heteroatom adjacent to the aromatic ring, different variation values were supposed, and therefore in each case the difference, Δm, between the last-occupied and the first-unoccupied molecular orbitals was calculated in β units. On the basis of the calculations—as shown in Fig. 9—it can be stated that with a decrease in the value of the coulomb-(α_E) and the resonance-(β_{E-C}) integrals the value of $\Delta m(\pi \rightarrow \pi^*$ transition) increases. The coulomb and resonance integrals of tin are smaller than the corresponding values for silicon, because with increasing atomic number the *d*-orbitals become more and more diffuse, and the length of the tin–carbon bond is greater than that of the silicon–carbon bond. Therefore, the value of Δm is higher in the case of the tin compound, than for the silicon derivative and the phenyl–tin group shows a hypsochromic shift as compared with the phenyl–silicon group. The change in dipole moment is in perfect accordance

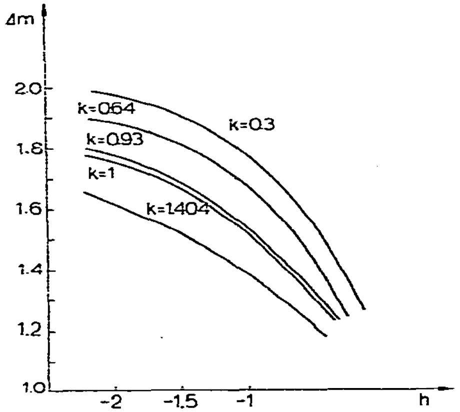

Fig. 9. Variation calculations for the π–π^* transitions (Δm) of the $(CH_3)_3$–E–C_6H_5 series where E = Si, Ge, Sn; h = parameters belonging to the coulomb integral; k = parameters belonging to the resonance integral.

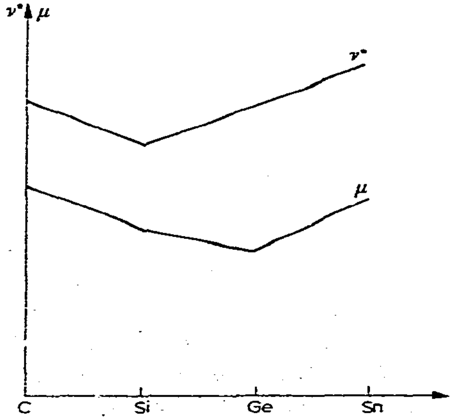

Fig. 10. The change of the wave number (ν^*) and the dipole moment (μ) of the compounds belonging to the $(CH_3)_3$–E–C_6H_5 series, where E = C, Si, Ge, Sn.

with this fact. As in the case of the carbon-analogue, there is only a $+I$-effect, the dipole moment is highest for the carbon compound. Although the inductive effect further increases in the silicon, germanium and tin compounds, at the same time the opposing mesomeric effect decreases the dipole moment originating from the inductive effect (Fig. 10). The dipole moments of the silicon and germanium derivatives ar lowest since for these compounds the $-M$ effect is still quite considerable.

Neopentylbenzene can be classed into group III. The term-scale of this type is shown in Fig. 11. The original benzene levels are moved upwards by the inductive effect of the CH_2-group in the above-mentioned manner and approximately to the same extent. The CH_2-group yields a hyperconjugation effect ($+M_h$) too, which

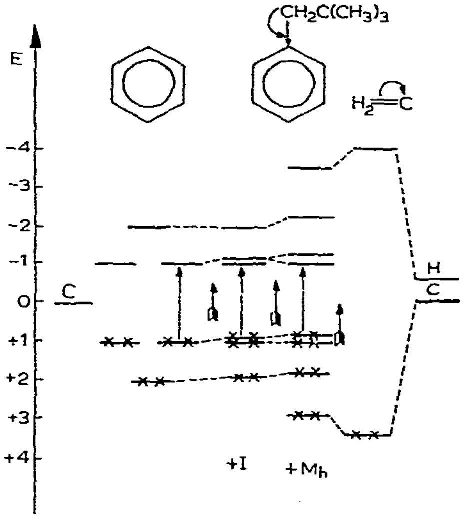

Fig. 11. Molecular orbital levels of neopentylbenzene.

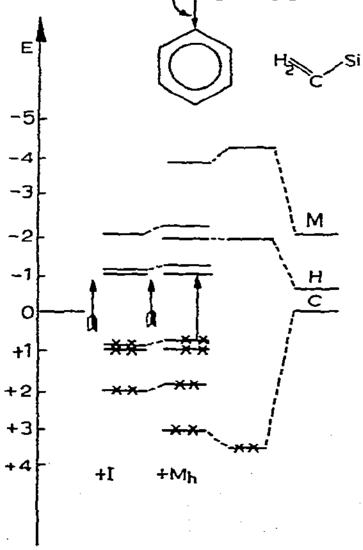

Fig. 12. Molecular orbital levels of the $(CH_3)_3$–E–$CH_2C_6H_5$ series, where E = Si, Ge, Sn.

shifts the levels downwards, the lower level to a larger extent than the upper. The tert-butyl radical slightly increases both effects. Therefore a stronger bathochromic effect is observable than for tert-butylbenzene.

The remaining members of the trimethylbenzyl–E series (E = Si, Ge, Sn) belong to type IV. The energy levels of the molecular orbitals are shown in Fig. 12. The CH_2-group—as with the previous type—causes, besides a $+I$-effect, a hyperconjugation effect, $(+M_h)$, but in this case in both directions, *i.e.*, towards the E-heteroatom (silicon, germanium, tin) and also towards the phenyl group. Thus, owing to the hyperconjugation, the electrons get to a molecular orbital of nine centres. The development of the nine-center π-system of trimethylbenzylsilane can be seen in Fig. 13 where the pseudo p-orbital of the $=H_2$ group causing the hyperconjugation and the $2p_\pi$-orbital of the carbon atom are also recorded. The tricentric hyperconjugation effect shifts the highest occupied level still farther upwards than in the case of the preceding neopentylbenzene. The inductive and hyperconjugation effects of identical direction cause a strong bathochromic shift, leading to further increase in the dipole moment. The dipole moment and the wave number of the absorption maxima of the compounds belonging to the trimethylbenzyl–E series show steady increase and decrease, respectively (Fig. 14). The difference between silicon and germanium is smaller than that between germanium and tin or carbon and silicon. The steady increase and decrease prove that the inductive and hyperconjugation effects increase from carbon to tin; this is a consequence of the different electronegativity of the heteroatoms. Thus, the electronegativity gradually decreases in Group IV/1, and is nearly equal for silicon and germanium. It is known, that the

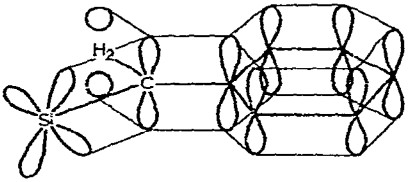

Fig. 13. The π-bond developing from the atomic orbitals of the benzyl–silicone group.

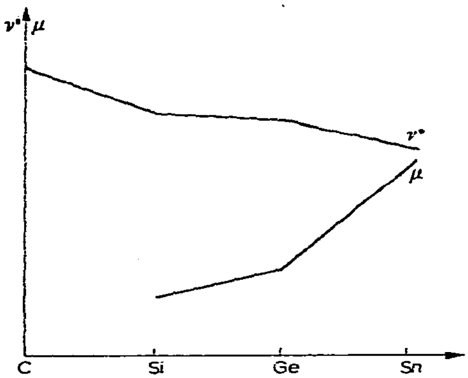

Fig. 14. The change of the wave number (ν^*) and the dipole moment (μ) of compounds belonging to the $(CH_3)_3$–E–$CH_2C_6H_5$ series, where E = C, Si, Ge, Sn.

electronegativity of silicon, germanium and tin depends to a greater extent on the substituents than that of the non-metallic elements in period II (B, C, N, O, F). On this basis and in agreement with other workers (Huang and Hui[1], Schmidtbauer[8]), the following two variations of the electronegativity sequence might be conceived for Group IV/1 : carbon, silicon, germanium, tin, lead or carbon, germanium, silicon, tin, lead.

By plotting the wave number of the absorption maxima of the benzyl compounds against the dipole moments (Fig. 15) a straight line is obtained both for the *p*-band and the α-band. The figure shows a strict agreement between the two kinds of measurements. Moreover, it proves that the following sequence for the electronegativity of the elements of Group IV/1 is correct: carbon, silicon, germanium, tin.

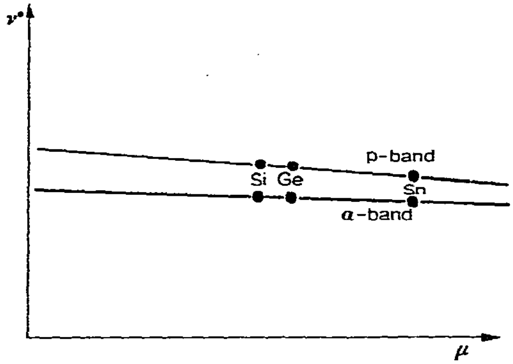

Fig. 15. The change of the wave numbers belonging to the α- and *p*-bonds of $(CH_3)_3$–E–$CH_2C_6H_5$ series in the function of the dipole moment (where E = Si, Ge, Sn).

SUMMARY

1. The character of the d_π–p_π bond formed between the phenyl group and the elements of Group IV/1 has been examined. On the basis of the ultraviolet spectra and dipole moments of the trimethylphenyl–E and trimethylbenzyl–E (where E represents carbon, silicon, germanium and tin) compounds synthesized by us, it has been established that the heteroatoms—except carbon—being directly bonded to the aromatic ring become conjugatively connected with the aromatic system.

2. The bathochromic effect appearing in the ultraviolet spectrum of trimethylphenylsilane was proved by means of quantum-chemical calculations. The partial charge shares and the bond orders of the atoms in the molecule were computed.

3. It was proved by a variation method that the ultraviolet spectrum of the trimethylphenyl compounds must show a hypsochromic shift from silicon to tin.

4. In the series of the trimethylbenzyl–E compounds (except the carbon analogue) a considerable bathochromic shift is caused by the hyperconjugation effect of the CH_2-group, since the hyperconjugation appears in both direction (both towards the heteroatom and the phenyl group).

5. On the basis of the experimental data, the value of the electronegativity in Group IV/1 decreases in the following sequence: carbon, silicon, germanium, tin.

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