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THE ROLE OF INDUCTIVE, HYPERCONJUGATIVE AND *d*-ORBITAL EFFECTS IN ORGANOSILICON COMPOUNDS

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Summary

The inductive hyperconjugative and *d*-orbital effects of $PhSiMe_3$, $PhSiH_3$, $PhSiF_3$ and of the respective carbon analogues have been investigated. Comparisons of calculated (CNDO/S method) and observed shifts for HOMO and LUMO levels indicate that all three effects have important roles in the organosilicon compounds. The relative importance of the effects depends on the compound; e.g. in $PhSiMe_3$ and $PhSiH_3$ hyperconjugation is the main effect, but in $PhSiF_3$ the effect of the *d*-orbitals is more important. The bathochromic shift in the UV transition of organosilicon compounds is not evident for the *d*-orbital effect.

Silicon gives stable covalent bonds with various types of organic groups. Most organosilicon compounds contain tetracoordinated silicon in a tetrahedral arrangement, but five or six coordination can occur when electronegative ligands are present. In these cases the chemical bonds are usually thought to involve participation of *d*-orbitals, but an alternative description of the bonding structure not involving *d*-orbitals has also been offered [1]. According to West the participation of 3*d* orbitals is fairly evident [2] but the degree of such participation is less than that expected for the simple hybridization model.

Much more controversial is the participation of vacant *d*-orbitals of silicon in dative π-bonds in organosilicon compounds. As silicon is less electronegative than carbon R_3Si groups could be expected to be more electron releasing than R_3C groups, but there are many examples of the opposite behaviour, and the usual explanation is that lone electron pairs or π-systems of the substituents donate electron to the vacant *d*-orbitals of silicon in partial $(d–p)\pi$ bonding [3]. As first noted by Pitt [4,5] most (if not all of the features concerned) can be alternatively, explained in terms of hyperconjugative effect of $\sigma^\star$ orbitals of proper symmetry, and that it is not necessary to use *d*-orbitals.

The outcome of the present work is to show that none of the effects can be separately used for explaining the experimental facts, and that it is better to use a combination of them.

Experimental

The UV photoelectron spectra of $PhSiMe_3$ and $PhSiF_3$ were recorded on an instrument at Tokyo University using Ne(I) resonance line (16.85 eV). For the analysis of the emitted electrons a hemispherical analyzer was used. The spectral data of other investigated substances were taken from the literature [6,7].

In order to evaluate the various electronic effects MO calculations were carried out with a modified version of the CNDO/S method described elsewhere [8].

Results

We first assume that the complex effect of a trimethylsilyl group is the resultant of the inductive (I), hyperconjugative (h) and d-orbital (d) effects. We then model such effects by quantumchemical calculations on the compounds $PhSiH_3$, $PhSiMe_3$, $PhSiF_3$ and their carbon analogues.

The calculations were made by the modified CNDO/S method with and without d-orbitals, with and without inclusion of hyperconjugation. Hyperconjugation was eliminated by setting the corresponding matrix element equal to zero. Bock et al. [9] made similar calculations for silyl and methylacetylenes. Since in the calculation including d-orbitals (and without hyperconjugation) the energy of the HOMO level was lower than that in acetylene they concluded that the d-orbital effect in these molecules is negligible.

The results of our calculations are shown in Figs. 1–3. The starting points are the e_{1g} (HOMO) and e_{2u} (LUMO) levels of benzene and their splittings and shifts under the effects of the various substituents are illustrated. The symbols + and − indicate the inclusion or neglect, respectively, of d or h effects. The experimental IP's and the calculated total charge of the groups (q) are also shown.

We consider the investigated effects in sequence and try to assess to their relative magnitudes values. The MH_3 and MMe_3 groups are considered first (Figs. 1, 2).

Inductive effect

The electronegativity of silicon is lower than that of the carbon so greater $+I$ effects are to be expected for SiH_3 and $SiMe_3$ groups. In fact, in the calculations without h and d $(\overset{-}{-})$ the SiH_3 and $SiMe_3$ groups show larger positive values of I than do the CH_3 or CMe_3 groups, the I effects being measured by the shifts from the benzene levels. From the Figs. 1–3 it can be deduced that MMe_3 groups are less electronegative than the MH_3 groups.

Hyperconjugation

On inclusion of h ($\mp$) an increase of positive charge on the substituents can be observed. The benzene levels are destabilized and markedly split. The $\psi_{a''}$ level rises more, since the substituent is not in the nodal plane, and the effect on $\psi_{a'}$ is far less. The splitting of the levels indicates that the hyperconjugative effects of CH_3 and CMe_3 groups are much greater than those of the groups containing silicon. In the carbon derivatives the positive charge on the substituent is raised by this greater hyperconjugative effect, but this does not compensate for the difference between the electronegativities of silicon and carbon.

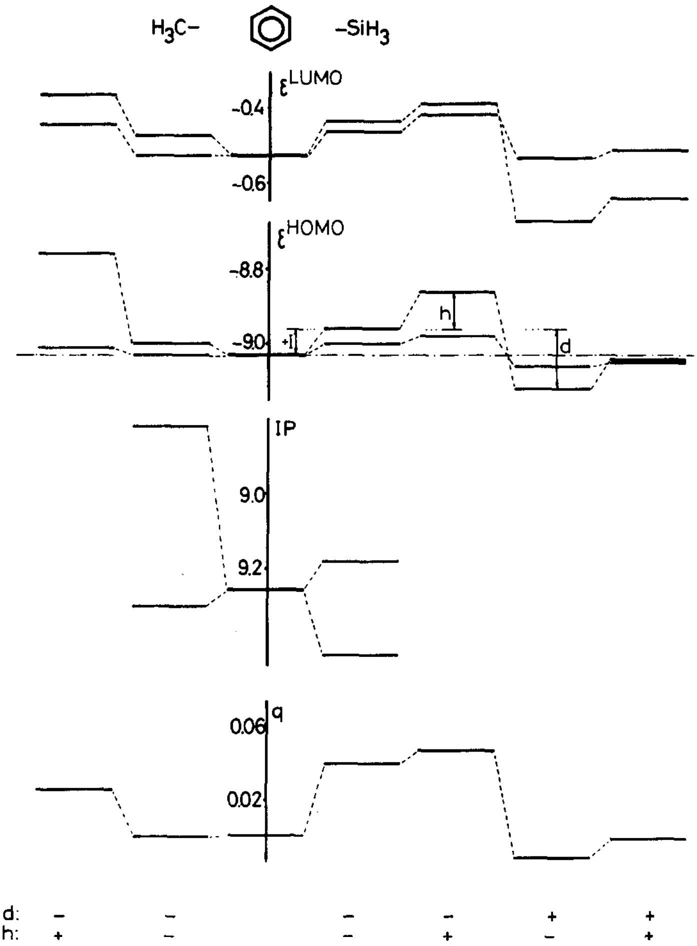

Fig. 1. Effect of CH_3 and SiH_3 groups on the energy levels of benzene.

d-Orbital effect

The *d*-orbitals (±) have opposite effects on the MOs compared with the *h* effects. As the vacant *d*-orbitals permit back-donation the positive charge on the group is expected to decrease. The shift and splitting of orbitals as a result of $+I$ are counterbalanced, and the shift and the splitting can even be in the opposite direction.

The effect of *h* is significant in every case as indicated by the considerable splitting, and it is greater for CH_3 and CMe_3 than for the silicon groups. This lower splitting for the silicon compounds may also arise from the *d*-orbital effect, as suggested by the absence of destabilization compared with benzene. There can even be a small stabilization; the exact value of it is difficult to specify because of the uncertainty in the experimental spectral data and the Jahn–Teller effect in benzene.

One can see that the calculated effects (shifts, splittings) are always smaller than the experimental values. This causes problem mainly in the case of the I effect and is the reason why the situation $(^{+}_{+})$ in $PhSiH_3$ leads to great distortion. If the $+I$ effect

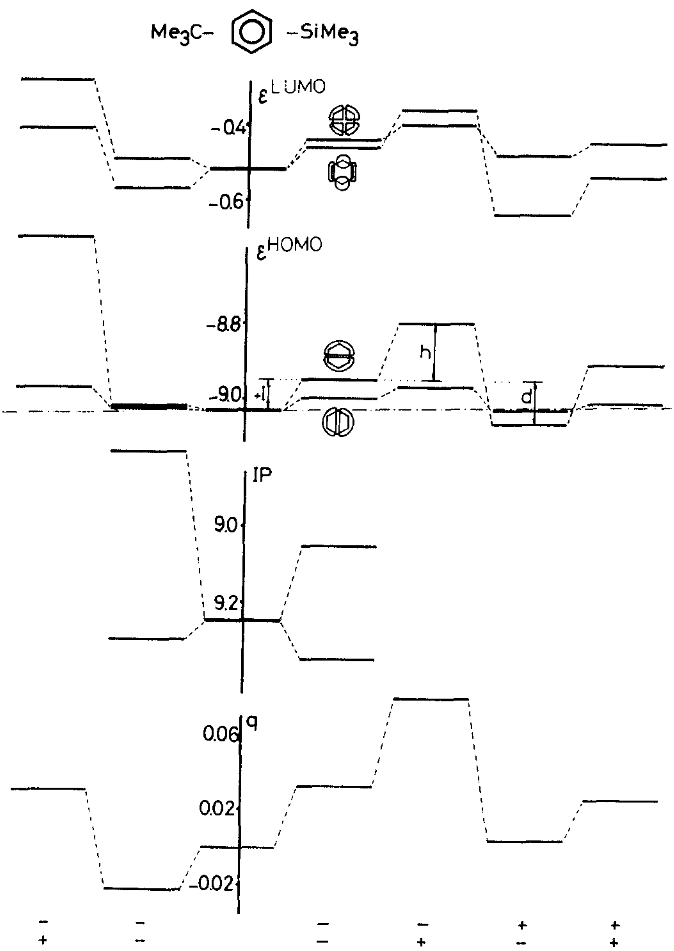

Fig. 2. Effect of CMe_3 and $SiMe_3$ groups on the energy levels of benzene.

is assumed to be greater than calculated, the *d*-orbital effect will not compensate for it and the situation $(^{+}_{+})$ will be more probable.

To clarify the effects of *d*-orbitals, calculations were made for CF_3 and SiF_3 groups (Fig. 3), for which only a very slight hyperconjugation is expected. It can be seen from the figure that there is little difference between the calculations made with or without *h*, and the dominant effects are *I* and *d*. As the CF_3 group is more negative the orbital energies of the carbon derivatives are smaller without *d*-orbitals. On inclusion of *d*-orbitals the order is upset and the splitting increases. In both compounds the HOMO level is certainly $\psi_{a'}$. The experimental spectra shows that the splitting of e_{2g} orbitals is actually almost the same in both compounds (or a little greater in case of $PhSiF_3$). At the same time the stabilization is also greater in $PhSiF_3$, and this can only be attributed to *d*-orbitals.

The various effects are similar on the LUMO levels, the only difference being in their relative magnitudes: *h* is smaller and *d* is greater than for the HOMO level. The unambiguous proof for *h* in carbon derivatives is that the LUMO is higher than in

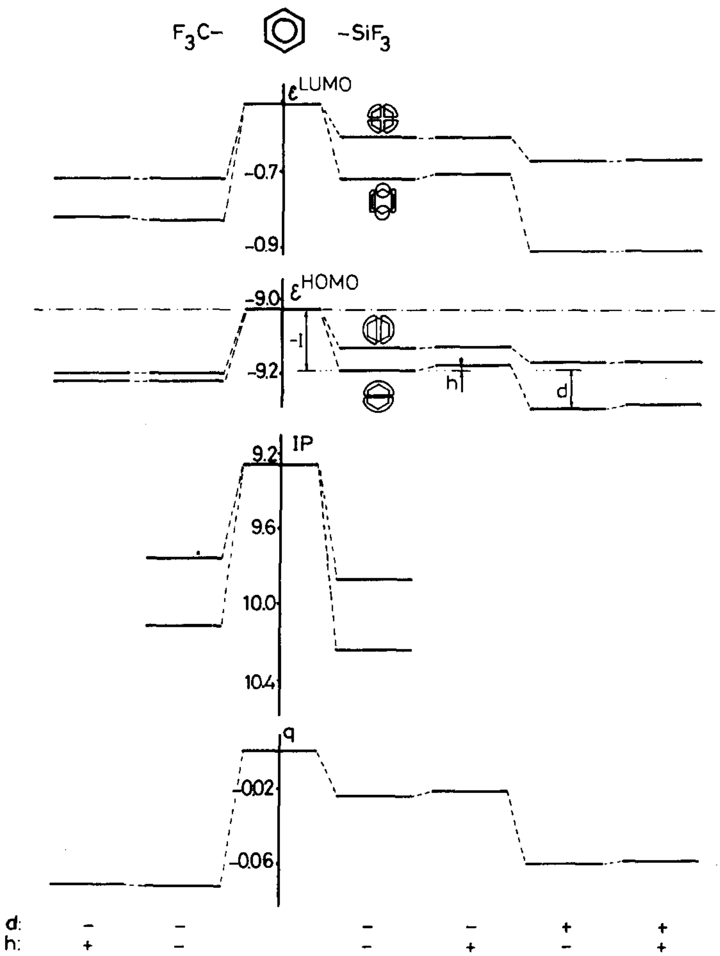

Fig. 3. Effect of CF_3 and SiF_3 groups on the energy levels of benzene.

benzene. Similarly, since the *I* and *h* effects for organosilicon groups are in the opposite direction to those of *d*, the proof of the participation of *d*-orbitals is that the LUMO is lower than in benzene. Unfortunately, there are no polarographic data for the investigated compounds, but the reduction of related biphenyl derivatives was in every case easier than that of the parent hydrocarbons [10,11].

The relative order of each effect on the basis of experiments and calculations is as follows:

$+I$: $CF_3 < SiF_3 \ll CMe_3 < CH_3 < SiH_3 < SiMe_3$

h: $CF_3 \sim SiF_3 \ll SiH_3 < SiMe_3 < CH_3 < CMe_3$

d: $SiH_3 \sim SiMe_3 < SiF_3$

For the influence of *d*-orbitals on electron transitions the following simple explanation can be given. The vacant *d*-orbitals are of the antibonding type lower both bonding and antibonding levels. As their levels are closer to the virtual levels in energy, the stabilization of virtual orbitals are greater and a bathochromic shift of the electronic transition is observed. The result of *h* is also a bathochromic shift but by a different mechanism. The excitation energy decreases as a result of the stronger destabilization of occupied orbitals. For both the HOMO and LUMO levels both effects can be seen in the figures. The calculations (Table 1) reveal one surprising fact which is that although the participation of *d*-orbitals stabilizes the LUMO levels more than the HOMO levels this does not mean that the given electron transition shows a red shift. The *d*-orbitals cause a small hypsochromic effect on the transition in all cases. The main reason for this is the mixing of transitions in configuration interactions included in the calculations. As mentioned above, the calculations underestimate the effects, and the absolute values of the shifts of the orbitals are

TABLE 1

EXPERIMENTAL AND CALCULATED UV TRANSITIONS (eV)

Compound	CNDO/S		Experimental
	with *d*	without *d*	
$PhSiH_3$	4.846	4.809	4.71 [12]
	6.001	6.013	5.77
	6.725	6.790	6.46
	6.879	6.865	
$PhCH_3$		4.750	4.75 [12]
		5.965	6.11
		6.771	6.81
		6.775	
$PhSiMe_3$	4.819	4.789	4.687 [14]
	5.952	5.921	5.766
	6.684	6.665	6.595
	6.843	6.833	
$PhCMe_3$		4.664	4.82 [12]
		5.824	5.96
		6.709	6.81
		6.731	
$PhSiF_3$	4.857	4.841	4.705 [13]
	6.027	6.019	5.904
	6.741	6.732	~ 6.7
	6.919	6.905	
$PhCF_3$		4.808	
		6.047	
		6.840	
		6.854	
$PhSiCl_3$	4.846	4.826	4.661 [13]
	6.002	5.985	5.700
	6.746	6.715	6.491
	6.870	6.880	
$PhCCl_3$	4.726	4.725	4.61 [12]
	5.871	5.874	5.51
	6.735	6.739	6.44
	6.757	6.761	

lower then the actual ones. It is thus possible that the difference between the HOMO and LUMO is lowered under the influence of *d*-orbitals causing a real decrease in excitation energy, but it is not really necessary to assume this. This means that a bathochromic shift in the UV spectrum does not necessarily prove the participation of *d*-orbitals. The opposite situation, in which the excitation energies for the carbon analogue are less (e.g. $PhCCl_3 - PhSiCl_3$) similarly does not prove the lack of *d*-orbitals.

References

1 T.B. Brill, J. Chem. Educ., 50 (1973) 392.
2 R.T. West and J. Barton, J. Chem. Educ., 57 (1980) 334.
3 E.A.V. Ebsworth in A.G. McDiarmid (Ed.), Organometallic Compounds of the Group IV elements. Vol. 1., Marcel Dekker, New York, 1968.
4 C.G. Pitt, J. Organomet. Chem., 23 (1970) C35.
5 C.G. Pitt, J. Organomet. Chem., 61 (1973) 49.
6 R.A.N. McLean, Can. J. Chem., 51 (1973) 2089.
7 G.G. Ramsey, J. Organomet. Chem., 135 (1977) 307.
8 T. Veszprémi, Chem. Phys. Letters, 88 (1982) 325.
9 W. Ensslin, W. Bock and G. Becker, J. Am. Chem. Soc., 96 (1974) 2757.
10 M.D. Curtis and A.L. Allred, J. Am. Chem. Soc., 87 (1965) 2554.
11 F. Correa-Duran, A.L. Allred, D.E. Glover and D.E. Smith, J. Organomet. Chem., 49 (1973) 353.
12 Z. Dinya, Elektronspektroszkópia. Tankönyvkiadó, Budapest, 1979.
13 T. Veszprémi, J. Nagy and J. Réffy, Kém. Közlemények, 46 (1976) 418.
14 T. Veszprémi, J. Réffy and J. Karger-Kocsis, J. Chim. Phys., 75 (1978) 1013.