σ–π Mixing in Phenylpentamethyldisilane

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Summary The photoelectron spectrum of phenylpentamethyldisilane, a substituted benzene in which the σ-electrons of the substituent are more easily ionized than the benzene π-electrons, has been determined; the highest occupied MO is assigned to a linear combination of $\pi(C_6H_5)$ and σ(SiSi) orbitals, resulting from σ–π mixing.

A NUMBER of publications[1–5] have demonstrated the importance of σ–π interaction in determining the electronic properties and reactivity of benzenoid π-systems containing organometallic substituents (*e.g.* $PhCH_2MX$, M = Si, Ge, Sn, Hg, Mn, Mo, W, Fe, or Co^{3-}). As well as its effect on the ionization potential of the π-electrons, it has been shown[3] that there is a good correlation between the magnitude of the σ–π interaction, and the σ^+ constant of the σ-substituent. However, thus far quantitative studies of σ–π interaction have been confined to $PhCH_2M$ systems where the σ-electron density of the substituent is primarily associated with the benzylic position, and where the I.P. of the participating σ-electrons is probably higher than that of the highest occupied π-MO of benzene. It is clearly of interest to determine the importance of σ–π interaction in other organometallic benzene derivatives, particularly where the relative energies of the σ and π electrons are the reverse of that normally found in organic systems. We report here on the use of photoelectron (p.e.) and charge transfer (c.t.) spectroscopy to determine the magnitude of σ–π mixing in phenylpentamethyldisilane ($PhSi_2Me_5$). The vertical I.P. of the σ(SiSi) electrons in $Me_3SiSiMe_3$ is reported[5] to be 8·69 eV, which is substantially lower than 9·25 eV, the corresponding I.P. of the highest occupied π-MO of benzene.[6]

The p.e. spectrum of $PhSi_2Me_5$, measured using a Perkin-Elmer PS16 instrument (He–I lamp, electrostatic sector 127°), shows three low energy bands, at 8·35, 9·07, and 10·03 eV, the latter being partially obscured by the onset of a broader unresolved band [σ(SiMe)][5] at 10 eV. The 9·07 eV band can unambiguously be assigned to ψ_{as} of the originally degenerate e_{1g} MOs of benzene, for this MO is nodal at the position of substitution and so only weakly perturbed. The bands at 8·35 and 10·03 eV are assigned to the linear combinations $C_1\ \psi_{SiSi} - C_2\ \psi_{sym}$ and $C_2\,\psi_{SiSi} + C_1\ \psi_{sym}$, respectively, where $C_1 > C_2$. The band at 8·35 eV cannot be assigned solely to an inductomerically shifted ψ_{sym} MO, for only a slightly smaller shift would then be expected for the monosilyl analogue $PhSiMe_3$, whereas in fact the ψ_{sym} band of the latter is at *ca.* 8·9 eV.[7]

Similarly the possibility that the 8·35 eV band arises solely from an inductively shifted σ(SiSi) orbital can also be ruled out on the basis of the tetracyanoethylene (TCNE) c.t. spectrum of $PhSi_2Me_5$. The TCNE c.t. spectra of monosubstituted benzenes generally consist of two bands in the visible spectrum, which are considered[8] to arise from the transitions $\psi_{as} \rightarrow \psi^*_{TCNE}$ and $\psi_{sym} \rightarrow \psi^*_{TCNE}$. Consistent with this assignment, the energies of these transitions are found to be linearly related to the absolute energies of ψ_{as} and ψ_{sym} when comparisons are made with the p.e. determined energies of ψ_{as} and ψ_{sym} of a variety of substituted benzenes.[6,8] Since the permethylated polysilanes do not form spectroscopically detectable c.t. complexes with TCNE[9] (presumably for steric reasons), despite their low I.P. values, the c.t. determined I.P. of $PhSi_2Me_5$ will correspond to the I.P. of the π electrons. The TCNE charge transfer spectrum of $PhSi_2Me_5$ is reported[10] to exhibit maxima at 25,000 and 20,400 cm^{-1}. Using the $\nu_{c.t.}$–I.P. correlation (1) of Farrell and Newton,[11] these transition

$$h\nu = 0{\cdot}83\ \text{I.P.} - 4{\cdot}42\ \text{eV} \qquad (1)$$

energies correspond to I.P. values of 9·06 (ψ_{as}) and 8·37 eV (ψ_{sym}), in good agreement with the p.e. values.† The 8·35 eV band in the p.e. spectrum must therefore be described in terms of a composite of σ(SiSi) and π_{sym} orbitals.

Assuming Koopmans' theorem,[12] the σ–π splitting in $PhSi_2Me_5$ is *ca.* 0·35 eV (Figure). This is substantially less than that observed for $PhCH_2SiMe_3$ (*ca.* 0·90 eV) and other substituents of the type $PhCH_2MX$. Theoretical calculations[13] suggest that this is partially related to the overlap (S) and resonance (β) integrals of the atom α to the π-system. The smaller values of S and β associated with silicon will

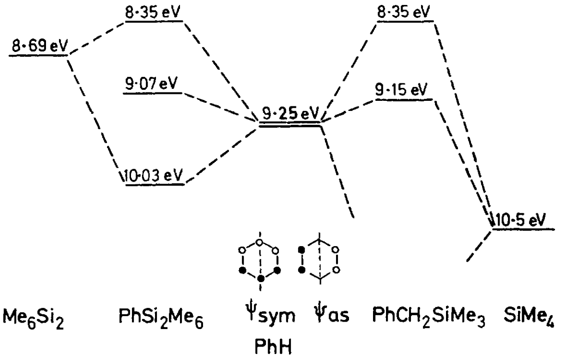

FIGURE. *Photoelectron energies of the highest occupied* MOs *of* $SiMe_4$, Si_2Me_6, PhH, $PhCH_2SiMe_3$, *and* $PhSi_2Me_5$, *and correlation diagram of σ–π mixing.*

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† Since the correlation (1) was developed for adiabatic I.P.s this agreement is not quite so exact, but is within ± 0·2 eV.

reduce the magnitude of α–π interaction relative to when carbon is adjacent to the benzene ring.

Manifestations of the large σ contribution to the highest occupied MO of $PhSi_2Me_5$ include (*a*) the long wavelength transition in the electronic spectrum at 236 nm which is partially $\sigma \rightarrow \pi^*$ in character,[14] and (*b*) a failure of the previously observed[15] correlation between the electrophilic aromatic reactivity, measured as $\sigma^+\rho$, and the I.P. The $\sigma^+\rho$ constant of the Me_5Si_2 group is reported[16] to be −0·23, substantially smaller than the value (−0·62) predicted by the correlation, $\nu_{c.t.} = (9300\,\sigma^+ + 26{,}200) \pm 500\ cm^{-1}$, which Hanstein, Berwin, and Traylor[3] showed to be valid for a variety of other substituents.

A more detailed discussion, including conformational aspects, will be published elswhere.

(*Received, October 29th*, **1971**; *Com.* 1884.)

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