

## NOTE

### PHENYL RING SILICON ATOM INTERACTION: THE HELIUM 584 Å PHOTOELECTRON SPECTRUM OF PHENYLTRIMETHYLSILANE

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The interaction between benzene ring and a substituent can be investigated by a number of spectroscopic methods. A direct estimation of the perturbation arising from the substituent on the degeneracy of the highest occupied  $\pi$  level ( $\pi_2, \pi_3$ ) of the benzene ring can be obtained by measuring vertical ionisation potentials of Ph-X derivatives<sup>1</sup>. This level undergoes changes due to two effects: (a) Alteration of its average energy, and (b) a splitting which is the more important when the occupied  $p$  levels of the substituent are very close in energy to the  $\pi$  levels of the benzene ring.

At first sight, a substituent that could contribute a  $p$ -electron pair to the aromatic system may be expected to decrease the ionisation potential. Conversely an electron-withdrawing substituent increases the ionisation energy. Preceding studies<sup>1,2</sup> have shown that, in the 584 Å photoelectron spectra of many monosubstituted benzenes of general formula Ph-X, where X is an electron-withdrawing group (NO, NO<sub>2</sub>, CN, CHO) the vertical ionisation potential is distinctly larger than 9.80 eV, (the value of benzene is 9.40 eV). On the other hand when X = Cl, Br, I, NH<sub>2</sub>, the vertical ionisation potential is less than 9.40 eV. Moreover the splitting of the highest  $\pi$  level, as measured by the difference between  $\pi_2$  and  $\pi_3$  ionisation potentials, is small for the substituents of the first class, and if a second substituent is introduced in *para*-position the splittings are additive.

In the present paper we have examined phenyltrimethylsilane I and *p*-fluorophenyltrimethylsilane II. Photoelectron spectra have been obtained using high resolution electrostatic sector energy analyser and recorded by keeping electron-focusing voltage constant and sweeping through a range of accelerating voltage applied to photoelectron just before admission to deflecting region.

The spectrum of I (Fig. 1a) shows that the lowest *I.P.* band is situated at 9.0 eV which is a lower *I.P.* than the corresponding band in benzene and that the splitting of the band is less than 0.2 eV. The shape of the band is very similar to that of PhCMe<sub>3</sub> (Fig. 1c) but the  $\pi_2, \pi_3$  splitting is not resolved. This can suggest that a ( $-M$ ) effect associated with the empty silicon  $d$ -orbitals is slightly more than balanced by an electron releasing effect owing to the presence of the three methyl groups. The overall

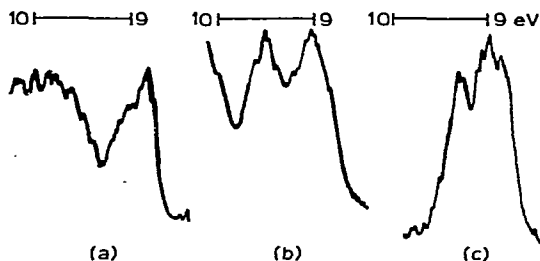


Fig. 1. Low I.P. bands in spectra of (a)  $\text{Ph} \cdot \text{SiMe}_3$ , (b)  $p\text{-FC}_6\text{H}_4 \cdot \text{SiMe}_3$  and (c)  $\text{Ph} \cdot \text{CMe}_3$ .

electron releasing effect of the  $\text{SiMe}_3$  group has been confirmed by  $^{14}\text{N}$  NMR spectroscopy<sup>3</sup>. The spectrum of II (Fig. 1b) appears to be quite similar to that of I except that the first band is clearly splitted into two components separated by about 0.45 eV, in agreement with what we could predict from the additivity rule<sup>1</sup> and the spectra of  $\text{PhF}$  ( $\approx 0.3$  eV) and I (less than 0.2 eV).

#### REFERENCES

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