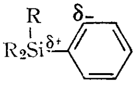
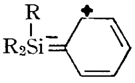
Interaction between a Phenyl Ring and Silicon Atom. The Nitrogen-14 Nuclear Magnetic Resonance of Nitrophenyltrimethylsilanes

By Y. VIGNOLLET and J. C. MAIRE*
(*Laboratoire des Organométalliques, Faculté des Sciences de Marseille, 13 Marseille, (13°), France*
and M. WITANOWSKI
(*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warszawa, Poland*)

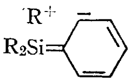
THE interaction between the phenyl ring and the silicon atom in phenylsilanes can be described as inductive (*I*) or mesomeric (*M*). The inductive effect will release electrons into the ring (a), whereas the resonance effect can either withdraw the ring π-electrons into the silicon *d*-orbitals (b) or transfer electronic charge to the *ortho*- and *para*-positions by hyperconjugation (c); structure (c) tends to reinforce the *I* effect (a).



(a)



(b)



(c)

In several studies of spectroscopic properties of silicon aromatic compounds[1-3] it has been suggested that the results could be best interpreted in terms of the participation of *d*-orbitals in the phenyl–silicon bond. However, there has been no definite evidence of this.

The ^{14}N chemical shifts of the nitro-group in aromatic nitro-compounds have been investigated.[4] The results were consistent with the trends previously reported for nitro-alkanes[5] where the electron-withdrawing effect resulted in an upfield shift of the resonance. Practically no effect (outside experimental error) of the difference in conjugation between the nitro-group and other substituent in the *ortho*-, *para*-, and *meta*-positions, respectively, was observed, and this was explained as due to insignificant changes in the total π-bond order at the nitrogen atom. However, if the other substituents is a silicon atom contributing its *d*-orbitals to the conjugated system, some effect might be expected. We have prepared and investigated three isomeric nitrophenyltrimethylsilanes (Table).

The ^{14}N shifts within this set of isomers show differences significantly larger than experimental error. In particular the *para*-isomer exhibits an extensive shielding with respect to the other isomers. This alone may be considered as a serious argument for an appreciable conjugation effect. If the inductive effect determines the shift, the expected order, based on the relative electronegativities of silicon (sp^3) and carbon (sp^2) atoms would be $\delta_{ortho} > \delta_{meta} \sim \delta_{para}$. The *M* effect should result in a difference between δ_{meta} and δ_{para}, while δ_{ortho} may be affected by the possible non-coplanarity of the nitro-group and the phenyl ring caused by steric interactions. In the latter case, the inductive effect should be dominant in the ^{14}N shift for the *ortho*-isomer. All this is in agreement with the experimental data, where the *ortho*-isomers show the resonance at the lowest field and the *para*-isomer at a field substantially higher than the other two isomers. It seems reasonable to conclude that some conjugation effect does exist between the silicon *d*-orbitals and the ring π-orbitals.

The half-height width of the signals decreases in order *para* > *meta* > *ortho*. Such a decrease was assumed[4] to be due to a decrease in conjugation; this is also in agreement with the arguments based on the chemical shifts.

The measurements of the ^{14}N spectra, using an internal reference technique, were carried out as in earlier work.[4,5] The compounds were prepared by nitration of phenyltrimethylsilane, followed by g.l.c. separation of isomeric nitro-derivatives.[6]

Compound	^{14}N shift* δ_N (p.p.m.)	Half-height signal width (c./sec.)
o-Nitrophenyltrimethylsilane	$+7\pm1$	100 ± 5
m-Nitrophenyltrimethylsilane	$+9\pm1$	139 ± 5
p-Nitrophenyltrimethylsilane	$+12\pm1$	182 ± 5

* Referred to nitromethane, but measured directly from dimethylformamide ($\delta_N = +\ 276$ p.p.m.); the positive sign denotes an upfield shift; measured at 4·33 Mc./sec., Varian HR-60.

(*Received, July 1st, 1968; Com.* 864.)

---

[1] J. F. Hemmert and J. C. Maire, *Bull. Soc. chim. France*, 1963, 2785.
[2] E. A. V. Ebsworth and S. G. Frankiss, *J. Amer. Chem. Soc.*, 1963, **85**, 3516.
[3] J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, 1963, **59**, 53.
[4] M. Witanowski, L. Stefaniak, and G. A. Webb, *J. Chem. Soc.* (*B*), 1967, 1065.
[5] M. Witanowski, T. Urbanski, and L. Stefaniak, *J. Amer. Chem. Soc.*, 1964, **86**, 2568.
[6] Y. Vignollet, Thesis, Marseille, 1968.