Journal of Organometallic Chemistry, 49 (1973) C19–C21
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Organosilicon compounds
CIV*. Silicon-29 NMR chemical shifts in some carbofunctional organosilicon compounds

J. SCHRAML, J. POLA, V. CHVALOVSKY

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague-Suchdol, (Czechoslovakia)

M. MÄGI and E. LIPPMAA

Institute of Cybernetics, Estonian Academy of Sciences, Tallinn (U.S.S.R.)

(Received December 18th, 1972)

Recent interest in silicon-29 resonance[2-9] prompts us to report some of our preliminary results on the ^{29}Si NMR spectra of the compounds $(CH_3)_{3-n}X_nSiCH_2Y$ (I) in which Y = $OC(O)CH_3$, and X = OC_2H_5 or $OC(O)CH_3$. These results represent a part of a wider study of compounds of the type $(CH_3)_{3-n}X_nSi(CH_2)_mY$ (II), studies of which were begun by several methods, including NMR of ^{1}H, ^{13}C, and ^{29}Si nuclei, a few years ago[10] with the aim of finding out what role hyperconjugation plays in such compounds.

^{29}Si NMR chemical shifts (on the δ-scale) are summarized in Table 1; the spectra

TABLE 1

SILICON-29 CHEMICAL SHIFTS[a], δ(Si), AND SUBSTITUENT INCREMENTS[b], Δδ(Si) FOR $(CH_3)_{3-n}X_nSiCH_2OC(O)CH_3$ AND $(CH_3)_{4-n}SiX_n$ COMPOUNDS

Group X	*n*	*δ(Si)*			*Δδ(Si)*	
		$Me_{3-n}X_nSiCH_2OAc$	*$Me_{4-n}SiX_n$*			
OC_2H_5	0	+ 0.3	0.0		+ 0.3	
	1	+ 9.0	+13.5		– 4.5	
	2	–16.1	– 6.1		–10.0	
	3	–58.2	–44.5		–13.7	
$O\underset{\underset{O}{\|}}{C}CH_3$	1	+13.8	+23.5[c]	+22.3[d]	– 9.7[c]	– 8.5[d]
	2	–18.1	+ 5.5[c]	+ 4.4[d]	–23.6[c]	–22.5[d]
	3	–82.5	–44.5[c]	–42.7[d]	–38.0[c]	–39.8[d]

[a] In ppm (± 0.3 ppm), relative to external tetramethylsilane; positive values correspond to downfield shifts. [b] As defined in the text. [c] Based on the data of ref. 3. [d] Based on the data of ref. 8.

---

*For part CIII see ref. 1.

were measured in neat liquids in natural ^{29}Si abundance (except for $(CH_3COO)_3SiCH_2OOCCH_3$ which was measured as a 30% solution in $CHCl_3$) using the spectrometer described earlier[11] (operating frequency 11.91 MHz, cw* absorption mode spectra accumulated both with and without proton decoupling, external referencing, maximum error 0.3 ppm). The preparation and some other properties of the studied compounds have been described elsewhere[1].

When the chemical shifts in $(CH_3)_{3-n}X_nSiCH_2Y$ compounds (δ(Si)(for $(CH_3)_{3-n}$-X_nSiCH_2OAc)) are combined with those in $(CH_3)_{4-n}X_nSi$ (δ(Si)(for $(CH_3)_{4-n}X_nSi$)) the shielding effect $\Delta\delta$(Si) of substituting a $CH_3C(O)O$ group for hydrogen in $SiCH_3$ can be calculated as the difference between the shifts in the pair of compounds with the same X and n, *i.e.*:

$$\Delta\delta(\mathrm{Si}) = \delta(\mathrm{Si})(\text{for } (CH_3)_{3-n}X_nSiCH_2OAc) - \delta(\mathrm{Si})(\text{for } (CH_3)_{4-n}X_nSi)$$

The shielding contributions or the substituent effects thus calculated are given in Table 1.

Inspection of Table 1 reveals the following facts:

(1) The substituent effect is not constant, it varies almost linearly with n in both series of compounds I.

(2) The slope of the plot of $\Delta\delta$(Si) against n is about twice as large in the series with X = OAc as in that with X = OEt.

(3) The substituent effect changes its sign from positive (+0.3 ppm, in the case $n = 0$) to negative when at least one oxygen atom is directly bonded to the silicon atom. Furthermore, an acetoxy group separated by one CH_2 group from the silicon atom increases the shielding of the silicon, which is the opposite to what one would expect from operation of the inductive effect of the acetoxy group alone.

Since interpretation of these findings would have to invoke such concepts as Si—O $(p\text{-}d)_\pi$ bonding, polarization of the Si—O bonds by electronegative substituents on silicon, and σ—π interaction (hyperconjugation), additional information was sought from ^{17}O, ^{13}C, and ^{1}H NMR spectra. ^{17}O NMR proved to be of little value, however[10], since the lines were very broad and rather insensitive to the structural changes. Chemical shifts of proton NMR resonances only varied within 0.5 ppm, except for those of the Si—CH_2—O protons which varied more, but irregularly. Of the ^{13}C NMR lines, those associated with the carbon atoms in the C_2H_5O and $CH_3C(O)O$ substituents on silicon were insensitive to substitution on the silicon. Chemical shifts of other carbon atoms varied to some extent but regularities in these variations were hardly discernible. Investigation of some carbon analogues provided no more insight.

Studies of more extensive series of compounds of type II with various substituents X and Y are in progress in the hope of throwing further light on the interpretation of the ^{29}Si shifts.

ACKNOWLEDGMENT

The authors wish to thank P. Novák for the preparation of studied compounds.

---

* cw = continuous wave.

REFERENCES

1 M. Jakoubková, P. Reich, Z. Papoušková, P. Novák, J. Pola and V. Chvalovský, *Coll. Czech. Chem. Commun.*, in press.
2 P.C. Lauterbur, in F.C. Nachod and W.D. Phillips (Eds.), *Determination of organic structures by physical methods, Vol. 2*, Academic Press, London, 1962, p. 465.
3 B.K. Hunter and L.W. Reeves, *Canad. J. Chem.*, 46 (1968) 1399.
4 G. Engelhardt, H. Jancke, M. Mägi, T. Pehk and E. Lippmaa, *J. Organometal. Chem.*, 28 (1971) 293.
5 M. Bacon, G.E. Maciel, W.K. Musker and R. Scholl, *J. Amer. Chem. Soc.*, 93 (1971) 2537.
6 H.C. Marsmann, *Chemiker Zeit.*, 96 (1972) 288.
7 G.C. Levy, *J. Amer. Chem. Soc.*, 94 (1972) 4793.
8 W. McFarlane and J.H. Seaby, *J. Chem. Soc. Perkin Trans. II*, (1972) 1561.
9 R.L. Scholl, G.E. Maciel and W.K. Musker, *J. Amer. Chem. Soc.*, 94 (1972) 6376.
10 V. Chvalovský, *Plenary lecture at IIIrd International Symposium on Organosilicon Chemistry*, Madison, U.S.A., 1972.
11 E. Lippmaa, T. Pehk and J. Past, *Eesti NSV Tead. Akad. Toim., Füüs.-Mat. Tehnikalead. Seer.*, 16 (1967) 345.