

SILICON-29 NMR CHEMICAL SHIFTS IN ORGANOSILICON COMPOUNDS CONTAINING CH₂Cl GROUP*

J. SCHRÁML, J. VČELÁK and V. CHVALOVSKÝ

Institute of Chemical Process Fundamentals

Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát 2

Received July 23rd, 1973

²⁹Si-, ¹³C- and ¹⁹F-NMR chemical shifts are reported for series of (CH₃)_{3-n}X_nSiCH₂Cl compounds with X = Cl and F. The substituent effect of the CH₂Cl group on the ²⁹Si-chemical shift varies with *n* in the two series of compounds investigated.

Lately, carbofunctional alkylsilanes have received considerable attention¹⁻⁶ various methods being used for the elucidation of the bonding situation in these compounds. Among the methods used ²⁹Si- and ¹³C-NMR appear promising, but before their potential could be fully exploited to the advantage of structural (and analytical) chemistry much more data than it is available now⁶⁻²¹, should be accumulated. This need of more data has been recently demonstrated¹¹ when the limited sets of ²⁹Si chemical shift data obtained in two laboratories^{9,11} were said¹¹ to lead to contradictory spectral assignments in chloromethylpentamethyldisiloxane and different signs of substituent effect of CH₂Cl group.

In order to provide more data and perhaps better insight into the controversial substituent effect of CH₂Cl group on the ²⁹Si shielding the compounds of the type (CH₃)_{3-n}X_nSiCH₂Cl with X = Cl and F were measured.

EXPERIMENTAL

Compounds

All the studied compounds were prepared by standard techniques. Some details of the preparation and other properties of the compounds can be found elsewhere^{16,22,23}.

NMR measurements

²⁹Si and ¹³C spectral data reported here were obtained using Bruker HFX 90 spectrometer. ¹³C- and ²⁹Si-NMR spectra were measured with the spectrometer ¹H locked, the former spectra were recorded at 22-62 MHz in the Fourier transform mode, the latter spectra were obtained by repetitive scanning and averaging (in a CAT) the frequency stabilized slow-passage, absorption

* Part CIX in the series Organosilicon compounds; Part CVIII: J. Organometal. Chem. 51, C5 (1973).

mode spectra at 17.87 MHz. The compounds were measured in 10 mm sample tubes containing mixtures of 90% (vol.) of the compound and 10% of tetramethylsilane as an internal standard and ^1H lock. ^{19}F -NMR spectra were measured at 56.4 MHz (Varian A 56/60, 5 mm sample tubes) using CCl_3F as internal standard.

RESULTS AND DISCUSSION

Contained in Table I are the carbon-13, fluorine-19 and silicon-29 chemical shifts for the studied compounds, included are also silicon-29 chemical shifts in $(\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_3$ compounds (taken from literature) and chemical shift increments of CH_2Cl group calculated according to Eq. (1).

$$\Delta\delta(\text{Si}) = \delta(\text{Si})(\text{for Me}_{3-n}\text{X}_n\text{SiCH}_2\text{Cl}) - \delta(\text{Si})(\text{for Me}_{4-n}\text{X}_n\text{Si}) \quad (1)$$

This increment is a collective measure of the substituent effect (either direct or indirect) of the CH_2Cl group on the silicon-29 shieldings.*

The important features of the data of Table I are as follows:

1) The dependences of silicon-29 chemical shifts on n in both series of chloromethylsilanes show overall pattern ("sagging") similar to that observed⁸ in the series of methylchlorosilanes and methylfluorosilanes, though

2) the substituent effect, $\Delta\delta(\text{Si})$, is not constant, *i.e.* the substituent effects are not directly additive in the series studied. The substituent effect varies with n in both series of compounds similarly, *i.e.* it changes its sign and its value becomes more negative as n increases. In contrast to this

3) the carbon-13 chemical shifts show different trends in the two series of compounds.

In comparison with the silicon-29 chemical shifts (the compound with $\text{X} = \text{Cl}$) measured elsewhere¹⁶, the higher precision achieved in the present work resulted only in minor corrections of the values (1.1 p.p.m. at the maximum) and has not affected the trends observed¹⁶. The only three values of $\Delta\delta(\text{Si})$ available for the series with $\text{X} = \text{F}$ seem to suggest that the substituent effect depends stronger on n in this series than in the series with $\text{X} = \text{Cl}$ resembling thus the series with $\text{X} = \text{OC}_2\text{H}_5$ or $\text{OC}(\text{O})\text{CH}_3$ ¹⁶. (The individual values of the substituent effect that are based on the literature data⁸ should be taken with a reserve since newer results^{10,16} show that in some unfavourable cases the data of ref.⁸ are subject to errors as large as 4 p.p.m.).

* The substituent effect thus defined is identical to the substituent chemical shift (SCS) of chlorine as defined by Dewar and Marchand²⁴. The reason for our preference to call the quantity the substituent effect of the CH_2Cl group is that it emphasises the fact that the chlorine is not directly bonded to the silicon atom.

TABLE I

Silicon-29, $\delta(\text{Si})$, Carbon-13, $\delta(\text{C})$, and Fluorine-19, $\phi(\text{F})$, Chemical Shifts^a and Substituent Increments, $\Delta\delta(\text{Si})$ ^b, for $(\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_2\text{Cl}$ and $(\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_3$ Compounds

Group X	n	$\text{Me}_{3-n}\text{X}_n\text{SiCH}_2\text{Cl}$				$\text{Me}_{4-n}\text{X}_n\text{Si}$	
		$\delta(\text{C})$		$\phi(\text{F})$	$\delta(\text{Si})$	$\delta(\text{Si})$	$\Delta\delta(\text{Si})$
		CH_3	CH_2				
Cl	0	-3.04	+30.57	—	+ 2.79	0.00	+ 2.79
	1	-0.13	+30.20	—	+23.08	+29.9 ^c	- 6.8
	2	+2.85	+30.75	—	+21.48	+31.8 ^c	-10.3
	3	—	+31.30	—	+ 1.65	+12.2 ^c	-10.6
F	1	-3.31	+28.27	-161.56	+24.83	+30.5 ^d	- 5.7 ^d
	2	-6.81	+24.31	-138.54	- 9.03	+ 4.5 ^d	-13.5 ^d
	3	—	+18.13	-143.99	-71.34	^e	—

^a Chemical shifts in p.p.m. positive value corresponds to a downfield shift. ¹³C- and ²⁹Si- shifts are relative to internal tetramethylsilane with a maximum error ± 0.1 p.p.m. ¹⁹F-shifts are relative to external CCl_3F with a maximum error ± 0.03 p.p.m. ^b Substituent increment $\Delta\delta(\text{Si})$ defined by Eq. (1). ^c Value taken from ref.¹⁶. ^d Value based on the data of ref.⁸. ^e Value not available.

The substituent effect of the CH_2Cl group has the sign expected on the electronegativity grounds only if $n = 0$. In order to explain the negative sign in the other cases it was suggested¹⁷ that the CH_2Cl group enhances the back bonding $\text{X}-\text{Si}$ bringing about an increase in the shielding. If it is really so, then the stronger dependence of the substituent effect in the series with $\text{X} = \text{F}$ reflects the well known fact that fluorine is better ($p \rightarrow d$) _{π} donor than chlorine. On the other hand, other interpretations of silicon-29 chemical shifts have been put forward^{18,25}. These two interpretations, though contradictory in some sense, do not consider ($p \rightarrow d$) _{π} bonds to play any major role in determining silicon-29 chemical shifts. Therefore any detailed interpretation of the present results must await till either the shifts are better understood or more data are available for a meaningful comparison to be made.

The authors are most grateful to Prof. D. Kummer, Technische Hochschule, Karlsruhe, for measuring the spectra.

REFERENCES

1. Fialová V., Bažant V., Chvalovský V.: This Journal 38, 3837 (1973).
2. Chvalovský V.: Plenary lecture at III. International Symposium on Organosilicon Chemistry, Madison U.S.A., 1972.

3. Komarov N. V., Roman V. K.: *Uspechi Chim.* 39, 1220 (1970).
4. Andrianov K. A., Petrashko A. I.: *Organometallic Chem. Rev.* 2, 383 (1967).
5. Brook A. G.: *Main Lecture at International Symposium on Organosilicon Chemistry, Prague, 1965*; *Pure Appl. Chem.* 13, 215 (1966).
6. Schraml J., Pola J., Chvalovský V., Mägi M., Lippmaa E.: *J. Organometal. Chem.* 49, C 19 (1973).
7. Lauterbur P. C., in the book: *Determination of Organic Structures by Physical Methods*, (F. C. Nachod, W. D. Phillips, Eds), Vol. 2, p. 465. Academic Press, London 1962.
8. Hunter B. K., Reeves L. W.: *Can. J. Chem.* 46, 1399 (1968).
9. Engelhardt G., Jancke H., Mägi M., Pehk T., Lippmaa E.: *J. Organometal. Chem.* 28, 293 (1971).
10. McFarlane W., Seaby J. H.: *J. Chem. Soc. Perkin Trans. II*, 1561 (1972).
11. Scholl R. L., Maciel G. E., Musker W. K.: *J. Am. Chem. Soc.* 94, 6376 (1972).
12. Marsmann H. C.: *Chemiker Ztg.* 96, 288 (1972).
13. Marsmann H. C., Horn H. G.: *Chemiker Ztg.* 96, 456 (1972).
14. Marsmann H. C., Horn H. G.: *Z. Naturforsch.* 27b, 1448 (1972).
15. Schraml J., Chuy N. D., Chvalovský V., Mägi M., Lippmaa E.: *J. Organometal. Chem.* 51, C 5 (1973).
16. Lippmaa E., Mägi M., Engelhardt G., Jancke H., Chvalovský V., Schraml J.: *This Journal*, in press.
17. Lippmaa E., Mägi M., Schraml J., Chvalovský V.: *Paper presented at XIth European Congress on Molecular Spectroscopy*, Tallin, USSR, 1973.
18. Engelhardt G., Jancke H., Lippmaa E., Mägi M.: *Paper presented at XIth European Congress on Molecular Spectroscopy*, Tallin, USSR, 1973.
19. Ernst C. R., Buell G. R., Spialter L.: *Paper presented at Organosilicon symposium*, Deuton, U.S.A., 1973.
20. Levy G. C.: *Paper presented at Organosilicon symposium*, Deuton, U.S.A., 1973.
21. Lambert R. L., Jr., Seyferth D.: *J. Am. Chem. Soc.* 94, 9246 (1972).
22. Jakoubková M., Reich P., Papoušková Z., Novák P., Pola J., Chvalovský V.: *This Journal* 38, 3471 (1973).
23. Včelák J., Chvalovský V.: Unpublished results.
24. Dewar M. J. S., Marchand A. P.: *J. Am. Chem. Soc.* 88, 3318 (1966).
25. Ljubimov V. S., Ionov S. P.: *Ž. Fiz. Chim.* 46, 838 (1972).

Translated by the autor (J. S.).