

**^{29}Si -NMR CHEMICAL SHIFTS IN ORGANOSILICON COMPOUNDS.
SUBSTITUENT EFFECT OF CH_2Cl GROUP***

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^{29}Si -NMR chemical shifts are reported and shown not to be a directly additive property of substituents.

^{29}Si -NMR chemical shifts of a series of compounds of formula $\text{Me}_{3-n}\text{X}_n\text{SiCH}_2\text{Cl}$ (*I*) and of some compounds of the type $\text{Me}_{4-n}\text{SiX}_n$ (*II*) with $\text{X} = \text{Cl}$, $\text{C}_2\text{H}_5\text{O}$ and CH_3COO have been measured. The chemical shifts δ_{Si} together with the shift increments $\Delta\delta_{\text{Si}}$ are listed in Table I. The increments $\Delta\delta_{\text{Si}}$ calculated as the difference between the ^{29}Si chemical shifts in the pair of compounds *I* and *II* of the same X and n

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

represent the shielding contribution or the substituent effect of CH_2Cl group^{1,2} as used in schemes of direct additivity of chemical shifts.

The $\Delta\delta_{\text{Si}}$ shielding contribution varies monotonously with n in the studied series. This variation has an important practical consequence, *i.e.* the direct additivity scheme does not hold for ^{29}Si chemical shifts even for such simple substituents as in CH_2Cl group.

Nonadditivity of the shielding effects of the substituents X in the $\text{Me}_{4-n}\text{SiX}_n$ series was already apparent from the work of Lauterbur⁴ and Hunter and Reeves⁵ who studied substituents X which they considered to be ($p \rightarrow d$) _{π} donors. Nevertheless, Maciel and coworkers⁶ have recently found that various substituents have roughly constant average substituent effects on ^{29}Si shieldings. Using the average value

* Part CX in the series Organosilicon Compounds; Part CIX: This Journal 39, 267 (1974).

(calculated from the shifts in five silanes not containing Si—O bonds) of +1.5 p.p.m. for the substituent effect of CH₂Cl group the authors⁶ assigned the two ²⁹Si resonance lines in chloromethylpentamethyldisiloxane which contained the Si—O bond.

The suggested assignment (*i.e.* the low field line assigned to the silicon atom bearing the CH₂Cl group⁶), is, we believe, erroneous and should be reversed for the following reasons: 1) the present data clearly indicate that the substituent effect of the CH₂Cl group is negative (−4.6 to −7.4 p.p.m.) when one oxygen atom is bonded to silicon. 2) In our previous study⁷, it was shown on four other linear siloxanes that the CH₂Cl group increases the silicon shielding in this class of compounds. 3) Data of Maciel and coworkers⁶ on chloromethylmethoxydimethylsilane yield in combination with the available data on methoxytrimethylsilane^{5,7} the substituent effect of −4.2 p.p.m.

In view of the present findings, the usefulness of additive scheme for ²⁹Si chemical shifts is questionable. Success of Maciel and coworkers⁶ in using substituent effects might be due to a fortuitous choice of alkylsilanes and to limited numbers of compounds with the same substituents. A detailed study of the possible causes of variations in the substituent effects is in progress.

TABLE I
²⁹Si Chemical Shifts^a δ_{Si} and Substituent Increments^b $\Delta\delta_{\text{Si}}$ for Me_{3−n}X_nSiCH₂Cl and Me_{4−n}SiX_n Compounds

X	n	δ_{Si}		$\Delta\delta_{\text{Si}}$
		Me _{3−n} X _n SiCH ₂ Cl	Me _{4−n} SiX _n	
Cl	0	+ 1.7 (+ 2.79 ^c)	0.0	+ 1.7
	1	+22.9 (+23.08 ^c)	+29.9	− 7.0
	2	+21.7 (+21.48 ^c)	+31.8	−10.1
	3	+ 0.8 (+ 1.65 ^c)	+12.2	−11.4
OC ₂ H ₅	1	+ 8.9	+13.5	− 4.6
	2	−17.2	− 6.1	−11.1
	3	−59.7	−44.5	−15.2
OC(O)CH ₃	1	+14.9	+22.3 ^d	− 7.4 ^d
	2	− 9.4	+ 4.4 ^d	−13.8 ^d
	3	−57.6	−42.7 ^d	−14.9 ^d

^a In p.p.m. (± 0.3); relative to external tetramethylsilane; positive values correspond to down-field shifts, the same experimental conditions as in ref.¹. ^b Defined by Eq. (1). ^c Value reported in ref.². ^d Based on the data of ref.³.

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