SILICON-29 AND CARBON-13 NMR SPECTRA OF MODEL ALKYLSILANES OF THE TYPE $(CH_3)_{3-n}X_nSi(CH_2)_mH$*,**

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^{29}Si- and ^{13}C-NMR chemical shifts are presented for the compounds of the type $(CH_3)_{3-n}X_n$. $Si(CH_2)_mH$ with various combinations of substituent X ($X = C_2H_5$, OC_2H_5, $OC(O)CH_3$, and Cl), their number n, and alkyl chain length m ($m = 1—5$). Silicon-29 chemical shifts are shown to follow general trends of the dependence on the total charge or on the number and nature of the substituents on the silicon atom, the alkyl chain playing only a minor role. It is demonstrated that the silicon upfield shift due to a γ-methyl group varies between is -0.9 and -1.8 ppm in the compounds, the silicon atom of which bears only one secondary carbon atom. The ^{13}C chemical shifts also follow the general dependence on the total charge. In the trimethylsilyl derivatives methylene carbon chemical shifts correlate with the corresponding shifts in carbon analogues and with those in hydrocarbons in which the trimethylsilyl group is replaced by a methyl group. For the short alkyls ($m = 1—3$) the substituent chemical shifts of various silyl groups depend on the alkyl chain length, α and β effects seem to depend on the number and nature of the substituents on the silicon atom.

In the previous papers[1−6] of this series we investigated the NMR spectra of compounds having the general formula $(CH_3)_{3-n}X_nSi(CH_2)_mY$ where the first atom of the substituent Y had an NMR active isotope (^{13}C, ^{14}N, ^{31}P, or ^{19}F) and was either p-bonded (benzene[1] and ethene[5] derivatives) or had unshared electrons (amines[3], πphosphines[6], and fluorides[3]). Before proceeding further to study the compounds with substituents Y like chlorine, hydroxy, alkoxy or acetoxy groups, the first atoms of which cannot be studied by the NMR technique (or the lines of which are broader than the chemical shift changes), it is necessary to examine first the compounds with Y = H.*** Data on such model compounds have been sporadically quoted before[1−6] but only now they are presented in full.

RESULTS AND DISCUSSION

The experimentally determined chemical shifts in alkylsilanes of the above type are summarized in Table I. It should be mentioned that the now reported data were obtained at the same time and by the same techniques as those discussed much earlier[1]. In the meantime the measuring techniques have been greatly improved and the precision increased. Occasionally, some other authors have reported chemical shifts with a higher accuracy for some of the compounds described here. But for the sake of consistency and in order to make comparisons possible, the data are presented here as obtained earlier. Though the more precise pieces of data are in some instances at difference with the values given in Table I they do not change the trends discussed here.

^{29}Si-Chemical Shifts

As it is apparent from the data in Table I, visualized in Fig. 1, the alkyl chain length m has only a minor influence on the silicon chemical shift. Similarly as in other compounds of this type[1-5] the substituents attached directly to the silicon atom (α substituents) have the dominating influence on its shift. For this reason good linear correlations exist between the chemical shifts in the corresponding compounds
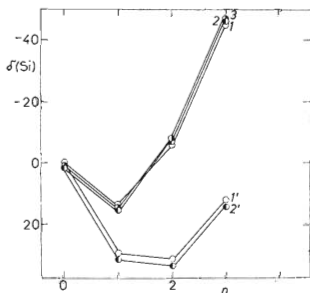
FIG. 1

^{29}Si-Chemical Shifts, $\delta(^{29}Si)$, *versus* Number n of Substituents X in the Compounds of the Type $(CH_3)_{3-n}X_nSi(CH_2)_mH$

1 $m = 1$, 2 $m = 2$, and 3 $m = 3$; 1–3 X = OC_2H_5, 1', 2' X = Cl.
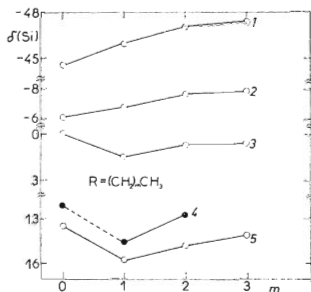
FIG. 2

^{29}Si-Chemical Shifts, $\delta(^{29}Si)$, *versus* Alkyl Chain Length m in the Compounds of the Type $(CH_3)_{3-n}X_nSiR$ where R = = $(CH_2)_mCH_3$ (Me = CH_3 and Et = C_2H_5)
1 $(EtO)_3SiR$, 2 $Me(EtO)_2SiR$, 3 Me_3SiR, 4 Cl_3SiR, 5 $Me_2(EtO)SiR$.

TABLE I

^{29}Si- and ^{13}C-NMR Chemical Shifts in the Compounds of the Type $(CH_3)_{3-n}X_nSi(CH_2)_mH^a$

m	X	n	δ(^{29}Si)	Δ(^{29}Si)^b	δ(SiCH$_3$)	δ(C-α)	δ(C-β)	δ(C-γ)	δ(C-δ)	δ(OC)	δ(OC^{13}C)
1	—	0	0.00	15.5^d	0.00	0.00					
	Cl	1	29.9		3.2	3.2					
		2	31.8		6.8	6.8					
		3	12.2	+21.8^d	9.7	9.7					
	OC$_2$H$_5$	1	13.5		−0.9	−0.9				57.5	18.3
		2	−6.1		−3.5	−3.5				57.4	18.2
		3	−44.5		−7.4	−7.4				57.6	17.8
	OC(O)CH$_3$	1	21.8		−0.6	−0.6				170.2	22.1
		2	4.6		−1.9	−1.9				170.0	21.8
		3	−43.7		−4.8	−4.8				168.6	21.1
2	—	0	1.6	1.6	−3.5	7.8	6.2				
	C$_2$H$_5$	1	4.6	3.0	−4.7	6.6	7.0				
		2	6.5	1.9	−7.0	4.8	7.0				
		3	7.1	0.6	—	2.8	6.9				
	Cl	1	31.9	2.0	1.0	11.1	6.5				

m	X	c	A							57.x	18.x
	OC_2H_5	2	34.0	2.2	5.2	14.8	6.7			57.9	18.4
		3	14.6	2.4	—	17.9	6.7			57.7	18.3
	F	1	15.8	2.3	−3.1	8.2	6.4			57.7	18.0
		2	−6.7	0.6	−6.2	5.7	6.3				
		3	−45.9	1.4	—	2.5	6.1				
3		1	32.0[e]	—	−2.3[f]	8.8[g]	6.1	18.2			
	OC_2H_5	0	0.7	0.9	−1.8	19.6	17.6	18.0			
		1	14.8	1.0	−2.3	19.3	16.9	17.8		57.8	18.5
		2	−7.6	0.9	−5.3	16.5	16.5	17.4		57.7	18.2
		3	−47.0	1.1	—	13.2	16.6	17.1		57.7	18.1
	Cl	3	12.8	1.8	—	27.3	16.8				
4		0	0.6	0.1	−2.1	16.3	26.0[h]	26.3[h]	13.4		
	OC_2H_5	1	14.1	0.7	−3.1	15.6	24.9[h]	25.6[h]	12.8	57.0	17.8
		2	−7.8	0.2	−5.9	12.9	24.5[h]	25.4[h]	12.9	56.8	17.5
		3	−47.4	0.4	—	9.5	24.3[h]	25.0[h]	12.4	56.9	17.2
5	—	0	0.2	0.4	−2.5	16.1	23.0[h]	35.3	21.8[h,i]		
5[j]	—	0	0.9	—	−1.9	14.1	33.1	31.0	22.0		

^{a} All the chemical shifts in δ-scale (ppm units relative to TMS line, paramagnetic shifts positive). ^{b} $\Delta = \delta(\mathrm{Si(CH_2)_mH}) - \delta(\mathrm{Si(CH_2)_{m-1}H})$. ^{c} The position of the carbon atoms relative to the silicon atom. ^{d} SCS value calculated from the shift in $HSiX_3$ compound as given in ref.[22]. ^{e} $J(^{29}\mathrm{Si}-^{19}\mathrm{F}) = 281$ Hz. ^{f} $J(^{13}\mathrm{C}-^{19}\mathrm{F}) = 15.4$ Hz. ^{g} $J(^{13}\mathrm{C}-^{19}\mathrm{F}) = 13.9$ Hz. ^{h} The assignment might be interchanged. ^{i} $\delta(\mathrm{C}-\varepsilon)$. 13.3. ^{j} Isomeric compound of the structure $(CH_3)_3SiCH_2CH_2CH(CH_3)_2$.

of different chain length m. The ^{29}Si-chemical shifts in ethoxy(methyl)alkylsilanes fit the U-shaped dependence on the total net charge on the silicon atom (Q_{Si} in Table II) (as calculated according to the Del Re method described earlier[3] and justified theoretically[7]).

If, instead of studying the dependence of the shift on the nature of the substituent X and their number n (Fig. 1), one follows the dependence of the shift on the alkyl chain length m for the fixed X and n as shown in Fig. 2, the trends in substituent chemical shifts (SCS) of the terminal methyl group on ^{29}Si-chemical shift are readily apparent as the vertical distance between the two consecutive points. Numerically, the methyl SCS values, $\Delta\,(^{29}\text{Si})$, are given as

$$\Delta(^{29}\text{Si}) = \delta(^{29}\text{Si} \quad \text{in} \quad (\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{CH}_2)_m\text{H}) -$$
$$-\delta(^{29}\text{Si} \quad \text{in} \quad (\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{CH}_2)_{m-1}\text{H}) .$$

In analogy to ^{13}C-NMR spectroscopy in which simple direct additivity of SCS values is usually well satisfied[8], the SCS values for $m = 1, 2$, and 3 are called the α, β, and γ effects, resp., of the methyl group. Nonadditivity of the α effects of various substituents on the silicon chemical shifts (which is also apparent from Fig. 1) has been recognized in early studies of ^{29}Si-NMR (ref.[9,10]) and relatively recently a pairwise additivity scheme was suggested by Vongehr and Marsmann[11] (and later theoretically justified by Radeglia[12]) to take account of the effects of the directly attached substituents. The α effects of methyl groups could not be evaluated for all the compounds studied here since the data for the corresponding silicon hydrides were not available. The effects in trimethyl and trichloro derivatives are considerably different.

The (β and γ) effects of electronegative substituents (like F (ref.[4]), Cl (ref.[13]), NH$_2$ (ref.[3]) or OC(O)CH$_3$ (ref.[13,14]) on the silicon shielding were shown to depend on the nature and number of the α substituents X (directly bonded to the silicon atom). The present data demonstrate that it is also so for the β effect of the methyl group. The γ effect is, however, in all the investigated compounds of the same sign (*i.e.* negative or upfield shift) and varies between -1.8 and -0.9 ppm only. (In contrast, the γ effect of chlorine varies between -2.0 to -6.4 ppm.)

The γ effect of the methyl group has received considerable attention in ^{13}C-NMR spectroscopy. In molecules without any sterical hindrance and with flexible methylene chain connecting the observed carbon with the γ methyl group the γ effect amounts[15] to about -2.5 ppm which is about 2 times larger effect than that observed on the silicon. The γ effects on the silicon shielding of such large magnitude (-2.7 ppm) were observed by Harris and Kimber[16] in compounds of the type R_3SiH and also by Maciel group[17] who found the γ effect of -2 ppm in tetraalkylsilanes (actually, those which contained γ methyl groups were either of $C_2H_5SiR_3$ or of $(C_2H_5)_3SiR$ type).

TABLE II

The Total Net σ-Electron Charges in $(CH_3)_{3-n}X_nSi(CH_2)_mH$ Compounds, Calculated by the Del Re Method

m	X	n	Q_{Si}	Q_C in Group						
				$SiCH_3$	C-α	C-β	C-γ	C-δ	OC	(OC)CH$_3$
1	—	0	0·016	−0·144	−0·144					
	OC_2H_5	1	0·299	−0·146	−0·146				0·023	−0·106
		2	0·440	−0·147	−0·147				0·022	−0·106
		3	0·648	−0·147	−0·148				0·022	−0·106
		4[a]	0·856	—	—				0·022	−0·106
2	—	0	0·021	−0·145	−0·098	−0·112				
	OC_2H_5	1	0·233	−0·147	−0·100	−0·112			0·023	−0·106
		2	0·443	−0·147	−0·101	−0·113			0·022	−0·106
		3	0·651	—	−0·102	−0·113			0·022	−0·106
	F	1	0·276	−0·143	−0·095	−0·110				
	C_2H_5	1	0·026	−0·146	−0·099	−0·112				
		2	0·030	−0·147	−0·100	−0·112				
		3	0·035	−0·101	−0·101	−0·113				
3	—	0	0·021	−0·145	−0·097	−0·069	−0·115			
	OC_2H_5	1	0·233	−0·147	−0·101	−0·068	−0·117		0·023	−0·106
		2	0·443	−0·148	−0·100	−0·068	−0·117		0·022	−0·106
		3	0·651	—	−0·103	−0·069	−0·117		0·022	−0·106
4	—	0	0·021	−0·145	−0·099	−0·068	−0·073	−0·118		
	OC_2H_5	1	0·233	−0·147	−0·101	−0·069	−0·073	−0·118	0·023	−0·106
		2	0·443	−0·148	−0·102	−0·070	−0·073	−0·118	0·022	−0·106
		3	0·651	—	−0·103	−0·070	−0·073	−0·118	0·022	−0·106
5	—	0	0·021	−0·145	−0·099	−0·068	−0·074	−0·074[b]		

[a] Compound of the X_4Si type. [b] $Q_C(C\text{-}\varepsilon) = -0.118$.

Since the latter authors[17] noticed roughly additive effects in tetraalkylsilanes, Harris[18] collated 18 pieces of data and treated them according to equations similar to those of Paul and Grant[15] for ^{13}C-chemical shifts (including correction terms for branching at the observed and α nuclei). Though with such corrections direct comparison of the effects is difficult, the obtained γ effect of methyl group, $-2\cdot24$ ppm, is still larger than that observed here. Since among the nine pieces of data which affected the value of the γ effect only two were derived from the compounds of the type $(CH_3)_3SiR$ while all the other compounds were either of $(C_2H_5)_3SiR$ or R_3SiH type, it seems that a condition for observing the larger γ effect is that at least three secondary carbon atoms must be bonded to the silicon atom in question. One can speculate that with three large alkyl groups the γ effect is amplified by a gear motion of the terminal methyl groups. It should be noted, however, that the γ effects observed on the silicon shift in trimethylsilyl derivatives should be compared with that observed on carbon in analogous compounds, *i.e.* in tert-butyl derivatives rather

TABLE III

^{13}C-Chemical Shifts in the Alkanes of the Type $R(CH_2)_mH^a$

m	R	Carbon chemical shift δ^b						
		C-α	C-β	C-γ	C-δ	C-ε	R(C)	R(CH₃)
1	H	$-2\cdot1$						
	t-C₄H₉	31·6					28·0	31·6
2	H	5·9	5·9					
	t-C₄H₉	36·5	8·5				30·3	28·7
3	H	15·6	16·1	15·6				
	t-C₄H₉	47·3	18·1	15·1			30·6	29·5
4	H	13·2	25·0	25·0	13·2			
	t-C₄H₉	44·1	27·0	23·7	13·9		30·1	29·2
5	H	13·7	22·6	34·5	22·6	13·7		
	t-C₄H₉	44·4	24·4	33·0	22·8	13·8	30·2	29·2
	H^c	11·5	31·6	29·9	21·9	—		
	t-C₄H₉^d	42·0	33·9	28·9	22·5	—	30·1	29·3
6	H	13·9	22·9	32·0	32·0	22·9		
	H^e	14·1	20·7	41·8	27·8	22·5		

^{a} The values for the alkanes with R = H converted from the original data[15] using $\delta(C_6H_5) = 128\cdot7$, those for the alkanes with R = t-C₄H₉ were taken from ref.[19]. ^{b} The carbon's position is relative to the substituent R. ^{c} Isomeric compound of the structure H—$CH_2CH_2CH(CH_3)_2$, data from ref.[19]. ^{d} Isomeric compound of the structure $(CH_3)_3C$—$CH_2CH_2CH(CH_3)_2$. ^{e} Isomeric compound of the structure H—$CH_2CH_2CH_2CH(CH_3)_2$, data from ref.[19].

than in the linear alkanes. Using the data on ^{13}C-chemical shifts in 2,2-dimethyl-butane and 2,2-dimethylpentane (Table III), the γ effect of the terminal methyl group appears much different ($+0\cdot3$ ppm) from the value usually quoted[15]. But, nevertheless, there is no apparent clear relationship between the ^{29}Si chemical shifts in trimethylalkylsilanes and the ^{13}C-chemical shifts in analogous tert-butylalkanes which both vary only little. Obviously, many more data on varied classes of organo-silicon compounds are needed in order to evaluate the true values of γ substituent effects.

The importance of the γ effects in ^{13}C-NMR spectroscopy stems from its steric origin which is conveniently demonstrated[20] by the difference in the methyl carbon shifts in cis- and trans-2-butene. Exactly analogous compounds of silicon have not yet been investigated, but we have shown[21] that different silicon chemical shifts are observed in cis- and trans-bis(trimethylsilyl)ethenes. Hence, it seems very likely that the γ effects of methyl group on the silicon shielding is also of steric nature.

^{13}C-Chemical Shifts

Similarly as the ^{29}Si-chemical shifts, the ^{13}C-chemical shifts in the studied compounds fit the described[3,23] approximate (linear) correlations of the shift with the total net charge on the carbon atom (Q_C in Table II) calculated by the Del Re method from the parameters given earlier[3]. Considerable deviations from the correlation line which occur for methylene carbon chemical shifts are in agreement with the complex nature of the shielding, while the correlation with the Del Re net charges takes only inductive influences into account.

In contrast to silicon chemical shifts, (methyl, α, and β methylene) carbon chemical shifts in trimethylsilyl derivatives show good linear correlations with the shifts of the corresponding carbons in tert-butyl derivatives as illustrated in Fig. 3. At the same
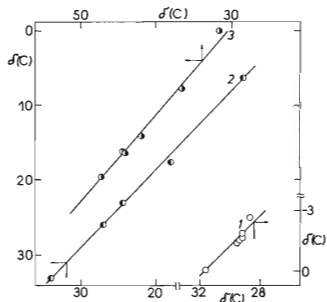

Fig. 3

^{13}C-Chemical Shifts of CH_3, C-α, and C-β Carbons in Trimethylalkylsilanes versus the Shifts of the Corresponding Carbons in Carbon Analogues (1 CH_3, 2 C-α, and 3 C-β)

time, the carbon chemical shifts in trimethylsilylalkanes show also linear correlations with the corresponding shifts in alkanes wherein a methyl group replaces the trimethylsilyl group. Parameters of the linear correlations of the type

$$\delta(C-p)^{RSi(CH_3)_3} = a \cdot \delta(C-p)^{RCH_3} + b$$

(where the index p runs through α, β, and γ carbon atoms) are listed in Table IV. Similar correlations have been found useful earlier by Roberts and coworkers[24] for alcohols and by Eggert and Djerassi[25] for amines. A comparison of the parameters of regression lines for the three substituents shows that while the slopes are rather similar (they are all in the range $0.8-1.0$) the corresponding intercepts for amino and hydroxy groups are of the same signs, but those for the trimethylsilyl group are of opposite signs. This observation is in agreement with the signs of the inductive effects of the involved groups, but the fact that different signs are also observed on γ carbon atoms (the trimethylsilyl group deshields while OH and NH_2 groups shield) indicates the complex nature of this carbon chemical shift to which certainly the paramagnetic δ effects of the three methyls of the trimethylsilyl group contribute.

It would be convenient, for the purpose of future comparisons, to have a method by which the chemical shifts in the not yet measured alkylsilanes could be predicted. Various mathematical schemes based on direct additivity of substituent effects have been used in this respect with considerable success in ^{13}C-NMR spectroscopy. Limited number of data and their precission do not allow a similar mathematical treatment of the present data as applied by Grant and Paul[15] to alkanes or more recently by Rakita and coworkers[26-29] to other organosilicon compounds. For trimethylsilyl derivatives the above correlations can be employed for this purpose but for other derivatives it is necessary to resort to substituent chemical shifts (SCS), i.e. to use the effects caused by replacement of a hydrogen atom in a hydrocarbon by a silyl group. Table V gives the SCS values as calculated from the data in Tables I

TABLE IV

Parameters of Linear Correlations $\delta(C-p)^{(CH_3)_3SiR} = a \cdot \delta(C-p)^{CH_3R} + b$

p^a	a	b, ppm	r^b	No^c
α	1·01	$-6·79$	0·990	6
β	1·00	$-9·03$	0·994	5
γ	0·90	$+5·93$	0·999	4

^{a} Position of the carbon atom relative to the substituent ($(CH_3)_3Si$ or CH_3 group). ^{b} Correlation coefficient. ^{c} Number of data points.

TABLE V

^{13}C-Substituent Chemical Shifts^a

Substituent R	m^b	Effects^c		
		α	β	$\gamma(\delta)$
$(CH_3)_3C^d$	1	33·7		
	2	30·6	2·6	
	3	31·7	2·0	−0·5
	4	30·9	2·0	−1·3 (−0·7)
	5	30·7	1·8	−1·5 (0·2)
$(C_2H_5)_3C^d$	1	25·3		
	2	21·2	1·2	
$(CH_3)_3Si$	1	2·1		
	2	1·9	0·3	
	3	4·0	1·5	2·6
	4	3·1	1·0	1·0 (0·2)
	5	2·4	0·4	0·8 (−0·8)
	5^e	2·6	1·5	1·1 (0·1)
$(CH_3)_2(C_2H_5O)Si$	1	2·1		
	2	2·3	0·5	
	3	3·7	0·8	2·4
	4	2·4	−0·1	0·6 (−0·4)
$CH_3(C_2H_5O)_2Si$	1	−1·4		
	2	−0·2	0·4	
	3	0·9	0·4	2·2
	4	−0·3	−0·5	0·4 (−0·3)
$(C_2H_5O)_3Si$	1	−5·3		
	2	−3·4	0·2	
	3	−2·4	0·5	1·8
	4	−3·7	−0·7	0·0 (−0·8)
$(C_2H_5)_3Si$	1	−4·9		
	2	−3·1	1·0	
$(CH_3)_2ClSi$	1	5·3		
	2	5·2	0·6	
CH_3Cl_2Si	1	8·9		
	2	8·9	0·8	
Cl_3Si	1	11·8		
	2	12·0	0·8	
	3	11·7	0·7	1·5

^{a} SCS values in ppm calculated as SCS = $\delta(R\text{—}(CH_2)_mH) - \delta(H\text{—}(CH_2)_mH)$, positive values indicate paramagnetic shift due to the substituent R. Data in Tables I and III used in deriving the SCS values. ^{b} m is the alkyl chain length $H\text{—}(CH_2)_mH$ or $R\text{—}(CH_2)_mH$. ^{c} The effects (SCS) are labelled according to the carbon's position relative to the substituent R. ^{d} Data from ref.[19] used. ^{e} Data for the isomeric compound of the structure $(CH_3)_3SiCH_2CH_2CH(CH_3)_2$.

and III, for the substituents studied here. As it is apparent from Table V, the SCS values of all the investigated substituents are for the first or the first two homologues $(m = 1, 2)$ different from those found in the longer alkyl chains. The same was also found in amines[25], alcohols[24], and sulphur derivatives[30]; in general, the trend in the effects can be described as increasingly diamagnetic with increasing alkyl chain length or with increasing number n of electronegative substituents on the silicon atom (α and β effects) but there are exceptions to such simplifying description. It should be noted that the γ effects of all silyl groups are downfield while tert-butyl or methyl groups show upfield γ effects as demonstrated by the γ effect of tert-butyl group in Table V and by about 2·7 ppm (average) upfield shift of methyl carbon on the silicon atom in ethane derivatives $(m = 2)$ as compared with methane derivative $(m = 1)$ in Table I.

REFERENCES

1. Nguyen-Duc-Chuy, Chvalovský V., Schraml J., Mägi M., Lippmaa E.: This Journal 40, 875 (1975).
2. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: This Journal 40, 897 (1975).
3. Schraml J., Nguyen-Duc-Chuy, Chvalovský V., Mägi M., Lippmaa E.: Org. Magn. Resonance 7, 379 (1975).
4. Schraml J., Včelák J., Engelhardt G., Chvalovský V.: This Journal 41, 3758 (1976).
5. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: This Journal 42, 306 (1977).
6. Čapka M., Schraml J., Jancke H.: This Journal, 43, 3347 (1978).
7. Engelhardt G., Radeglia R., Jancke H., Lippmaa E., Mägi M.: Org. Magn. Resonance 5, 561 (1973).
8. Stothers J. B.: Carbon-13 NMR Spectroscopy, p. 56. Academic Press, New York 1972.
9. 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, New York 1962.
10. Hunter B. K., Reeves L. W.: Can. J. Chem. 46, 1399 (1968).
11. Vongehr M., Marsmann H. C.: Z. Naturforsch. 31b, 1423 (1976).
12. Radeglia R.: Z. Naturforsch. 32b, 1091 (1977).
13. Schraml J., Včelák J., Chvalovský V.: This Journal 39, 267 (1974).
14. Schraml J., Pola J., Chvalovský V., Mägi M., Lippmaa E.: J. Organometal. Chem. 49, C—19 (1973).
15. Grant D. M., Paul E. G.: J. Amer. Chem. Soc. 86, 2984 (1964).
16. Harris R. K., Kimber B. J.: Advan. Mol. Relax. Proces. 8, 15 (1976).
17. Scholl R. L., Maciel G. E., Musker W. K.: J. Amer. Chem. Soc. 94, 6376 (1972).
18. Harris R. K. in the book: NMR of the Periodic System (R. K. Harris, B. E. Mann, Eds). M. Dekker, New York, in press.
19. Lindeman L. P., Adams J. Q.: Anal. Chem. 43, 1245 (1971).
20. Seidman K., Maciel G. E.: J. Amer. Chem. Soc. 99, 659 (1977).
21. Lippmaa E., Mägi M., Chvalovský V., Schraml J.: This Journal 42, 318 (1977).
22. Löwer R., Vongehr M., Marsmann H. C.: Chem.-Ztg. 99, 33 (1975).
23. Lazzeretti P., Taddei F.: Org. Resonance 3, 113 (1971).
24. Roberts J. D., Weigert F. J., Kroschwitz J. I., Reich H. J.: J. Amer. Chem. Soc. 92, 1338 (1970).

25. Eggert H., Djerassi C.: J. Amer. Chem. Soc. *95*, 3710 (1973).
26. Rakita P. E., Srebro J. P., Worsham L. S.: J. Organometal. Chem. *104*, 27 (1976).
27. Rakita P. E., Worsham L. S., Srebro J. P.: Org. Magn. Resonance *8*, 310 (1976).
28. Rakita P. E., Worsham L. S.: J. Organometal. Chem. *137*, 145 (1977).
29. Rakita P. E., Worsham L. S.: J. Organometal. Chem. *139*, 135 (1977).
30. Barbarella G., Dembech P., Garbesi A., Fava A.: Org. Magn. Resonance *8*, 108 (1976).

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