Journal of Organometallic Chemistry, 190 (1980) 9—33
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE NMR STUDY AND CNDO/2 MOLECULAR ORBITAL CALCULATION OF SILACYCLOBUTANES

A.M. KRAPIVIN *, M. MÄGI **, V.I. SVERGUN, R.Z. ZAHARJAN, E.D. BABICH and N.V. USHAKOV

Topchiev Institute of Petrochemical Synthesis, U.S.S.R. Academy of Sciences, Moscow, 117071 (U.S.S.R.)

(Received September 7th, 1979)

Summary

^{29}Si, ^{13}C and ^{1}H chemical shifts have been determined for twenty-four substituted silacyclobutanes. Coupling constants, ^{1}J(SiC), for directly-bonded silicon and carbon atoms have been measured. Six substituted silacyclopentanes have been also studied for comparison with the strained 4-membered cyclic compounds. Molecular orbital calculations for cyclic silanes have been carried out using the CNDO/2 method. Net atomic charges, bond-order and other quantum chemical parameters have been obtained from SP- and SPD-basis set computations. Only for the SPD calculation was generally good agreement obtained between experimental data and computed values. The effect of substitution in silacyclobutanes on the chemical shifts and coupling constants is compared to that for silacyclopentanes and acyclic silanes. The unusual trend in the screening of Si nuclei and the sensitivity of C3 to substitution on the Si atom in the silacyclobutanes are explained by the existence of a strong 1—3 transannular interaction, which is confirmed by the measurements of ^{2}J(SiC$_3$) and by computed resonance energies $-E^{R}_{AB}$.

Introduction

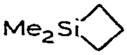
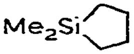
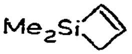
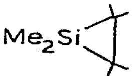
Small, strained, four-membered organosilicon rings have been satisfactorily described by chemical experiments [reviews 1,2], but the high reactivity of silacyclobutanes to nucleophilic and electrophilic reagents has not been explained on the basis of their electronic structure.

Despite the fact that ^{29}Si and ^{13}C NMR spectroscopy is widely used for investigating the electronic distributions in organosilicon compounds, very few

---

* To whom correspondence should be addressed.

** Institute of Cybernetics, Estonian Academy of Sciences.

NMR studies have been made to characterize the cyclocarbosilanes. The ^{29}Si chemical shifts in ,  and  have been reported [3] and a comprehensive examination of ^{29}Si and ^{13}C data in 1,3-disilacyclobutanes is available [4]. Such novel organosilicon cycles as  [5] and  [6] have been characterized by NMR data.

The interpretation of ^{13}C and especially ^{29}Si NMR data is still complicated by the limited number of successful theoretical investigations of NMR parameters in organosilicon compounds. Molecular orbital (MO) calculations including SCF MO methods in CNDO/2 approximation have been applied to the explanation of the trends in ^{29}Si screening constants of acyclic silanes [7—11], but the results obtained are not reliable because of *1*) variations in the diamagnetic contribution to the screening constant are neglected and *2*) the large number of simplifications necessary for the calculation of the paramagnetic contribution.

The directly-bonded ^1J(SiC) coupling constants for a variety of acyclic silanes have been reported [12—17]. But, to our knowledge, the only value of ^1J(SiC) in strained, cyclic silanes has been measured for a Si—C(Me) bond in a silacyclopropane derivative [6], where J(SiC) was found to be equal to 58 Hz (^1J(SiC) for the *endo*-cyclic Si—C bond has not been determined).

It has been shown that ^1J(SiC) strongly depends on the "s-character" of the carbon and silicon hybrid orbitals [12—14]. This experimental trend was confirmed by calculations based on the maximum overlap approximation method [18], and on the INDO scheme [19,20]. Summerhays and Deprez [19] found that the calculated values of the Fermi-contact term in J(SiC) were in good agreement with the experimental ^1J(SiC) in the Me_3SiX series. The results were similar to those obtained by INDO calculation for all terms appearing in the general expression for J(SiC). It has been established [20] that the Fermi-contact term provides the dominant contribution (~99%) to the coupling constant between silicon and carbon atoms. Thus, the experimental J(SiC) might be a sensitive probe of "s-character" in the Si—C bond and can be used for a determination of hybridization states of interacted Si and C atoms.

Clearly, there is a need for a systematic study of the NMR spectra of strained organosilicon rings. The second purpose of our study is to calculate electronic distributions in cyclic silanes using SP- and SPD-basis sets and to compare the results of CNDO/2 computations with NMR data. This is required to determine the proper guidelines in calculation of electronic structure of four-membered cycles and for evaluation of the role of 3*d*-orbitals of Si atom in the physical and chemical properties of silacyclobutanes.

Experimental

(a) NMR measurements

Proton magnetic resonance measurements were made as 30% solutions in CCl_4 on a Tesla BS-487C or a Tesla BS-467 spectrometer at 80 MHz and 60 MHz, respectively. A small amount of benzene, C_6H_6, ($\approx$1%) was used to provide a lock signal and to serve as an internal reference peak. Sometimes, a small amount of tetramethylsilane (TMS $\approx$ 1%) was added to samples for precise determination of ^{1}H chemical shifts. From the ^{1}H spectra of silacyclobutanes it is possible to discern only highly perturbed triplet character (α-CH_2 protons) and quintet character (β-CH_2 protons) signals which allow an estimation of ^{1}H chemical shifts by multiplet center positions. ^{1}H chemical shifts are given in δ-scale (TMS) and chemical shifts for CH_3 protons were measured to an accuracy of ±0.01 ppm.

Carbon-13 NMR spectra were obtained from either a Bruker WP-80 or Bruker WH-90 spectrometer at 20.1 MHz and 22.62 MHz, respectively, and the samples were neat liquids. 1% of C_6H_6 was used as the internal standard peak. The ^{13}C resonance assignments given in Tables 1 and 3 are based on chemical shifts, intensity information, off-resonance decoupling and ^{29}Si—^{13}C coupling constants. ^{13}C chemical shifts are given relative to TMS ($\delta^{13}C(C_6H_6) = 128.5$ ppm from TMS) with the accuracy of ±0.03 ppm.

The values of ^1J(SiC), ^2J(SiC) and ^1J(CC) were measured from ^{13}C spectra with the accuracy of ±0.5 Hz. All ^1J(SiC) were assumed to have a negative sign [21]. A typical spectrum is shown in Fig. 1.

The ^{29}Si chemical shifts were obtained by ^{1}H-{^{29}Si} INDOR technique at frequency ν(Si) 15.894 MHz with the accuracy of ±0.05 ppm. The measurements were carried out on a Tesla BS-487C spectrometer equipped with r.f. units for the heteronuclear double resonance procedure [22]. In some cases, the ^{29}Si spectra were recorded on a multinuclear spectrometer in the FT mode at 11.92 MHz with gated proton decoupling. Most of the compounds (III, V, XI, XV—XIX) were examined as 50% solutions in $CHCl_3$ with hexamethyldisiloxane (HMDS) or TMS as internal reference.

For several compounds the ^{29}Si measurements were performed using both INDOR-experiment and FT-mode, but the differences in the chemical shifts of one sample did not exceed ±0.3 ppm. We also examined the solvent effects on ^{29}Si chemical shift for I. No effects of concentration, temperature and type of solvent (C_6H_6, C_6D_{12}, CD_3OD and R_2NH) on the ^{29}Si resonance frequency were observed.

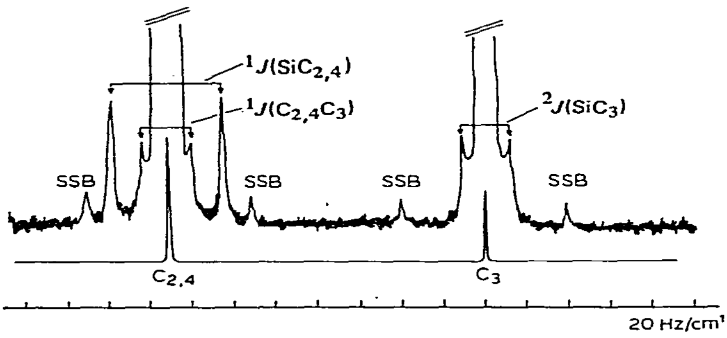
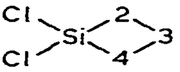


Fig. 1. ^{13}C spectrum of  (V) after 18000 scans.

All ^{29}Si chemical shifts for silacyclopentanes (Table 3) were measured using only the INDOR technique. The ^{29}Si chemical shifts are given in ppm, negative values denote an upfield shift from TMS.

(b) Semi-empirical calculations

The semi-empirical SCF LCAO-MO calculations in CNDO/2 approximation [23] were carried out on a BESM-6 computer using a modified version of the CNINDO [24] programm. All computations were performed using two basis sets: SP-basis and SPD-basis extended by the inclusion of vacant 3*d*-orbitals for elements of the Second Period (Si and Cl).

The geometries of compounds investigated were taken from electron diffraction studies [25—29]. For computation facilities the atomic charges and bond-order parameters were calculated for $\mathrm{XY\underline{SiCH_2CH_2CH_2}}$, where X, Y = OH or NH_2 instead of OEt or NEt_2. The structure of Si—OH and Si—NH fragments have been determined [30,31].

The geometrical parameters for silacyclobutanes: Si—C(Me) = 1.898, Si—H = 1.49, Si—Cl = 2.035, Si—N = 1.740, Si—O = 1.630, Si—C(CH_2) = 1.898, C—C = 1.590, C—H = 1.13 (Å); ∠CSiC(*exo*-cyclic) = 107—108°, ∠HSiH = 112°, ∠ClSiCl = 106°, ∠CSiC(*endo*-cyclic) = 80—81°, ∠SiCC = 87—88°, ∠CCC = 100°, ∠HCH = 110°.

(c) Chemical compounds

All samples studied were purified by distillation; The purities (95—99%) were checked by gas chromatography-mass-spectrometry on an LKB-2091 spectrometer and by NMR spectra. The mass spectra revealed the parent ions and the $[M-15]^+$ and $[M-28]^{+\cdot}$ ions.

Compounds I, IV, V and XIV were prepared by the literature methods [32a], II and III [32b], XV—XVII [32c], VII—IX [32d], XXI, XXIV, XXIX and XXX [32e], XIX [32f], XXII and XXIII [32g], XX [32h], X and XIII [32i], XII [32j].

1,1-Diallyl-1-silacyclobutane (XVIII). To a solution of 0.5 mol allylMgCl in 250 ml ether or THF was added a solution of 0.2 mol V in ether at 30—35°C. The mixture was stirred for 3 h at 35°C. After the usual treatment, 22.5 g (≈75%) of crude product was obtained. Purification was achieved by column chromatography (neutral Al_2O_3, n-hexane) followed by vacuum distillation. 16.6 g of XVIII was obtained. B.p. 57—60°C (10—12 mmHg), n_d^{20} = 1.4830, d^{20} = 0.8496.

1,1-Diethoxy-1-silacyclobutane (XI). To a solution of 0.05 mol V and 0.1 mol C_5H_5N in C_6H_6 (50 ml) was added 0.15 mol absolute C_2H_5OH at 10°C, under an inert atmosphere. After one hour, $C_5H_5N \cdot HCl$ was filtered off, solvent was removed and vacuum distillation gave rise to XI. Yield 60%, b.p. = 66°C (25 mmHg), n_d^{20} = 1.4206, d^{20} = 0.9230.

1-Methyl-1-ethoxy-1-silacyclobutane (VI). The procedure is similar to the preparation of XI: IV, 0.05 mol; C_5H_5N, 0.05 mol; absolute C_2H_5OH, 0.08 mol; C_6H_6, 40 ml. Yield 66%, b.p. 80—83°C (82 mmHg), n_d^{20} = 1.4244.

1-Methyl-1-ethoxy-1-silacyclopentane (XXVI). The procedure is similar to the preparation of XI and VI: XXV, 0.05 mol; C_5H_5N, 0.05 mol; absolute C_2H_5OH, 0.08 mol; C_6H_6, 40 ml. Yield 85%, b.p. 100—102°C (90 mmHg).

1-Methyl,1-diethylamino-1-silacyclopentane (XXVIII). To a solution of 0.05 mol XXV in C_6H_6 (20 ml) was added 0.1 mol of $(C_2H_5)_2NH$ in C_6H_6 (15 ml), at room temperature under an inert atmosphere. Filtration, solvent removal and vacuum distillation gave the product XXVIII. Yield 90%, b.p. 99—100°C (50 mmHg).

Results

The experimental NMR data obtained for silacyclobutanes (SiCB) are presented in Table 1.

In four-membered ring systems, such as SiCB with a rapidly inverting non-planar structure, the ring protons constitute spin system of A_4B_2 type or $[AA'A''A'''BB']$ type and, hence, a computer analysis is required for determination of ^1H chemical shifts and H—H coupling constants.

Analysis of the proton NMR spectrum was carried out as described previously [33] for I. LACX programme [34] was employed using the 100 MHz data. A good fit was obtained as evidenced by a low rms error (rms = 0.05 Hz for 80 lines iterated). The results are given in Table 2.

The angle of "puckering", ψ, was determined from a modified Karplus expression as reported previously [35] for rapidly averaging $^3J_{cis}$ and $^3J_{trans}$ coupling constants in the $-CH_2-CH_2-$ fragment of the cyclic molecule due to ring inversion. ψ for molecule I was found to be equal to 36.7° (experimental ψ 30—35° [25,26]).

NMR experimental results for substituted silacyclopentanes (SiCP) are given in Table 3.

For a more detailed investigation of substitution effects on NMR parameters, the studied SiCB and SiCP series were compared with acyclic silanes. The results are tabulated in Tables 4—6. NMR data for the Me_2SiXY series were taken from the literature.

The semi-empirical calculations were performed to elucidate the lower values of $^1J(SiC)$ for *exo-* and *endo*-cyclic Si—C bonds in SiCB, the unusual trends in screening ^{29}Si nuclei and the sensitivity of C3 to substitution on the Si atom in SiCB. It was also necessary to study the effect of the participation of 3*d*-orbitals on physical parameters in SiCB. The results of calculations which will be used in the discussion are given in Tables 7—9.

Discussion

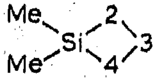
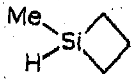
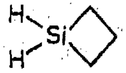
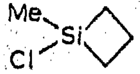
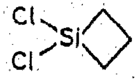
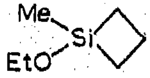
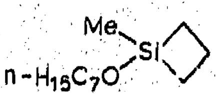
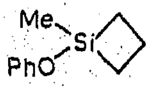
(a) ^{29}Si chemical shifts

The results of the ^{29}Si NMR study for cyclic silanes are presented in Tables 1, 3 and 4. As is apparent from Table 4, the substituent effects on ^{29}Si screening in the SiCB are considerably different from those observed in the SiCP and Me_2SiXY series. The decrease in the shielding of ^{29}Si nucleus, normal for organosilicon compounds of type $Me_{4-n}SiX_n$ [3,13], under replacement of the first methyl group by an electronegative substituent, such as Cl, OR, NR_2 etc., is observed only for the SiCP series. In the SiCB series, except for IV, such a substitution leads to upfield shifts. To provide some understanding of these results, the electronic distributions in the compounds SiCB, SiCP and Me_2SiXY

(Continued on p. 17)

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS ^1J(SiC) FOR SILACYCLOBUTANES

Compounds		$^{29}Si_1$ (ppm)	^{13}C (ppm)			$^1J(^{29}Si^{13}C)$ (Hz)		$^1H_{2,4}$			Additional data
			Me(Si)	$C_{2,4}$	C_3	Si—Me	Si—$C_{2,4}$	Me	$H_{2,4}$	HC_3	
	(I)	18,4 [a]	0,3	14,8	18,1	45	42	0,258	1.06	2.15	$^2J(Si_1C_3)$ 16 Hz $^1J(C_2C_3)$ 22 Hz
	(II)	6,0	−2,2	13,3	20,3	45	42	0.300	1,03	2.15	^{1}H—SiH 4.84 ppm ^1J(SiH) 187.3 Hz
	(III)	−5,0		9,5	22,7		42		1,1	2,3	^{1}H—SiH 4.7 ppm [d] ^1J(SiH) 194.4 Hz
	(IV)	32,5	3,5	20,9	15,9	49	45	0,619	1,4	2,0	$^2J(Si_1C_3)$ 17 Hz $^1J)C_2C_3)$ 24 Hz
	(V)	18,1		27,7	14,0		52		1,95	1,95	$^2J(Si_1C_3)$ 19 Hz $^1J(C_2C_3)$ 24 Hz
	(VI)	14,1	−2,7	18,6	13,5			0,238	0,9—2,0		
	(VII)	14,5	−4,2	18,5	14,2			0,23			^{13}C—OCH_2 63,3 ppm ^1H—OCH_2 3,64 ppm
	(VIII)	17,0	−0,8	19,4	14,3	54	47	0.358	1,1—2,0		^{13}C—C_x 155,3 ppm C_0 122,6 ppm C_m 130,2 ppm C_p 120,6 ppm

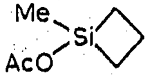
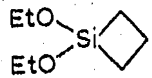
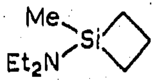
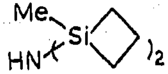
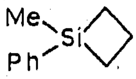
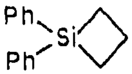
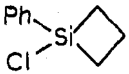
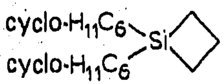
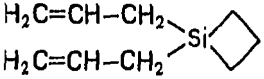
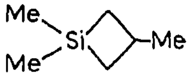
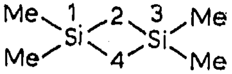
	(IX)	22.7	−0.8	18.3	15.0			0.383	1.2—2.0		$^{13}\mathrm{C}{-}\mathrm{OC}\overset{*}{\mathrm{C}}\mathrm{H_3}$ 21.9 ppm CO 170.7 ppm
	(X)	7.0	0.8	20.6	13.7	53	48	0.225	1.1	1.78	
	(XI)	−17.1		20.8	11.7		55		1.4	1.4	$^2J(Si_1C_3)$ 19 Hz $^{13}C{-}OCH_2$ 58.8 ppm
	(XII)	7.8	−2.3	19.5	14.5	52	45	0.288	0.9—1.9		$^{13}C{-}NCH_2$ 41.1 ppm $^1H{-}NCH_2$ 2.91 ppm
	(XIII)	7.6	0.5	20.4	14.5	50	45	0.125	1.0	1.8	
	(XIV)	11.9	−1.8	14.4	18.3	46 Si_1C_x 60	43	0.513	1.3	2.3	$^{13}C{-}C_x$ 138.4 ppm C_o 133.4 C_m 127.9 C_p 129.4
	(XV)	7.0		14.0	18.4	Si_1C_x 62	44		1.5	2.3	$^{13}C{-}C_x$ 136.3 ppm C_o 134.5 C_m 128.0 C_p 129.6
	(XVI)	21.4		20.4	16.3						$^{13}C{-}C_x$ 134.7 ppm C_o 133.2 C_m 128.2 C_p 130.8 ppm
	(XVII)	23.8		8.8	18.8	Si_1C_x 48	41		0.9	2.0	$^{13}C{-}C_x$ 24.4 ppm C_α 27.9 C_β 28.3 C_γ 27.2 ppm

TABLE 1 (continued)

Compounds		$^{29}Si_1$ (ppm)	^{13}C (ppm)			$^1J(^{29}Si^{13}C)$ (Hz)		$^1H_{2,4}$			Additional data
			Me(Si)	$C_{2,4}$	C_3	Si—Me	Si—$C_{2,4}$	Me	$H_{2,4}$	HC_3	
	(XVIII)	17.1		12.2	18.2				1.03	2.07	^{13}C—$SiCH_2$ 22.7 ppm =CH 133.5 ppm =CH_2 114.0 ppm
	(XIX)	37.2		18.3	18.2		37		1.25	2.2	
	(XX)	5.7	1.0 [b] −1.8	23.6	27.8	44 [b] 46	43	0.26	0.4—2.4		^{13}C—CCH_3 27.8 ppm ^1H—CCH_3 1.14 ppm
	(XXI)	2.1 [c]	2.8 [c]	4.1 [c]		49	35	0.230	−0.004		
	(XXII)	Si_1 25.5 Si_3 0.0	1.7 1.8 Me(Si_1) 6.1	10.5		Si_1—Me 54 Si_3—Me 51	$Si_1C_{2,4}$ 40 $Si_3C_{2,4}$ 36	0.238 0.325 Si_1Me 0.575	0.5		
	(XXIII)	Si_1 17.6 Si_3 −4.9	1.0	17.8		52	$Si_1C_{2,4}$ 48 $Si_3C_{2,4}$ 32	0.331	1.00		

[a] Literature value 18.9 ppm [3]. [b] Tentative assignment to *trans*-Me. [c] For compound XXI ^{29}Si 2.3 ppm, ^{13}C—CH_3 2.8 and CH_2 3.7 ppm [4]. [d] For compound III, $^2J(Si_1C_3)$ 17 Hz, $^1J(C_2C_3)$ 26 Hz.

TABLE 2

^{1}H NMR PARAMETERS [a] FOR I

$\nu(\alpha\text{-CH}_2)$	$\nu(\beta\text{-CH}_2)$	$(^2J_\alpha - ^2J_\beta)$ [b]	$^3J_{cis}$	$^3J_{trans}$	$^4J_{cis}$	$^4J_{trans}$
105.6	215.1	−1.195 (0.019)	9.912 (0.011)	6.495 (0.012)	−1.648 (0.021)	0.990 (0.107)

[a] ν in Hz relative to TMS, J(HH) in Hz, standard deviations are given in Hz in parentheses, spectrum of I was recorded on Varian XL-100. [b] At fixed $^2J_\beta$ −10.57 Hz, $^2J_\alpha$ −11.765 Hz.

were calculated with minimal SP- and extended SPD-basis sets. The results of the computations for the series SiCB are given in Tables 7, and 8.

According to the theoretical investigations available to date, the variations in the ^{29}Si screening constant are mainly due to changes in the paramagnetic contribution [7—11]. Although the methods used for calculation of a paramagnetic term have a number of drawbacks, their benefit resides in the explanation of experimentally found "Λ"-type dependence for the variations in the ^{29}Si chemical shifts [7,9,11],

Based on the scheme proposed by Engelhardt, Radeglia and others [7,9,11] the upfield shifts of ^{29}Si nuclei are explained by the increase in positive charge ($+q$) on the silicon when the electronegative groups are introduced, but not by the participation of d-orbitals of Si atom in p—d interaction with substituent. However, due to the large number of assumptions this model has not been rigorously proved, and therefore the possibility of p—d interactions is not ruled out. The computed values of charges ($+q$) on the Si atom in the SiCB, SiCP, and Me_2SiXY series were compared and it was found that, irrespective of the basis employed, the charge in the SiCB was always less than in the corresponding SiCP or Me_2SiXY compound. Thus, the scheme of Engelhardt et al. [7] failed to explain the distinctive features of the substitution effect on the Si chemical shifts in SiCB.

Because of uncertainties over the calculation of total ^{29}Si screening constants the measured values of ^{29}Si chemical shifts in SiCB (see Table 1) were correlated with the calculated values of net atomic charges on Si atoms ($+q_{Si}$) obtained from SP- and SPD-basis computations (see Tables 7 and 8). The correlations found are presented in Figs. 2 and 3.

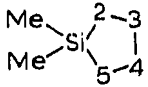
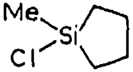
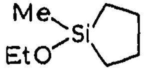
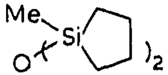
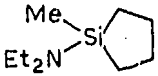
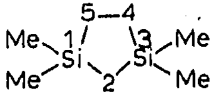
It is seen that the omission of d-orbitals leads to a complete failure of any correlation ($r = 0.51$, Fig. 3), but the inclusion of d-orbitals into the calculation gives rise to some dependence ($r = 0.83$, Fig. 2). This correlation improves ($r = 0.93$) when the value of charge on Si for X, Y = Cl is excluded. It is evident from the relationship in Fig. 2 that the upfield shift increases with the positive charge on the Si atom. Although a valid theoretical explanation for such a dependence of ^{29}Si chemical shifts on net atomic charge has not yet been established, a similar slope for such a dependence has been obtained by Réffy et al. [38] for other acyclic silanes.

In our opinion, the comparison of the correlations shown in Figs. 2 and 3 displays the correctness of using SPD-basis set for the calculation of the electronic distributions in SiCB. Furthermore, the inclusion of silicon d-orbitals into the interaction with the substituent is discussed as a possible reason for a

(Continued on p. 20)

TABLE 3

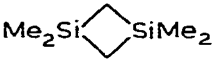
CHEMICAL SHIFTS AND COUPLING CONSTANTS ^1J(SiC) FOR SILACYCLOPENTANES

Compound		^{29}Si (ppm)	^{13}C (ppm)			$^1J(^{29}Si^{13}C)$ (Hz)		^{1}H (ppm)		
			Me(Si)	$C_{2,5}$	$C_{3,4}$	Si—Me	Si—$C_{2,5}$	Me	$HC_{2,5}$	$HC_{3,4}$
	(XXIV)	16.4 [a]	−0.3	13.6	28.0	50	51 [b]	0.10	0.54	1.48
	(XXV)	45.4	1.7	16.1	26.4	55	57	0.525	0.84	1.68
	(XXVI)	29.9	−2.4	12.1	26.3			0.20	0.53	1.56
	(XXVII)	24.2	−1.3	14.0	26.8			0.15	0.52	1.56
	(XXVIII)	20.0	−1.4	13.0	27.1	55	56	0.165	0.56	1.61
	(XXIX)	14.0	−0.3	C_2 −1.8	$C_{4,5}$ 11.2	50	Si_1—C_5 Si_3—C_4 52 $Si_{1,3}$—C_2 42	0.09	HC_2 −0.41	$HC_{4,5}$ 0.663
	(XXX)	Si_1 41.8 Si_3 12.8	Me(Si_1) 3.0 −0.3 −0.4	C_2 1.5	C_5 14.2 C_4 9.8	Si_1—Me 58 Si_3—Me 51	Si_1—C_2 50 Si_1—C_5 58 Si_3—C_2 43 Si_3—C_4 53	Me(Si_1) 0.463 0.163 0.050	HC_2 −0.03 — 0.01	$HC_{4,5}$ 0.34 — 1.2

[a] Literature value 16.8 ppm [3]. [b] $^2J(Si_1C_{3,4}) < 7$ Hz (see Text).

TABLE 4

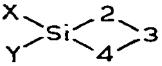
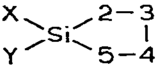
SUBSTITUENT INCREMENTS $\Delta(^{29}Si)$ FOR THE SiCB, THE SiCP AND ACYCLIC SILANES OF THE TYPE Me_2SiXY (IN PPM)

X	Y	$YX\overline{SiCH_2CH_2CH_2}$ $\Delta_I(^{29}Si)$ [a]	Me_2SiXY $\Delta_{II}(^{29}Si)$ [b]	$XY\overline{SiCH_2CH_2CH_2CH_2}$ $\Delta_{III}(^{29}Si)$ [c]
H	H	−23.4	−37.3 [d]	
Me	H	−12.4	−16.3 [e]	
Me	Me	0	0	0
Me	Cl	14.1	29.5 [f]	29.0
Cl	Cl	−0.3	32.0 [f]	
Me	OEt	−4.3	14.5 [g]	13.5
Me	OSi(Me)RR′	−11.4	6.6	7.8
		(R + R′ = $(CH_2)_3$)	(R, R′ = Me)	(R + R′ = $(CH_2)_4$)
OEt	OEt	−35.5	−5.7 [g]	
Me	NEt_2	−10.6		3.6
Me	HNSi(Me)RR′	−10.8	2.2 [e]	
		(R + R′ = $(CH_2)_3$)	(R, R′ = Me)	
Me	Ph	−6.5	−4.4 [e]	
Ph	Ph	−11.4	−8.2 [h]	
			$(Me_3Si)_2CH_2$	
		−16.3	−0.5 [i]	−2.4

[a] $\Delta_I(^{29}Si) = \delta^{29}Si$(subst. SiCB) − $\delta^{29}Si$(I). [b] $\Delta_{II}(^{29}Si) = \delta^{29}Si(Me_2SiXY) - \delta^{29}Si(Me_4Si)$. [c] $\Delta_{III}(^{29}Si) = \delta^{29}Si$(subst. SiCP) − $\delta^{29}Si$ (XXIV). [d] [36]. [e] [13]. [f] [7]. [g] [16]. [h] [3]. [i] [37].

TABLE 5

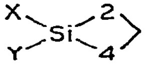
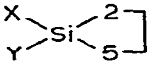
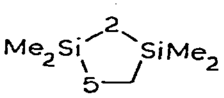
SUBSTITUENT INCREMENTS $\Delta(^{13}C)$ FOR THE SiCB, THE SiCP AND ACYCLIC SILANES OF THE TYPE Me_2SiXY (IN PPM)

								Me_2SiXY
X	Y	$\Delta(^{13}C)$ [a]			$\Delta(^{13}C)$ [b]			$\Delta(^{13}C)$ [c]
		C(Me)	C2,4	C3	C(Me)	C2,5	C3,4	C(Me)
H	H		−5.3	4.6				
Me	H	−2.5	−1.5	2.2				−2.6 [d]
Me	Me	0	0	0	0	0	0	0
Me	Cl	3.2	6.1	−2.2	2.0	2.5	−1.6	3.4 [d]
Cl	Cl		12.9	−4.1				6.8
Me	OEt	−3.0	3.8	−4.6	−2.1	−1.5	−1.7	−0.5 [d]
Me	OPh	−1.1	4.6	−3.8				0.2
OEt	OEt		6.0	−6.4				−3.5
Me	OSi(Me)RR′	0.5	5.8	−4.4	−1.0	0.4	−1.2	2.4 [d]
			(R + R′ = $(CH_2)_3$)		(R + R′ = $(CH_2)_4$)			(R, R′ = Me)
Me	NEt_2	−2.6	4.7	−3.6	−1.1	−0.6	−0.9	
Me	HNSi(Me)RR′	0.2	5.6	−3.6				2.9 [d]
			(R + R′ = $(CH_2)_3$)					(R, R′ = Me)
Me	Ph	−2.1	−0.4	0.2				−0.6 [d]
Ph	Ph		−0.8	0.3				−0.2

[a] $\Delta(^{13}C) = \delta^{13}C$(subst. SiCB) − $\delta^{13}C$(I). [b] $\Delta(^{13}C) = \delta^{13}C$(subst. SiCP) − $\delta^{13}C$ (XXIV). [c] $\Delta(^{13}C) = \delta^{13}C(Me_2SiXY) - \delta^{13}C(Me_4Si)$. [d] [13].

TABLE 6

SUBSTITUENT INCREMENTS $\Delta(^1J_{SiC})$ FOR THE SiCB, THE SiCP, AND ACYCLIC SILANES OF TYPE Me_2SiXY (IN HZ)

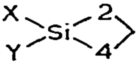
				Me_2SiXY		
X	Y	$\Delta(^1J_{SiC})$ [a]		$\Delta(^1J_{SiC})$ [b]	$\Delta(^1J_{SiC})$ [c]	
		Si—C(Me)	Si—C2,4	Si—C(Me)	Si—C(Me)	Si—C2,5
Me	Me	0	0	0 [f]	0	0
Me	Cl	+4	+3	+8	+5	+6
Cl	Cl		+10	+18 [d]		
Me	OSi(Me)RR′	+8	+6	+9		
	Me		(R + R′ = $(CH_2)_3$)	(R, R′ = Me)		
OEt	OEt		+13	+23 [e]		
Me	NEt_2	+7	+3		+5	+5
Me	HNSi(Me)RR′	+5	+3	+6		
	RR′		(R + R′ = $(CH_2)_3$)	(R, R′ = Me)		
Me	Ph	+1	+2	+1		
						
		+4	−8		0	−9

[a] $\Delta(^1JSiC) = {}^1JSiC(\text{subst. SiCB}) - {}^1JSiC(I)$. [b] $\Delta(^1JSiC) = {}^1JSiC(Me_2SiXY) - {}^1JSiC(Me_4Si)$. [c] $\Delta(^1JSiC) = {}^1JSiC(\text{subst. SiCP}) - {}^1JSiC(XXIV)$. [d] [14]. [e] [16]. [f] [12].

shielding effect on Si nuclei in organosilicon compounds [13].

The other effect which has to be mentioned in the discussion is a strong upfield shift of Si nuclei resonance when a donor group such as CH_3 (XX) or $SiMe_2$ (XXI) is introduced at a position β to Si1 in the four-membered ring. These shifts (Δ^{29}Si(XXI) −16.3 ppm, and Δ^{29}Si(XX) −12.7 ppm).could be associated neither with +*J* inductive effect of the substituent, nor with changes

TABLE 7

NET ATOMIC CHARGES AND BOND ORDER PARAMETERS FOR  CALCULATED WITH SPD-BASIS SET

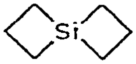
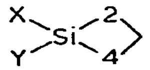
X	Y	q(Si)	$q(C_{Me})$	$q(C_{2,4})$	$P_{sSisC(Me)}$	$P_{sSisC_{2,4}}$
H	H	+0.3420		−0.1577		0.2061
H	Me	+0.2347	−0.1995	−0.1452	0.2638	0.2095
Me	Me	+0.1563	−0.1913	−0.1405	0.2630	0.2104
Me	Cl	+0.1142	−0.1807	−0.1284	0.2721	0.2151
Cl	Cl	+0.0602		−0.1175		0.2247
Me	OH	+0.2369	−0.1998	−0.1412	0.2758	0.2189
OH	OH	+0.3407		−0.1580		0.2287
Me	NH_2	+0.1928	−0.1921	−0.1 '04	0.2737	0.2169
		+0.1421		−0.1373		0.2168

TABLE 8

NET ATOMIC CHARGES AND BOND ORDER PARAMETERS FOR  CALCULATED WITH SP-BASIS SET

X	Y	$q(\mathrm{Si})$	$q(\mathrm{C_{Me}})$	$q(\mathrm{C_{2,4}})$	$p_{sSi\,sC_{Me}}$	$p_{sSi\,sC_2}$
H	H	+0.5379		–0.1370		0.1991
Me	H	+0.5429	–0.1578	–0.1401	0.2714	0.2006
Me	Me	+0.5333	–0.1666	–0.1462	0.2602	0.1968
Me	Cl	+0.6666	–0.1768	–0.1589	0.2740	0.2010
Cl	Cl	+0.8151		–0.1800		0.2096
Me	OH	+0.7927	–0.2002	–0.1757	0.2759	0.2056
OH	OH	+1.0209		–0.2105		0.2139
Me	NH_2	+0.6874	–0.1801	–0.1670	0.2748	0.2029
		+0.4635		–0.1263		0.2034

in geometry. An analogous substitution in the SiCP and in acyclic silanes gives a shift to upper field of only 3 ppm (see Table 4). The most reasonable explanation for the effect is the existence of direct bonding between the atoms at positions 1 and 3 in the strained cycles of SiCB. The 1—3 transannular interaction has been already accepted for cyclobutanes [39,40] and it has been noted in SiCB [41].

The shielding of Si1 caused by electron donor groups at position β to Si1 becomes clear after an examination of the structure of the highest occupied molecular orbitals for SiCB, constructed from the calculation and depicted in Fig. 7: the electrons are donated from the substituent into the antibonding orbital formed by C3 or Si3 and Si1 atoms and, consequently, the electrons of Si1 participating in this interaction are localized closer to the silicon nucleus and the shielding of Si increases.

The concept of 1—3 transannular interaction allows a satisfactory explanation of the downfield shift of ^{29}Si in spirosilacyclohexane (XIX), where the Si atom interacts with two β-carbons (Δ^{29}Si(XIX) +18.8 ppm). The bonding reduces significantly the spherical symmetry of electronic distributions around the Si nucleus relative to that in I and increased deshielding on ^{29}Si is observed.

(b) ^{13}C chemical shifts

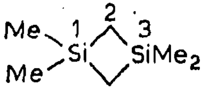
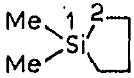
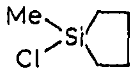
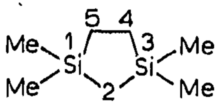
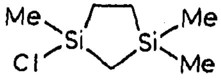
In this study we have an opportunity to examine the effect of screening of carbon nuclei (C2,4 and C3) on substitution at silicon atoms and to compare the results of ^{29}Si and ^{13}C investigations for determining the proper guideline in the calculation methods.

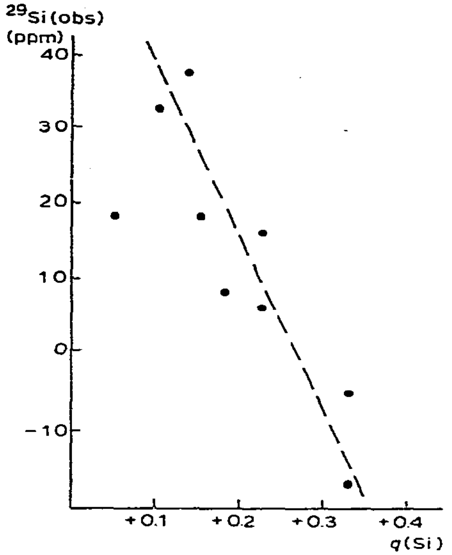
The data obtained for cyclic silanes (see Tables 1, 3 and 5) suggest that of the α-carbons the largest electronic perturbations under the effect of substitution on Si occure in the SiCB series. For example, the range of substituent chemical shift (SCS) for α-C atoms in the SiCB is 18.2 ppm (see Table 5), but in the series Me_2SiXY, the range of SCS for α-carbons is only 10.3 ppm (Table 5), which does not increase for the series Et_2SiXY [42]. A small SCS range was also observed for the SiCP series.

We have explored the empirical correlation between C2,4 chemical shifts

TABLE 9

BOND ORDER PARAMETERS CALCULATED WITH SPD-BASIS AND WITH SP-BASIS FOR CYCLIC SILANES

P_{sAsB} for	SPD-calculation						SP-calculation					
	$Si_1C(Me)$	Si_1C_2	Si_1C_5	$Si_3C(Me)$	Si_3C_2	Si_3C_4	$Si_1C(Me)$	Si_1C_2	Si_1C_5	$Si_3C(Me)$	Si_3C_2	Si_3C_4
	0.2677	0.2209					0.2525	0.2134				
	0.2759	0.2257		0.2679	0.2215		0.2615	0.2160		0.2540	0.2139	
		0.2324		0.2680	0.2221			0.2203		0.2579	0.2147	
	0.2569	0.2628					0.2475	0.2560				
	0.2724	0.2738					0.2647	0.2658				
	0.2592	0.2360	0.2485				0.2448	0.2405	0.2558			
	0.2665	0.2409	0.2563	0.2594	0.2362	0.2479	0.2490	0.2411	0.2632	0.2459	0.2488	0.2542



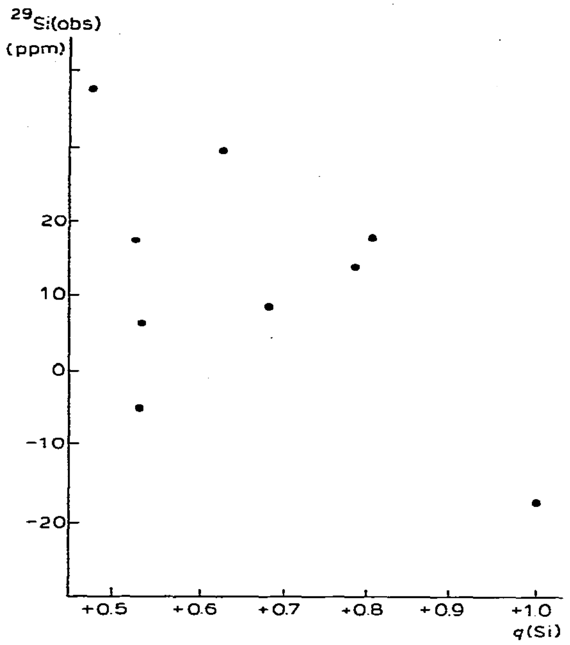
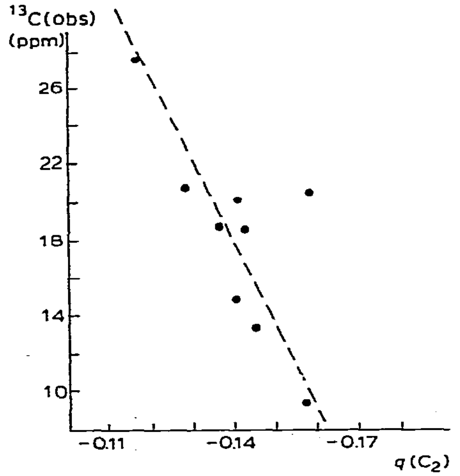


Fig. 2. Plot of δSi vs. q(Si), obtained from SPD-calculations for type $XY\overline{SiCH_2CH_2CH_2}$.

Fig. 3. Relationship between δSi and q(Si) obtained from SP-calculation for type $XY\overline{SiCH_2CH_2CH_2}$.

in the $XY\overline{SiCH_2CH_2CH_2}$ series and values of SP- and SPD-basis set computed electronic densities on the corresponding carbons (the results are given in Tables 7 and 8). The dependences found are presented in Figs. 4 and 5.

A linear correlations ($r = 0.95$, X, Y = OH excluded) was noted only for



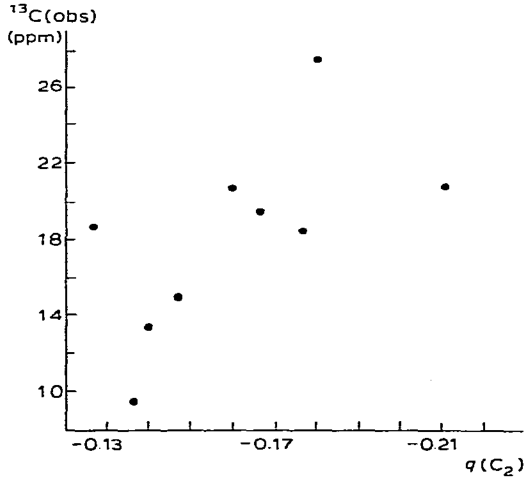


Fig. 4. Plot of δC_2 vs. $q(C_2)$, obtained from SPD-calculation for type $XY\overline{SiCH_2CH_2CH_2}$.

Fig. 5. Plot of δC_2 vs. $q(C_2)$, obtained from SP-calculation for type $XY\overline{SiCH_2CH_2CH_2}$.

SPD-calculation. The slope of the curve on Fig. 4 indicates the expected relationship between δ C2,4 and q(C): an increase in electronic density on carbon causes an upfield shift.

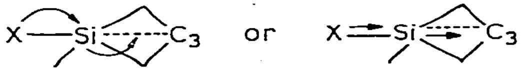
The correlation found for SP-calculated values of net atomic charge on carbon ($r = 0.63$, Fig. 5) has an opposite slope even if we omit the two extreme points.

However, it has been recommended [43] that the discussion of substituent effects should not include any implied assumption that ^{13}C shielding varies linearly with the electron density, unless a reliable theoretical treatment demonstrates that such a dependence is at least approximately valid for the relationship of interest. On the other hand, a good linear correlation has been found between δ(C-*para*) and electronic density on those carbons in substituted benzenes [44].

The correlations obtained in this study (Figs. 2 and 4), which were the criterion for the correctness of the computation basis used, clearly demonstrate that SPD-calculation reflects closes the valence electron distributions in the SiCB, and that *d*-orbitals of Si atom play the role not only in a silicon screening effect, but also in α-carbons shielding.

Another result was achieved in the study of C3 chemical shifts in cyclic silanes. The range of SCS for C3 was found to be surprisingly large in the SiCB, 11 ppm (see Table 5). A replacement of H in III by a methyl group or heteroatoms causes an upfield shift of C3 similar to that in acyclic silanes [42], while in the latter case the SCS for β-carbons do not exceed 2 ppm [42], the SCS for C3 in the SiCB has a much larger range: Δ(C3) is equal to −6.4 ppm for X, Y = OEt (XI). The SCS for C3,4 in the SiCP is small.

The diamagnetic shift of carbon nuclei at 4-position to a substituent (γ-effect) has been widely investigated in ^{13}C NMR spectroscopy and is mainly connected with the steric repulsion effect [45]. Taking into account the small range of SCS Δ(C-β) increments for unstrained cyclic and acyclic silanes, the shielding effect on C3 in the SiCB could be hardly explained by steric interactions only. The 1—3 transannular bonding might also be involved in the interpretation of C3 chemical shifts in four-membered cycles. In this way, substitution to the Si atom of substituents capable of *p*—*d* conjugation (Cl, O, N, C_6H_5, CH_3 etc.) has to increase the electronic population on transannular bond by the scheme:



which causes the shielding effect on C3. The donating abilities of the substituents can be estimated approximately from the values of Δ(C3) given in Table 5. The order found follows the sequence: OEt > NEt_2 > Cl > CH_3 ≈ C_6H_5. When the substituent is a hydrogen atom, the electron density on the transannular bond is pushed towards silicon and a downfield shift of C3 is observed.

This result is partially confirmed by examining the ^{13}C chemical shifts of C-*para* in Me_3SiPh and in $\mathrm{MePh\overline{SiCH_2CH_2C}H_2}$ (XIV). The chemical shifts were obtained from the spectra recorded under identical conditions (50% solutions in $CHCl_3$).

Δ(C-*para*) between XIV and Me_3SiPh was found to be equal to +0.6 ppm. This indicates that the $\mathrm{Me\underline{SiCH_2CH_2C}H_2}$ group is a better acceptor than Me_3Si

group [44] and that the electronic charge on *para*-carbon is decreased in XIV relative to that in Me_3SiPh. The conclusion was supported by SPD-calculation for these compounds: $Q(\text{C-}para(\text{XIV})) - Q(\text{C-}para(\text{Me}_3\text{SiPh})) = -0.006\ e$. The SP-calculation yielded equal values of $Q(\text{C-}para)$.

(c) J(SiC) coupling constants

Of special concern in our study was the sensitivity of nuclear spin couplings, $J(\text{SiC})$, to the changes in electronic structure of organosilicon compounds governed by geometrical deformations and electronegativity effect. We studied the magnitude of coupling constants, $^1J(\text{SiC})$, for *exo*- and *endo*-cyclic Si—C bonds as a probe of hybridization state of the Si atom in organosilicon rings studied. The data presented in Tables 1 and 3 reveal that the SiCB differ from the SiCP and acyclic silanes in the magnitudes of $^1J(\text{SiC})$ as much as they differ in the chemical shifts.

The inspection of $J(\text{SiC})$ in the compounds studied shows that four-membered rings are characterized by smaller values of coupling constants both for *endo*-cyclic Si—C2,4 bonds and *exo*-cyclic Si—C bonds. The substituent increments, $\Delta J(\text{SiC})$, were also found to decrease especially in Si—C2,4 links in the SiCB (see Table 6).

The decrease in $J(\text{SiC})$ for the Si—CH_2 bond in going from silacyclopentane or acyclic silane (e.g. Me_2SiEt_2*: $^1J(\text{SiC(Me)}) = 50$ Hz, $^1J(\text{SiC(CH}_2))= 51$ Hz) to silacyclobutane is consistent with the decrease in $^1J(\text{CC})$ in cycloalkanes [46,47]: $J(\text{CC})$ was found to reduce in going from cyclopentane or acyclic alkane ($J = 33$—34 Hz) to cyclobutane (J 28—29 Hz) and then to cyclopropane ($J = 10$—12 Hz). But a striking feature of $J(\text{SiC})$ in the SiCB was noted by examining the coupling constants for Si—C(Me) bonds: the reduction of $J(\text{Si—C(Me)})$ was found to follow the sequence: silacyclopropane [6] > silacyclopentane > silacyclobutane. In the case of carbon—carbon couplings in Me-substituted cycloalkanes, the decreasing $J(\text{CC(Me)})$ was observed in the order: cyclopropane [46] > cyclobutane [47] > cyclopentane ≈ acyclic alkane [48].

The smaller magnitudes of $^1J(\text{SiC})$ for *exo*-cyclic bonds were measured not only in methyl substituted, but also in phenyl substituted SiCB. In order to elucidate the reasons for such an effect we attempted to calculate the values of $J(\text{SiC})$ by the CNDO/2 method.

It is known that $^1J(\text{SiC})$ might be expressed as sum of three contributions:

$$J(\text{SiC}) = J(\text{orbital}) + J(\text{spin-dipolar}) + J(\text{contact})$$

As has been shown in the literature [20], the orbital and spin-dipolar contributions to $J(\text{SiC})$ are not only small, relative to the Fermi-contact contribution, but also mutually cancelling.

From MO treatment, the Fermi-contact contribution to the coupling constant is normally given by eq. 1:

$$J_{\text{SiC}} = (4\beta/3)^2 h\gamma_{\text{Si}}\gamma_{\text{C}}(\Delta E)^{-1}S^2_{\text{si}}(\text{O})S^2_{\text{c}}(\text{O})P^2_{s_{\text{si}}s_{\text{c}}} \qquad (1)$$

---

* This study.

(where β, h, γ_{Si}, γ_{C} are the constants, $S^2_{\text{si}}(\text{O})$ and $S^2_{\text{c}}(\text{O})$ are the s-orbital densities at the nuclei of Si and C, ΔE is an average exitation energy and $P^2_{s\text{Si}s\text{C}}$ is the silicon 3s—carbon 2s element of the density matrix or bond-order parameter.)

Interpretations of J(SiC) in terms of hybridization or "silicon and carbon s-character" arguments largely pivot on the factor $P^2_{s\text{si}s\text{c}}$ and assume the factor $(\Delta E)^{-1}S^2_{\text{si}}(\text{O})S^2_{\text{c}}(\text{O})$ to be constant [19,20]. But the general MO approach, which does not make the average ΔE approximation, is very difficult to apply satisfactorily because of the problems associated with constructing good excited-state wave functions and because of serious cancellation difficulties. Variation in $S^2(\text{O})$ might also become appreciable as Maciel et al. [49,50] have noted for J(CC) and J(CF).

Under these circumstances we examined a relationship between experimental values of J(SiC) for *exo*- and *endo*-cyclic Si—C bonds and the factor $P^2_{s\text{Si}s\text{C}}$

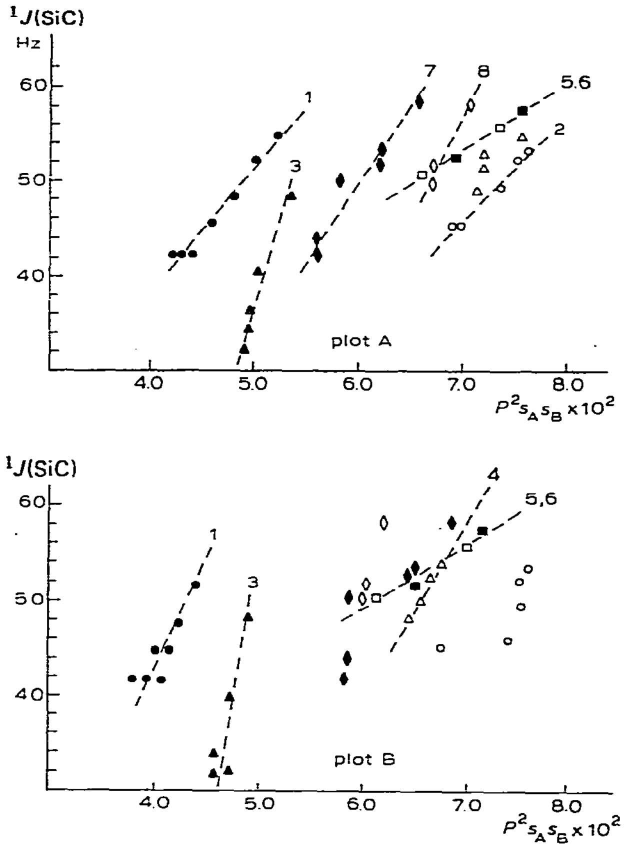
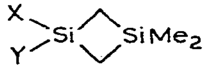
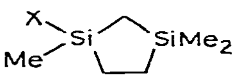


Fig. 6. Dependence of ^1J(SiC)(expt) on $P^2_{s_As_B}$, obtained from SPD-calculation (plot A) and from SP-calculation (plot B) for Si—C bonds in cyclic carbosilanes; A-B corresponds to: (1●) Si_1—C_2, (2○) Si_1—C(Me) in $\text{XY}\overline{\text{SiCH}_2\text{CH}_2\text{C}}\text{H}_2$; (5■) Si_1—C_2, (6□) Si_1—C(Me) in $\text{XMe}\overline{\text{SiCH}_2\text{CH}_2\text{CH}_2\text{C}}\text{H}_2$; (3▲) Si_1—C_2, Si_3—C_2, (4△) Si_1—C(Me), Si_3—C(Me) in



(7♦) Si_1—C_2, Si_1—C_5, Si_3—C_2, Si_3—C_4, (8◇) Si_1—C(Me), Si_3—C(Me) in



obtained from SP- and SPD-calculations for the cyclic silanes studied. The computed P^2-parameters are given in Tables 7, 8, and 9. The relationships found are shown in Fig. 6.

Regarding the correlations shown in Fig. 6, it must be noted that although the plots A and B are similar, the SPD-calculation (plot A) gives a more regular curve. Another feature is that the curves 1—8 for each type of cycle differ by the slope (tg α). On returning to eqn. 1, it becomes clear that the differences in tg α can be defined by the factor $S^2_{\mathrm{Si}}(\mathrm{O})S^2_{\mathrm{C}}(\mathrm{O})/\Delta E$.

When the linear dependence of ${}^1J(\mathrm{SiC})$ on P^2-parameter has been established for cyclic silanes, the values of $J(\mathrm{SiC})$ in I were computed using the scheme of calculation by eq. 1 where $S^2(\mathrm{O})$ and ΔE were assumed to be constant as is published [19,20]. It was found that the large differences between calculated and experimental $J(\mathrm{SiC})$ occurred for Si—C(Me) and Si—C 2,4 bonds where the errors were +15% and —17% respectively (SPD-calculation of P^2; SP-calculation gave much larger differences). This result displays that either P^2-parameter was calculated for the geometry of I which was not adequate to describe the real structure, or factor $S^2_{\mathrm{Si}}(\mathrm{O})S^2_{\mathrm{C}}(\mathrm{O})/\Delta E$ could not be taken as a constant for the organosilicon compounds of different type. Since the latter problem needs further detailed studies which are beyond the scope of the present work, only the reasons for a decrease in the magnitude of $J(\mathrm{SiC})$ for *exo*-cyclic Si—C bonds were investigated.

Two explanations may be given for such an effect:

(a). A geometrical factor due to the deformation of *exo*-cyclic CSiC angle or to the increase in Si—C(Me) bond length which might result in the decrease of P^2-parameter.

(b). An electronic factor depending on the changes in electron distributions basically on 3*s* and 3*p* orbitals of the Si atom due to a possible occupation of 3*d* orbitals in the SiCB.

To investigate the factor *a* we varied the geometrical parameters, such as *exo*-cyclic CSiC angle and the length of the Si—C(Me) bond in I, and calculating the changed geometry using SP- and SPD-basis sets. The P^2-parameter was found to be practically insensitive to the deformations: alteration of CSiC angle from 120 down to 95° and of the length Si—C(Me) from 1.86 to 1.92 Å gave a change P^2 of about ± 0.005 (SPD) and about ± 0.007 (SP). This shows that the geometrical deformations, which can be due to the steric interaction of periplanar hydrogen atoms at C3 with the methyl group at Si1, is not the main reason for the decrease of the Si—C coupling constant of the *exo*-cyclic bond in the SiCB.

Another approach for an explanation of the reduced $J(\mathrm{SiC})$ in *exo*-cyclic bonds of the SiCB can be made by comparing the electronic distributions in the SiCB I with those in XXIV and in $\mathrm{Me_4Si}$.

The comparison of P^2-parameters calculated for Si—Me bonds in I, XXIV and $\mathrm{Me_4Si}$ revealed that SPD- and SP-computations gave almost equal values of P^2, excluding P^2 in I for which this value was slightly higher. Other terms which are important for the determination of the net value of $J(\mathrm{SiC})$ are $S^2_{\mathrm{Si}}(\mathrm{O})$, $S^2_{\mathrm{C}}(\mathrm{O})$ and ΔE from eqn. 1. As mentioned above, the evaluation of ΔE is associated with many problems and, therefore, the effect of variation of this parameter on $J(\mathrm{SiC})$ in I, XXIV and $\mathrm{Me_4Si}$ cannot be considered.

As has been mentioned for the cases of ${}^1J(\mathrm{CH})$, ${}^1J(\mathrm{CC})$ and ${}^1J(\mathrm{CF})$ coupling constants [49,50], $S^2(O)$ parameter might be influenced by the effective nuclear charge (Z^*), which depends on the changes in electronic density on the atom, if Slater's screening rules are used. The greater electronic density on the atom gives a decrease in Z^* and, hence, $S^2(O)$. It was of interest to see how the calculated net atomic charges on silicon and carbon atoms would alter the magnitude of $J(SiC)$.

For this purpose we used eqn. 2, which was based on the assumptions described in [49,50]:

$$S^2_{Si}(O)S^2_C(O)/\{S^2_{Si}(O)S^2_C(O)\}_0 = \{(4.15+0.35q_{Si})(3.25-0.35q_C)/(4.15)(3.25)\}^3 \tag{2}$$

(where $\{S^2_{Si}(O)S^2_C(O)\}_0$ stands for the value appropriate to neutral, nonpolar Si—C fragment, and q_{Si} and q_C present the net atomic charges on silicon and carbon atoms.)

It was found that the omission of silicon 3*d* orbitals from basis set effectively eliminated a possibility of decreasing $J(SiC)$, but inclusion of *d* orbitals into the computation led to a greater electronic charge on the Si atom in I and reduced $S^2_{Si}(O)S^2_C(O)$ factor in I relative to that in Me_4Si. Such a correction gave a decrease in $J(SiC)$ in I to the values of about 40 Hz. By taking into account the larger value of P^2-parameter in I, an increase in the calculated magnitude of $J(SiC)$ for the *exo*-cyclic Si—C bond can be supposed to be close to the measured one. However, this result should be considered as indicative rather than final.

In phenyl substituted SiCB (XIV and XV) the $J(SiCx)$ values were also decreased and equal to 60—62 Hz, while in Me_3SiPh the coupling constant was found to be 66.5 Hz [12]. By the method already described [51] we estimated the "*s*-character" of silicon ($f_{Si}(s)$) and carbon ($f_c(s)$) "hybrid" orbitals forming the Si—C(Me) and Si—C*x* bonds in XIV and Me_3SiPh. If a linear dependence of $J(SiC)$ on $f_{Si}(s) \times f_C(s)$ is valid in our case, the reduced $J(SiC)$ were found only from the SPD-valence shell density matrix for Si—C bonds in XIV compared with that in Me_3SiPh.

From these results it can be concluded that $J(SiC)$ is the parameter more sensitive to the electronic distributions rather than to the geometrical deformations. The latter is obviously confirmed by comparison of $J(SiC)$ in Me_4Si, Me_2SiEt_2 and XXIV.

It is also necessary to note here the $^1J(SiC)$ in 1,3-disilacyclobutanes (Table 1). The magnitude of $J(SiC)$ of the *exo*-cyclic Si—C bond in these compounds is close to that in the SiCP and in acyclic silanes, but $^1J(SiC)$ in *endo*-cyclic bonds are the lowest known to date for organosilicon compounds. However, if another Me_2Si group is taken into consideration ($\Delta J(SiC) \approx -7$ Hz), then an approximate equality will be observed between Si—C coupling constants for *endo*-cyclic linkages in monosilacyclobutanes and 1,3-disilacyclobutanes. But the computation of $P_{s_{Si}s_C}$ for compounds XXI, XXII and XXIII (see Table 9) gave rise to the increased bond-order parameters when the second Si atom was introduced into the silacyclobutane ring. The explanation for such a divergence might be given perhaps in the terms of variation in $S^2_{Si}(O)S^2_C(O)/\Delta E$ factor.

$^2J(SiC3)$ coupling constant. The existence of 1—3 bonding in the SiCB was

demonstrated by determining the nuclear spin coupling constant between Si and C3 nuclei. The values of ^2J(SiC) were found to be unexpectedly large (16—19 Hz). To varify this result an attempt was made to measure ^2J(SiC) in the SiCP XXIV, but no ^2J coupling was observed although the width of C3,4 peak at the ^1J(CC) satellite height in ^{13}C spectrum of XXIV did not exceed 6—7 Hz. Thus, ^2J(SiC) in XXIV was found to be less than 7 Hz.

The value of ^2J(SiC) has been previously measured only in $R_3Si—C≡C—X$ compounds [12,17], where it varied between 10—16 Hz. The comparison of ^1J(SiC) and ^2J(SiC) obtained in I and $Me_3Si—C≡C—Ph$ [12] displays the nuclear spin-spin interaction through two bonds in I is weakened 2.6 times with respect to direct interaction, while the interaction through the triple bond is weakened as much as 5 times (^1J(SiC) = 83.6 Hz and ^2J(SiC) = 16.1 Hz [12]).

The only reason for such a strong interaction between Si1 and C3 nuclei can be attributed to the transannular 1—3 bonding in the SiCB. The nuclear spin information is transfered in this interaction through space directly, without participation of α-carbon electrons.

^{1}H NMR data were not studied in detail because of the very complicated spectra and the uncertainties in the determination of ^{1}H chemical shifts. Only the comparatively strong downfield shift for all protons in the SiCB, especially for α-protons, should be mentioned.

(d) Electronic structure of silacyclobutanes

Although discussions on relative energies and forms of MO in I and in III have been made earlier on the basis of EHT [41] and ab initio STO-3G [52] methods, it was of interest to study the MO's in the SiCB constructed by CNDO/2 method with or without the inclusion of the silicon 3*d* orbital. In CNDO calculation the neglect of *d* orbitals led to a degenerated pair of the highest occupied MO in III, which were similar to e_u - MO's constructed in cyclobutane [52]. This is inconsistent with the experimental results obtained from photoelectron spectrum of III [41]. As 3*d* orbitals were accounted for in the computation of III, the degeneracy of two uppermost MO was lifted and e_u. MO were transformed into a_1 and b_2 MO, shown schematically in Fig. 7. As is seen, the $d_{x^2-y^2}$ and d_{xy} orbitals have the appropriate symmetry to be incorporated into $a_1(\sigma)$MO, especially by mixing the $3p_x$ orbital with $3d_{x^2-y^2}$ on the silicon atom, and into $b_2(\pi)$MO, if the planar form with C_{2v} symmetry is assumed for III. The $3p_x + 3d_{x^2-y^2}$ orbital interacts with $2p_x$ orbital of the C3 atom forming a transannular bond.

An approximate stability for this bonding was evaluated by the values of calculated resonance energies (E^R_{AB}) [53]. The E^R_{AB} were computed by CNDO procedure for the two basis sets. The SPD-basis calculation revealed a significant stability of the 1—3 transannular bond (E^R for Si···C3 was about 1/4 of E^R for Si—C2 bond), while the SP-calculation led to a negligible one.

The results obtained from analysis of the dependence of total energy ($E_{tot.}$) of molecule I on geometrical factors should be also pointed out here. The optimization has been carried out for the geometry of I in the four variables: dihedral angle ψ, *exo*-cyclic Si—C bond length, *endo*-cyclic Si—C bond length and *exo*-cyclic CSiC angel (see Fig. 8). The $E_{tot.}$ was calculated using SP- and SPD-basis sets for each variation. The results are given in Table 10.

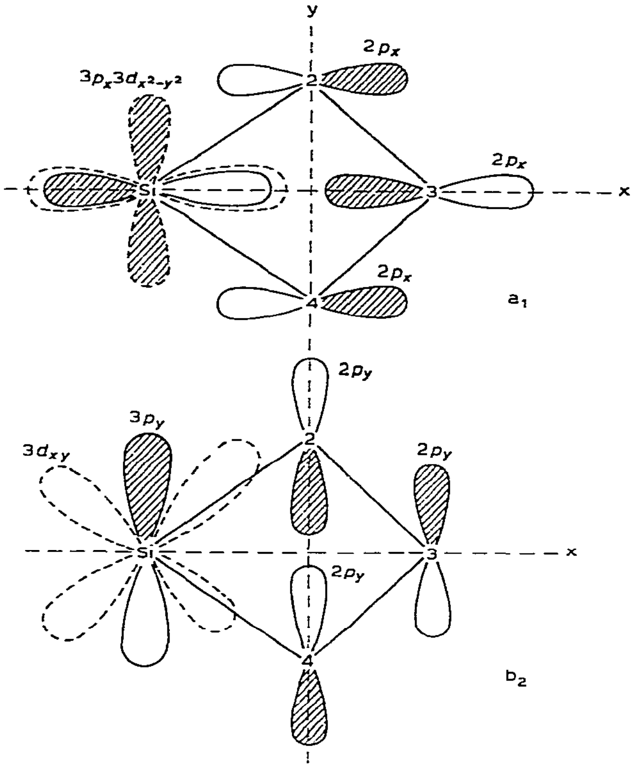
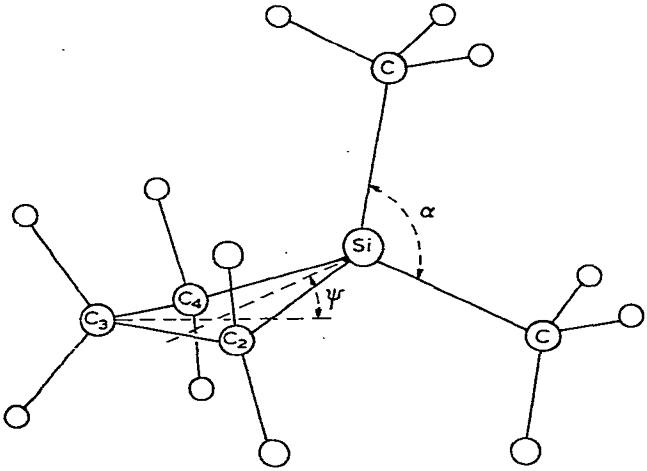


Fig. 7. Form of the uppermost ring molecular orbitals for III.



∠α MeSiMe 108°
Si–Me 1.898 Å
Si–C 2,4 1.898 Å
ψ 30 ± 5°

Fig. 8. Structure of I.

TABLE 10

THE EFFECT OF VARIATIONS IN GEOMETRICAL PARAMETERS ON CALCULATED TOTAL ENERGY FOR I

SP-calculation $E_{tot.}$ (a.u.)	Parameter changed geometry	SPD-calculation $E_{tot.}$ (a.u.)
	Experimental	
−48.12255		−49.03152
	Planar form	
−48.14027	$\psi = 0°$	−49.02443
−48.13591	l(Si—Me) = 1.92 Å	−49.03032
−48.09500	l(Si—Me) = 1.86 Å	−49.02688
−48.13860	l(Si—C_2) = 1.93 Å	−49.02950
−48.09048	l(Si—C_2) = 1.84 Å	−49.03018
−48.12275	∠MeSiMe = 112°	−49.03093
−48.11750	∠MeSiMe = 120°	−49.02193
−48.11957	∠MeSiMe = 100°	−49.02844

The SP-computation fails to yield a minimum value of $E_{tot.}$ for a geometry close to that found experimentally: the planar form with increased *exo*-cyclic angle and bond lengths is more stable. Contrary to this, the SPD-calculation gives a minimum $E_{tot.}$ for the puckered form with parameters identical to the experimental values. This provides an additional support to the fact that consideration of *d*-orbitals is important both for determination of electronic distributions in the SiCB, and for the structural properties.

The chemical experiment [1,2] displays the high reactivity of the SiCB both to cleavage and to substitution reactions with nucleophiles, in contrast to cyclobutanes. In this study we examined the shape and the energy of lowest unoccupied MO (LUMO) in the SiCB, constructed from CNDO/2 calculation, and found that: (1) the lowering of LUMO energies in molecules I—V and XI is correlated with the relative reactivity of these compounds in the reaction of nucleophilic cleavage of *endo*-cyclic Si—C bond; (2) the "*s*-character" of LUMO or the contribution of 3*s* atomic orbital of silicon to the LUMO is significantly increased. This is consistent with the smaller "*s*-character" on Si—C bonds in four-membered rings discovered by *J*(SiC) measurements. The $3d_{x^2-y^2}$ orbital was also found to be incorporated into LUMO.

Hence, it is possible to suggest that a donation of electron density from nucleophile on LUMO of SiCB should result in a destabilization of 1—3 antibonding interaction and in weakening of *endo*-cyclic Si—C bond due to the changes in hybridization state of the silicon atom. An increase in the "*s*-character" on Si atom should naturally lead to the relaxation in the strained molecule by a cleavage of the Si—C bond. The more detailed discussion of the electronic structure and comparative reactivity of organosilicon cyclic compounds will be the subject of our next report.

Conclusions

On the basis of NMR studies of cyclic silanes an appreciable differences between four-membered rings of SiCB and acyclic or cyclic unstrained organosilicon compounds have been noted.

On the basis of the comparison of experimental data and parameters calculated with SP- and SPD-basis sets the following conclusions may be drawn: (a) the computation in extended basis set reflects more realistically the electronic distributions in the SiCB studied and the effect of 3*d*-orbitals on NMR parameters is significant. (b) the investigation of substituent increments and the measurement of ^2J(SiC) enables us to conclude that in the SiCB strong 1—3 transannular interaction is displayed; (c) the high reactivity of SiCB to the ring opening can be attributed to the decreased "*s*-character" on Si atomic orbitals forming the *endo*-cyclic bonds with the carbon atoms.

However, based on semiempirical CNDO/2 method, which has many inherent deficiencies, these results leave room for further improvements, especially for the case of 3*d*-orbital participation, and a final result on this subject requires computations using the other levels of approximation.

References

1 N.S. Nametkin and V.M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., 5 (1974) 1153.
2 R. Damrauer, J. Organometal. Chem., Rev. A, 8 (1972) 67.
3 R.L. Scholl, G.E. Maciel and W.K. Musker, J. Amer. Chem. Soc., 94 (1972) 6376.
4 G. Fritz and E. Matern, Z. Anorg. Allg. Chem., 426 (1976) 28.
5 E. Block and L.K. Revelle, J. Amer. Chem. Soc., 100 (1978) 1630.
6 R.L. Lambert and D. Seyferth, J. Amer. Chem. Soc., 94 (1972) 9246.
7 G. Engelhardt, R. Radeglia, H. Jancke, E. Lippmaa and M. Mägi, Org. Magn. Reson., 5 (1973) 561.
8 C.R. Ernst, L. Spialter, G.R. Buell and D.L. Wilhite, J. Amer. Chem. Soc., 96 (1974) 5375.
9 R. Wolff and R. Radeglia, Z. Phys. Chem., Leipzig, 258 (1977) 145.
10 F.F. Roelandt, D.F. van de Vondel and E.V. van den Berghe, J. Organometal. Chem., 94 (1975) 377.
11 R. Wolff, Ph.D. Thesis, Berlin (1978).
12 G.C. Levy, D.M. White and J.D. Cargioli, J. Magn. Reson., 8 (1972) 280.
13 R.K. Harris and B.J. Kimber, J. Magn. Reson., 17 (1975) 174.
14 H. Dreeskamp and K. Hildenbrand, Justus Liebigs Ann. Chem., 3 (1975) 712.
15 K.G. Sharp, P.A. Sutor, E.A. Williams, J.D. Cargioli, T.F. Farrar and K. Ishibitsu, J. Amer. Chem. Soc., 98 (1976) 1977.
16 R.K. Harris and B.J. Kimber, Org. Magn. Reson., 7 (1975) 460.
17 B. Wrackmeyer, J. Organometal. Chem., 166 (1979) 353.
18 K. Kovacevic and Z.B. Maksic, J. Mol. Struct., 17 (1973) 203.
19 K.D. Summerhays and D.A. Deprez, J. Organometal. Chem., 118 (1976) 19.
20 M.D. Beer and R. Grinter, J. Magn. Reson., 31 (1978) 187.
21 R.R. Dean and W.McFarlane, Mol. Phys., 12 (1967) 289.
22 M.F. Larin, Ph.D. Thesis, Irkutsk, 1978.
23 J.A. Pople and G.A. Segal, J. Chem. Phys., 44 (1966) 3289.
24 P.A. Dobosh, CNINDO : CNDO and INDO MO Programm (FORTRAN IV), Quantum Chemistry Programm Exchange, Prog. 141.
25 V.S. Mastryukov, O.V. Dorofeeva, L.V. Vilkov, B.N. Cyvin and S.U. Cyvin, Zh. Struct. Khim., 16 (1975) 473.
26 V.S. Mastryukov, L.V. Vilkov and N.A. Tarasenko, J. Mol. Struct., 27 (1975) 216.
27 L.V. Vilkov, V.S. Mastryukov, V.D. Oppenheim and N.A. Tarasenko, in S.J. Cyvin (Ed.), Molecular Structure and Vibrations, Amsterdam, Elsevier Sc. Publ. Co., 1972, 18/1, p. 310.
28 V.T. Aleksanyan, G.M. Kuz'yantz, V.M. Vdovin, P.L. Grinberg and O.V. Kuzmin, Zh. Strukt. Khim., 10 (1969) 397.
29 A.V. Golubinsky, Ph.D. Thesis, Moscow Univer., 1978, Moscow.
30 B. Csakvari, Z. Vaguer, P. Govory and F.C. Mijlhoff, J. Organometal. Chem., 107 (1976) 287.
31 A.G. Robiette, D.W.H. Raukin, C. Slidewell and G.M. Sheldrick, Chem. Commun., (1968) 909.
32 (a) V.M. Vdovin, N.S. Nametkin and P.L. Grinberg, Dokl. Akad. Nauk SSSR, 150 (1963) 799; (b) N.S. Nametkin, V.M. Vdovin, E.D. Babich and P.L. Grinberg, ibid., 161 (1965) 358; (c) N.S. Nametkin, N.V. Ushakov and V.M. Vdovin, Zh. Org. Khim., 44 (1974) 1970; (d) P.L. Grinberg, Ph.D. Thesis 1968, Moscow; (e) V.N. Karelsky, Ph.D. Thesis 1970, Moscow; (f) N.S. Nametkin, N.A. Lepetukhina, O.V. Kuzmin, E.D. Babich and T.N. Chernyscheva, Dokl. Akad. Nauk SSSR, 198 (1971) 112; (g) N.S. Nametkin, V.M. Vdovin and A.V. Zelenaia, ibid., 170 (1966) 1088; (h) N.S. Nametkin, E.D. Babich,

V.N. Karelsky and V.M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., 5 (1971) 1033; (i) N.S. Nametkin, V.M. Vdovin, E.D. Babich and V.D. Oppenheim. Zh. Geterocikl. Soed., 3 (1965) 455; (k) N.S. Nametkin, V.M. Vdovin and P.L. Grinberg. Dokl. Akad. Nauk SSSR, 155 (1964) 849.
33 A.M. Krapivin and V.A. Chertkov, Zh. Strukt. Khim., in press.
34 C.W. Haig, Org. Magn. Res., 4 (1971) 203.
35 J.B. Lambert, J.J. Papay, S.A. Khan, K.A. Kappauf and E.S. Maguar, J. Amer. Chem. Soc., 96 (1974) 6112.
36 R. Löwer, M. Vongehr and H.S. Marsmann, Chem. Zeit., 99 (1975) 33.
37 B.K. Hunter and L.W. Reeves, Can. J. Chem., 46 (1968) 1399.
38 J. Réffy, T. Veszprémi, P. Hencsei and J. Nagy, Acta Chim. Acad. Sci. Hung., 96 (1978) 95.
39 R. Hoffmann and R.B. Davidson, J. Amer. Chem. Soc., 93 (1971) 5699.
40 N.L. Bauld, J. Cessac and R.L. Holloway, J. Amer. Chem. Soc., 99 (1977) 8140.
41 C.S. Cundy, M.F. Lappert, J.B. Pedley, W. Schmidt and B.T. Wilkins, J. Organometal. Chem., 51 (1973) 99.
42 J. Schraml, V. Chvalovsky, M. Mägi and E. Lippmaa, Collection, Czech. Chem. Commun., 44 (1979) 854.
43 G.E. Maciel, in G.C. Levy (Ed.), Topics in Carbon-13 NMR Spectroscopy, Wiley-Interscience, New York, London, 1974, vol. 1, p. 61.
44 G.L. Nelson, G.C. Levy and J.D. Cargioli, J. Amer. Chem. Soc., 94 (1972) 3089.
45 J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, London, 1972.
46 F.J. Weigert and J.D. Roberts, J. Amer. Chem. Soc., 94 (1972) 6021.
47 M. Stöcker and M. Kleissinger, Org. Magn. Reson., 12 (1979) 107.
48 K.D. Summarhays and G.E. Maciel, J. Amer. Chem. Soc., 94 (1972) 8348.
49 G.E. Maciel, J.W. McIver, N.S. Ostlund and J.A. Pople, J. Amer. Chem. Soc., 92 (1970) 1.
50 G.E. Maciel, J.W. McIver, N.S. Ostlund and J.A. Pople, J. Amer. Chem. Soc., 92 (1970) 11.
51 K.R. Fountain, Tetrahedron. Lett., 31 (1970) 2655.
52 P.D. Mollere and K.N. Houk, J. Amer. Chem. Soc., 99 (1977) 3226.
53 H. Fisher and H. Kollmar, Theor. Chim. Acta, 16 (1970) 163.