Journal of Organometallic Chemistry, 406 (1991) 283–298
Elsevier Sequoia S.A., Lausanne
JOM 21352

Synthesis and ^{1}H, ^{13}C, ^{14}N, ^{15}N, ^{29}Si NMR study of trimethylsilylquinolines and their methiodides

Edmunds Lukevics *, Edvards Liepiņš, Izolda Segal and Mendel Fleisher
Institute of Organic Synthesis, Latvian Academy of Sciences, Riga, Latvia (USSR)

(Received August 28th, 1990)

Abstract

2-, 3-, 4-, 5-, 6-, 7- and 8-trimethylsilylquinolines and their methiodides as well as some 2-silylalkylquinolines were obtained by lithium synthesis in order to elucidate intramolecular donor–acceptor interactions between nitrogen and silicon atoms. ^{1}H, ^{13}C, ^{14}N, ^{15}N and ^{29}Si NMR spectra of the compounds were studied and quantum-chemical calculation of charges on individual atoms in the unsubstituted quinoline and in trimethylsilylquinoline molecule was carried out. The two-centred component of the total system energy for various bonds was calculated. The findings suggest donor-acceptor interaction between nitrogen and silicon atoms in 2-trimethylsilylquinoline that reduces electron density at nitrogen atoms. An apparently weaker interaction is observed in 8-trimethylsilylquinoline.

Introduction

The electron-donating properties of the organosilicon substituent bonded to the phenyl ring in arylsilanes are opposed by an electron-accepting effect and either significantly decreased or completely overlapped [1]. A popular explanation is a hypothetical interaction of the π-electron systems and free *d*-orbitals of silicon.

A similar interaction is possible in pyridylsilanes as well. Results of the study of basicity [2,3] and of ionization potentials of silyl derivatives of pyridine [4] encourage us to consider the pronounced contribution of π–d interaction. Comparison of the calculated and experimental electron spectrum of 2-trimethylsilylpyridine [5] also suggests the interaction between π-electrons of the heterocycle and the vacant *d*-orbitals of silicon.

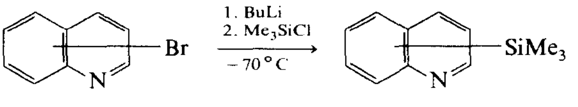
On the other hand, an α-effect leading to decreased electron density at the nitrogen atom has been observed in α-aminoalkylsilanes [6–8].

In continuation of our study of electron effects in the molecules of organosilicon derivatives of nitrogen-containing heterocycles we synthesized trimethylsilyl substituted quinolines (**1**) and their methiodides (**2**) as well as 2-silylalkylquinolines (**3**) containing a silyl group in the side chain. ^{1}H, ^{13}C, ^{14}N, ^{15}N and ^{29}Si NMR spectra of the compounds revealed the aforesaid effects in quinolylsilanes. Quantum-chemical calculation of charges on separate atoms in unsubstituted quinoline and in trimethylsilylquinoline and a calculation of the two-centred component of the total system energy for various bonds were made [9].

Results and discussion

Synthesis

2-, 3-, 5-, 6-, 7- and 8-trimethylsilylquinolines were obtained by means of lithium synthesis involving metallation of the corresponding bromoquinolines by butyllithium in ether or in the mixture ether : THF = 1 : 1 at low temperature. The resulting lithium derivative of quinoline was treated with trimethylchlorosilanes [10,11]. 4-Substituted product was synthesized from quinoline according to [12]. The reaction of trimethylsilylquinolines with methyl iodide in ether or without solvent (in the case of 2-substituted product) afforded methiodides.

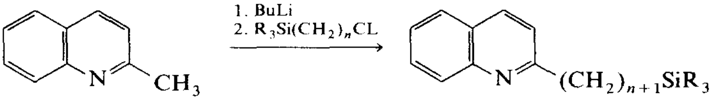


(1a–g)

(**a**: 2- (substituent position); **b**: 3-; **c**: 4-; **d**: 5-; **e**: 6-; **f**: 7-; **g**: 8-)

2-, 3- and 4-trimethylsilylpyridines (**4a–c**) and their methiodides (**5a–c**) were synthesized for the comparison using the same methods [11,12].

The lithium derivative of quinaldine [10,11] resulting from its interaction with butyl lithium (in ether), was reacted with chloro- or chloroalkylsilane to produce compounds with a silyl group in the side chain.



(3a–c)

(**a**: $n = 0$, $R_3 = Me_3$; **b**: $n = 0$, $R_3 = Me_2H$; **c**: $n = 1$, $R_3 = Me_3$)

The values of chemical shifts (CS) and spin–spin coupling constants (SSCC) obtained from the NMR spectra of trimethylsilylquinolines are given in Table 1. The quantumchemical calculations for molecules **1** are presented in Table 2.

The interaction between N and Si atoms was expected to be particularly manifest when analyzing ^{15}N and ^{29}Si CS, so these values will be considered first.

^{15}N and ^{14}N NMR spectra

The ^{15}N CS measured for I are given in Table 1. A comparison of $\delta(^{15}N)$ with the calculated charges on nitrogen atoms (Fig. 1) shows that the ^{15}N CS for 3-, 4-, 5-, 6- and 7-trimethylsilyl substituted compounds depend on the charge on the nitrogen atom. An increase in the positive charge is accompanied by a downfield shift of the ^{15}N resonance. However, 2- and 8-$SiMe_3$ derivatives display a considerably larger downfield shift of the ^{15}N signal indicating the positive charge on the nitrogen atom is larger than expected. Calculations based on the correlation from Fig. 1 demonstrate that the positive charge is increased on the nitrogen atom of 2-trimethylsilylquinoline by ~ 0.03 units and to a smaller extent on the nitrogen

Table 1

^{13}C, ^{15}N and ^{29}Si NMR spectral parameters of trimethylsilylquinolines in $CDCl_3$

Substituent	$\delta(^{29}Si)$ (ppm)	$\delta(^{15}N)$ (ppm)	Chemical shifts, $\delta(^{13}C)$ ppm										$^1J(^{29}Si-^{13}C_i)$ (Hz)	$^1J(^{29}Si-^{13}CH_3)$ (Hz)
			C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	$SiCH_3$		
H	–	−71.1 [18]	150.73	121.55	136.43	128.37	127.01	129.85	129.94	148.78	128.76	–	–	–
2-$SiMe_3$	−5.07	−47.9	170.25	124.85	133.10	127.60	126.23	129.95	128.84	148.85	127.51	−1.67	75.5	52.7
3-$SiMe_3$	−3.75 [a]	−76.6	153.88	132.71	142.03	127.90	126.40	129.37	129.65	148.54	127.81	−1.25	62.7	52.8
4-$SiMe_3$	−3.26	−67.0	149.45	126.39	148.98	128.18	127.65	129.00	130.90	147.87	132.08	+0.29	64.0	53.0
5-$SiMe_3$	−4.07	−70.2	149.71	121.16	135.96	139.22	133.64	128.73	131.16	148.69	131.84	+0.30	62.6	52.8
6-$SiMe_3$	−3.84	−73.1	150.63	121.06	135.97	133.63	139.20	133.48	128.50	148.66	127.76	−1.14	64.0	52.5
7-$SiMe_3$	−3.67	−69.7	150.33	121.27	135.80	126.79	130.43	142.67	135.18	147.74	128.41	−1.21	63.2	52.5
8-$SiMe_3$	−4.49	−65.5	148.74	120.38	135.77	128.82	125.72	135.42	141.49	152.46	126.36	−0.32	64.9	53.3

[a] According to Ref. 19: $\delta(^{29}Si) = -3.7$ ppm (TMS/C_6D_6).

Table 2

Quantum-chemical calculations of charges on atoms of quinoline and trimethylsilylquinoline molecules

Location of substituent	Charge, *e*										
	N	Si	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
–	5.1642	–	3.8969	4.0255	3.9658	4.0021	3.9950	3.9839	4.0203	3.8974	3.9871
2	5.1151	3.8288	4.0274	3.9750	3.9891	4.0094	3.9896	3.9907	4.0146	3.9168	3.9698
3	5.1770	3.8358	3.8564	4.1404	3.9082	3.9968	4.0000	3.9780	4.0250	3.8850	4.0015
4	5.1424	3.8243	3.9188	3.9668	4.0922	4.0247	3.9914	3.9889	4.0165	3.9148	3.9451
5	5.1570	3.8280	3.9064	4.0197	3.9914	4.1236	3.9327	4.0062	3.9965	3.9157	3.9467
6	5.1647	3.8298	3.8957	4.0289	3.9616	3.9391	4.1140	3.9394	4.0368	3.8852	4.0033
7	5.1538	3.8264	3.9058	4.0175	3.9743	4.0208	3.9503	4.1047	3.9565	3.9177	3.9710
8	5.1659	3.8197	3.9005	4.0282	3.9649	3.9809	4.0148	3.9229	4.1366	3.8623	3.9997

atom of 8-trimethylsilylquinoline. Thus, ^{15}N NMR spectra provide evidence for electron density transfer from the nitrogen atom to the C_2–Si and C_8–Si bond in the respective compounds.

The ^{14}N signals for protonated species (Table 3) are rather wide and their CS, in contrast to those of the bases, lie in the narrow range. This also shows that the downfield shift of the ^{15}N resonance in 2-trimethylsilylquinoline is caused by electron density transfer in space.

Comparing $\delta(^{15}N)$ CS for compounds **1a**, **3a** and **3c**, which are equal to -47.9, -79.1 and -75.9 ppm, respectively, it should be noted that the introduction of a methylene group between the quinoline ring and the silicon atom causes considerable upfield shift of the ^{15}N resonance. This implies the effects observed in the case of 2-trimethylsilylquinoline are either weakened or abolished and is a manifestation of the electron-donating properties of trimethylsilylalkyl groups. As expected, the replacement of the trimethylsilyl substituent from the ring by another methylene

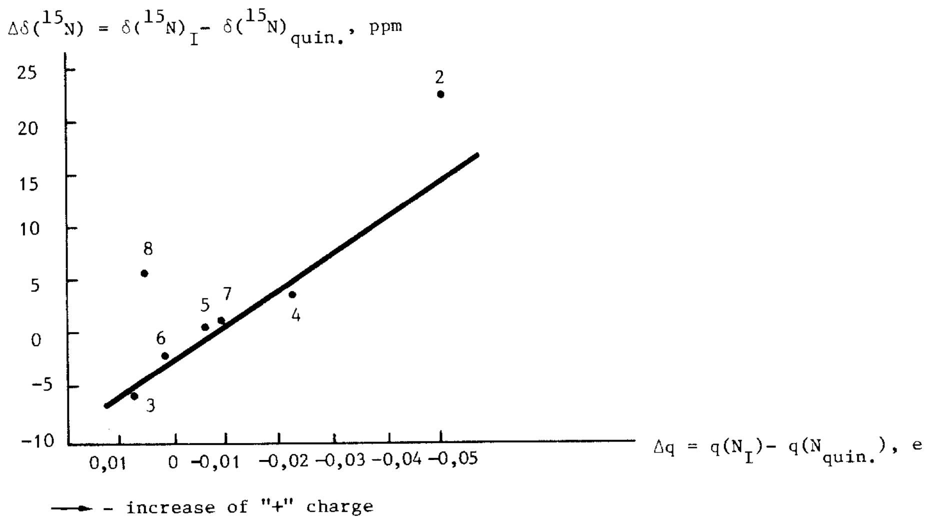


Fig. 1. Dependence of $\delta(^{15}N)$ CS on charge variation on the nitrogen atom caused by the introduction of a trimethylsilyl group into various positions of the quinoline ring.

Table 3

^{13}C, ^{14}N and ^{29}Si CS for methiodides of trimethylsilylquinolines in DMSO-d_6

Substituent	$\delta(^{29}Si)$ (ppm)	$\delta(^{14}N)$ (ppm)	Chemical shifts, $\delta(^{13}C)$ ppm										
			C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	NCH_3	$SiCH_3$
H	–	−191.6 [a] (140)	150.00	121.83	146.90	129.78	130.16	135.34	118.97	138.17	129.05	45.37	–
2-SiMe$_3$	+3.53	−188.8 (200)	169.04	128.19	143.94	129.92	130.19	135.42	119.29	140.46	129.30	45.77	−0.76
3-SiMe$_3$	−0.40	−192.0 (200)	152.40	133.96	152.75	129.70	130.05	135.52	118.75	137.98	128.68	44.99	−1.60
4-SiMe$_3$	+0.32	−191.4 (200)	147.09	127.84	163.75	129.73	129.89	134.47	119.89	136.58	132.37	45.45	−0.81
5-SiMe$_3$	−1.88	−190.2 (200)	146.17	122.02	149.35	142.48	136.55	134.23	120.18	139.35	132.05	45.80	−0.14
6-SiMe$_3$	−1.90	−192.1 (220)	146.77	121.86	149.95	135.63	143.07	139.11	117.84	138.46	128.33	45.18	−1.60
7-SiMe$_3$	−0.67	−192.8 (220)	146.71	122.02	149.92	128.84	133.48	150.59	123.96	137.20	129.16	45.26	−1.60

[a] Half-width (Hz) of line is given in brackets.

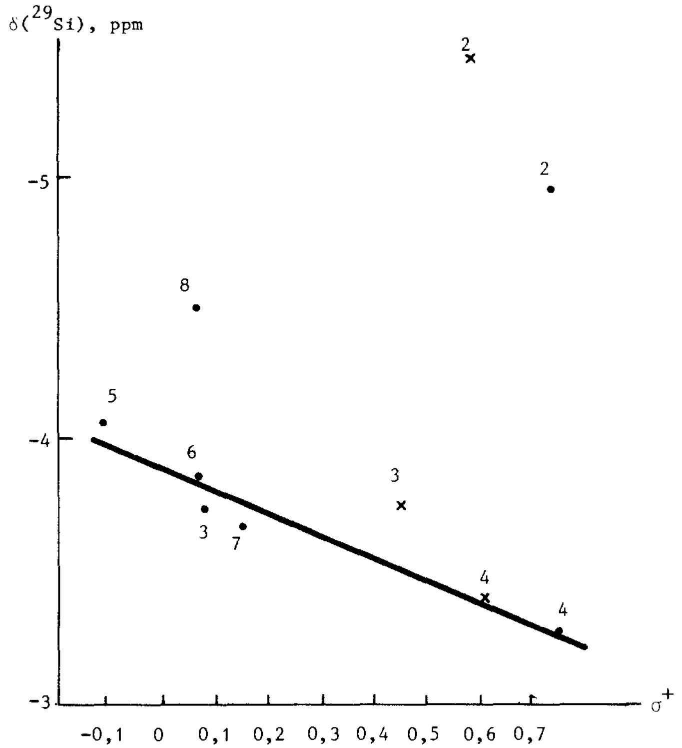


Fig. 2. Relationship between $\delta(^{29}Si)$ CS for compounds **1** (**4**) and σ^+ reactivity constants for various locations of the quinoline (pyridine) cycle; • - for quinoline derivatives, × - for pyridine derivatives. σ^+ value for positions 2, 3, 4, 5, 6, 7, 8 of the quinoline ring is equal to 0.73, 0.08, 0.75, −0.11, 0.07, 0.15, 0.07 respectively; for 2, 3, 4 locations of pyridine 0.56, 0.45, 0.60 [22].

group (**3c**) or substitution of the methyl group for a hydrogen atom (**3b**, $\delta(^{15}N) = -77.65$ ppm) results in a small downfield shift of the ^{15}N signal compared with that for compound **3a**.

^{29}Si NMR spectra

^{29}Si CS for compound **1** are presented in Table 1. Comparison with the σ^+ reactivity constants determined for various positions of the quinoline cycle reveals a linear correlation between these values (Fig. 2). 2-SiMe$_3$-quinoline, and to a lesser degree 8-SiMe$_3$ quinoline deviates from this correlation. The observed values are shifted upfield or toward more negative σ^+ values. Thus, ^{29}Si CS are indicative of a considerably increased negative charge on the ^{29}Si nuclei of 2-trimethylsilylquinoline in comparison with the "normal" or σ^+ value. It is 2.5 times stronger than the corresponding increase of the negative charge on the ^{29}Si nuclei in 8-trimethylsilylquinoline.

Owing to the parabolic dependence of ^{29}Si CS on the charge on the silicon atom, quantitative analysis based on a direct comparison of ^{29}Si CS with the calculated charge cannot be carried out [13]. Qualitative analysis of ^{29}Si CS and the charge calculated on the silicon atom in **1** also shows some excess of the negative charge on it in 2- and 8-trimethylsilylquinoline (Fig. 3).

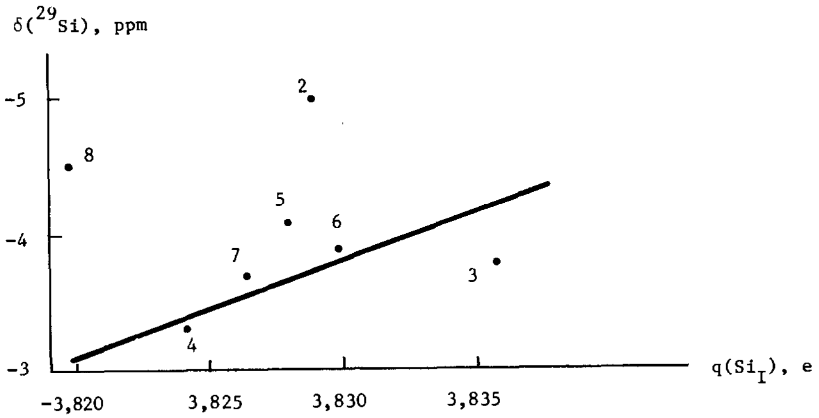


Fig. 3. Relationship between $\delta(^{2(}\mathrm{Si})$ CS of compounds **1** and the charges calculated on the silicon atom.

A comparison of $^{29}\mathrm{Si}$ CS in quinolines **1** with those for *N*-methylquinolinium salts **2** also provides evidence, stronger for **1**, for additional contribution to the shielding of $^{29}\mathrm{Si}$ nuclei (Fig. 4).

Consequently, $^{29}\mathrm{Si}$ CS demonstrate the existence of N → Si interaction in 2-$\mathrm{SiMe_3}$-quinoline. Probably, this interaction, though weaker, occurs in 8-trimethylsilylquinoline too.

As for compounds **1a** and **3a, f**, it must be noted that the changes in $^{29}\mathrm{Si}$ CS have a similar character to those in $^{15}\mathrm{N}$ CS. Thus, the most upfield $^{29}\mathrm{Si}$ shift, -5.07 ppm, corresponds to the most downfield shift of the $^{15}\mathrm{N}$ signal in 2-trimethylsilylquinoline. The $^{29}\mathrm{Si}$ CS values becomes more positive ($\delta(^{29}\mathrm{Si}) = +2.82$ ppm) with increased shielding of the nitrogen atom in compound **3a** accompanied by an upfield displacement of the $^{15}\mathrm{N}$ CS. The CS for compound **3c** has an intermediate though similar CS value ($\delta(^{29}\mathrm{Si}) = +2.10$ ppm).

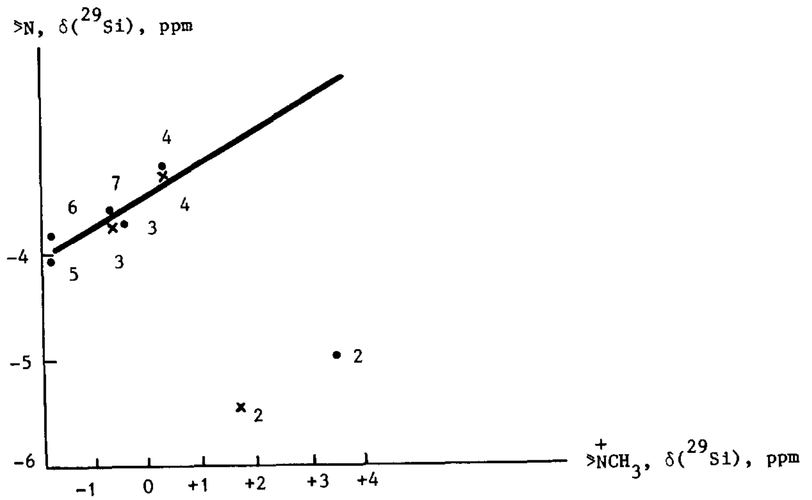


Fig. 4. Relationship between $\delta(^{29}\mathrm{Si})$ CS of trimethylsilylquinolines (-pyridines) and their methiodides: • - for quinoline derivatives, * - for pyridine derivatives.

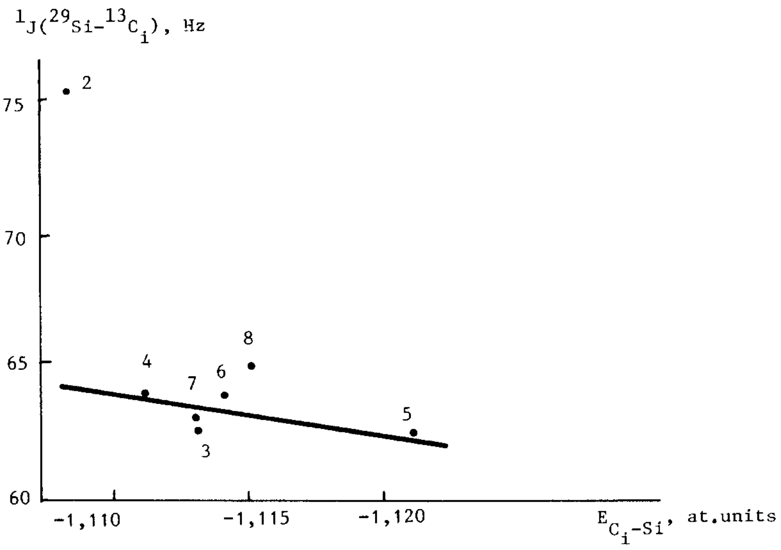


Fig. 5. Relationship between $^1J(^{29}Si-^{13}C)$ SSCC and the two-centred component of the total energy system for the Si–C bond in trimethylsilylquinolines **1**.

The study of $^1J(^{29}Si-^{13}C)$ SSCC provides information on the mechanism of N → Si interaction. SSCC values compared for various locations of the quinoline cycle show a considerable increase for the 2-trimethylsilyl derivative (see Table 1). According to Ref. 14, this increase in SSCC might be due to increased electron density on the antisymmetric orbitals of the N=C–Si fragment. Thus, the possible mechanism of electron density transfer from nitrogen to silicon atom in 2-silyl-substituted quinoline involves interaction of the unpaired electron pair of the nitrogen atom and the antibonding orbitals of the N=C–Si fragment.

On the other hand, quantum-chemical calculations can reveal the stability of bonds by means of the two-centred component of the total system energy for the corresponding bond. A linear correlation for all locations of quinoline except position two (Fig. 5) resulted from the comparison of $^1J(^{29}Si-^{13}C)$ SSCC with the two-centred component of the total energy system for the Si–C bond (Table 4). This

Table 4

Two-centered component of the total system energy for C–Si and N · · · Si bonds in trimethylsilylquinolines

Substituent location	E_{C-Si} (unit of energy)	$E_{N\cdots Si}$ (unit of energy)
2	−1.108	−0.045
3	−1.113	−0.009
4	−1.111	−0.003
5	−1.121	−0.001
6	−1.114	0
7	−1.113	0
8	−1.115	−0.025

Table 5

$^{13}C-^{1}H$ SSCC (Hz) for trimethylsilylquinolines

Substituents	H [20]	2-$SiMe_3$	3-$SiMe_3$	4-$SiMe_3$	5-$SiMe_3$	6-$SiMe_3$	7-$SiMe_3$	8-$SiMe_3$
C_2H_2	178	–	175.5	177.0	177.5	176.3	176.4	176.9
C_3H_3	165	160.9	–	161.0	161.8	161.7	162.0	161.9
C_4H_4	162	160.9	160.2	–	158.0	160.1	160.8	161.0
C_5H_5	160	160.1	159.9	159.8	–	159.0	159.0	159.5
C_6H_6	161	160.7	161.6	160.9	158.8	–	157.0	161.1
C_7H_7	162	160.6	161.0	160.8	161.1	160.2	–	159.3
C_8H_8	161	163.0	164.0	164.1	163.0	163.2	158.0	–
C_2H_3	3.7	[a]	–	3.3	3.5	3.2	3.0	3.3
C_3H_2	9.0	–	[a]	9.0	9.1	8.9	8.6	8.9
C_2H_4	7.6	[a]	8.8	–	7.5	7.9	7.4	7.7
C_4H_2	5.4	–	5.1	[a]	5.4	5.3	5.0	5.2
C_4H_5	5.4	4.7	5.1	[a]	–	5.0	5.0	5.2
C_5H_4	5.2	5.8	5.0	–	[a]	5.0	4.5	5.1
C_5H_7	7.3	7.3	7.2	7.0	[a]	7.1	–	7.2
C_6H_8	8.6	8.8	8.4	8.4	8.4	[a]	9.2	–
C_7H_5	8.5	8.5	8.7	8.6	–	8.6	[a]	8.8
C_8H_6	6.3	5.9	5.2	5.7	5.3	–	8.0	[a]

[a] Not measured.

fact speaks in favour of additional interactions along the C–Si bond that are not implied by quantum-chemical calculation. The possibility of charge transfer from nitrogen to silicon is partially confirmed by calculation of the two-centred component of the total system energy for the N · · · Si bond (Table 4). For example, $E_{N \cdots Si}$ in 2-trimethylsilylquinoline is considerably higher than in other trimethylsilyl derivatives of quinoline. However, in 8-trimethylsilylquinoline this component is noticeably increased compared with other derivatives.

^{13}C NMR spectra

^{13}C CS for trimethylsilylquinolines are presented in Table 1. ^{13}C signals in compound I were assigned with the aid of spectra without proton decoupling. The $^{13}C-^{1}H$ SSCC found for I differ slightly from those for unsubstituted and methyl-substituted quinolines (Table 5) [15].

The ^{13}C resonance of $SiMe_3$ in the 2-substituted derivative is shifted further upfield than when the substitution is made at other locations, indicating increased donor capacity of the 2-quinoline substituent in reference to silicon atom. The considerable downfield shift of the ^{13}C resonance of $SiMe_3$ in positions 4 and 5 of the quinoline cycle is apparently caused, for the most part, by steric effects which are to be expected for these positions. A certain downfield shift of the ^{13}C signal of the 2-trimethylsilyl group of quinoline salt **2** is probably due to steric interaction between the NCH_3 group and the 2-$SiMe_3$ substituent.

Smaller deviations, possibly due to charge transfer between nitrogen and silicon atoms, can be observed for ^{13}C resonances in the quinoline ring. Moreover, direct comparison of ^{13}C CS with the charge on the given carbon atom is difficult owing to the specific shielding characteristic of every quinoline position. We therefore used for the comparison the shift values resulting from the introduction of the $SiMe_3$ group (Table 6). Charge variation on separate carbon atoms, brought about by the

Table 6

Effect of trimethylsilyl substituent on the shielding of quinoline cycle nuclei in trimethylsilylquinolines, $\Delta = \delta_{Z(I)} - \delta_{Z(\text{quin.})}$ ($Z = {}^{15}N$ or ${}^{13}C_i$) ppm[a]

Substituent location	Nucleus									
	N	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
2	+23.2	+19.52	+3.3	−3.33	−0.77	−0.78	+0.10	−1.1	+0.07	−1.25
3	−5.5	+3.15	+11.16	+5.60	−0.47	−0.61	−0.48	−0.29	−0.24	−0.95
4	+4.1	−1.28	+4.84	+12.55	−0.19	+0.64	−0.85	+0.96	−0.91	+3.32
5	+0.9	−1.02	−0.39	−0.47	+10.85	+6.63	−1.12	+1.22	−0.09	+3.08
6	−2.0	−0.10	−0.49	−0.46	+5.26	+12.19	−3.63	−1.44	−0.12	−1.00
7	+1.4	−0.40	−0.28	−0.63	−1.58	+3.43	+12.82	+5.24	−1.04	−0.35
8	+5.6	−1.99	−1.17	−0.66	+0.45	−1.29	+5.57	+11.55	+3.68	−2.40

[a] Sign "+" stands for the downfield shift, sign "−" stands for the upfield shift in regard to the unsubstituted quinoline.

$SiMe_3$ group, was calculated in an analogous way (Table 7). A comparison of these values demonstrates that the calculated charges on carbon atoms are closely connected with changes in ^{13}C CS (Fig. 6). Growth of the positive charge on the carbon atoms is accompanied by a downfield shift of the ^{13}C resonance. Deviations can be observed only in some cases: the C_9 and C_{10} points deviate in the 2-substituted quinoline **1a**; C_5 and C_4 do so in the sterically hindered 4-$SiMe_3$ and 5-$SiMe_3$ derivatives, respectively. Probably, these deviations are caused either by electron density transfer from nitrogen to silicon in the 2-substituted derivative or by steric affects in 4- and 5-trimethylsilylquinolines. Thus. several changes in the ^{13}C CS in NMR spectra for compounds **1** can be explained by the concept of charge transfer from the nitrogen to silicon atom through space.

The unpaired electron pair of nitrogen may possibly exert its influence on the C_8–C_9 bond, whose location is similar to that of the C_2–Si bond in 2-trimethylsilylquinoline. However, if this influence exists then it must be observable in all quinolines and not be eliminated by alkylation.

Comparison of ^{13}C CS in **1** and in **2** demonstrates the existence of two types of carbon atoms (Fig. 7). The points corresponding to C_2, C_9 and C_8 form a straight line, with other points below. Thus, the effect of the unpaired electron pair of

Table 7

Variation of charge on separate atoms of quinoline cycle during the introduction of trimethylsilyl substituent, Δq (e)[a]

Substituent location	Nucleus									
	N	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
2	−0.049	+0.131	−0.051	+0.023	+0.007	−0.005	+0.007	−0.006	+0.019	−0.017
3	+0.013	−0.041	+0.115	−0.058	−0.005	+0.005	−0.006	+0.005	−0.012	+0.014
4	−0.022	+0.022	−0.059	+0.126	+0.023	−0.004	+0.005	−0.004	+0.017	−0.042
5	−0.007	+0.020	−0.006	+0.026	+0.122	−0.062	+0.022	−0.024	+0.018	−0.040
6	+0.001	−0.001	+0.003	−0.004	−0.063	+0.119	−0.045	+0.017	−0.012	+0.016
7	−0.010	+0.009	−0.008	+0.009	+0.019	−0.045	+0.121	−0.064	+0.020	−0.016
8	+0.002	+0.004	+0.003	−0.001	−0.021	+0.020	−0.061	+0.116	−0.035	+0.013

[a] Sign "−" means the growth of "+" charge at the introduction of $SiMe_3$ group.

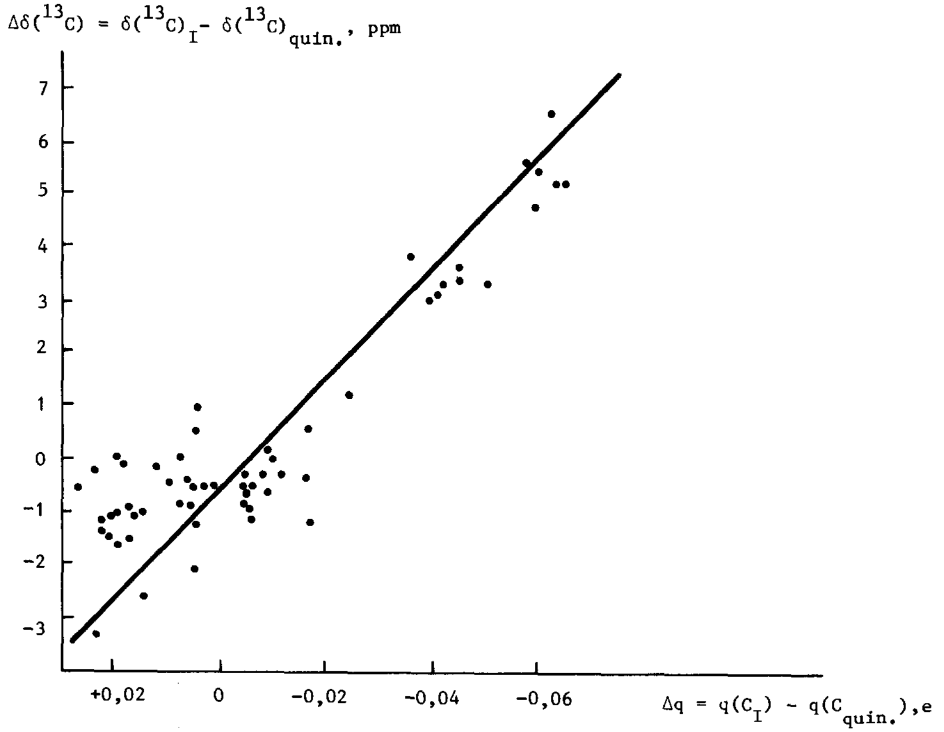


Fig. 6. Changes of $\delta(^{13}C)$ CS connected with changes of charge on the carbon atoms in various locations due to the introduction of a trimethylsilyl group.

nitrogen on the shielding of the neighbouring ^{13}C nuclei is equal to 12–15 ppm; it is considerably higher than in the case of ^{29}Si nuclei, and, in contrast to ^{29}Si nuclei, explains the downfield shift of ^{13}C resonance.

^{1}H NMR spectra

^{1}H nuclei are more distant from the scene of possible N → Si interaction compared with other nuclei. As a result, one would expect changes in ^{1}H NMR spectra to be less obvious, due to the geminal N → Si interaction.

Table 8

^{1}H chemical shifts of trimethylsilylquinolines [a]

Substituent location	$\delta(^{1}H)$ ppm							
	H_2	H_3	H_4	H_5	H_6	H_7	H_8	$SiMe_3$
2	–	7.59	8.03	7.76	7.49	7.68	8.17	0.42
3	9.00	–	8.26	7.80	7.53	7.71	8.10	0.39
4	8.82	7.48	–	8.02	7.50	7.63	8.15	0.45
5	8.91	7.36	8.42	–	7.68	7.73	8.14	0.47
6	8.88	7.35	8.10	7.94	–	7.83	8.10	0.37
7	8.90	7.37	8.10	7.79	7.66	–	8.19	0.37
8	8.90	7.30	8.08	7.78	7.45	7.88	–	0.46

[a] Assignment was done using the long-range SSCC $^{5}J(H_4{-}H_8) \sim 0.6$ Hz, and the double resonance as well.

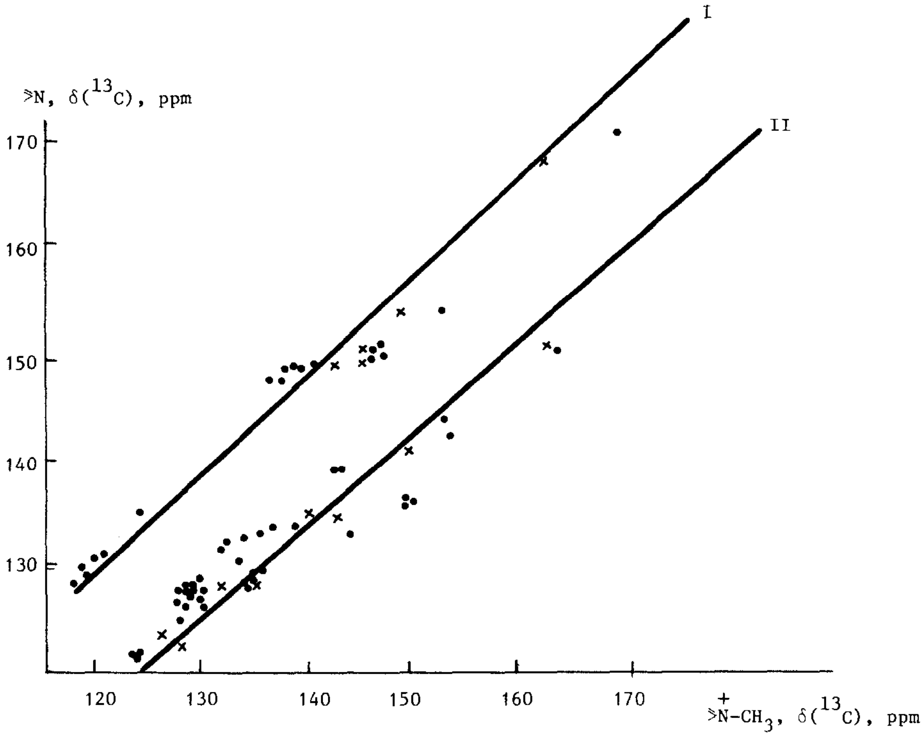


Fig. 7. Relationship between $\delta(^{13}C)$ CS of trimethylsilylquinolines (-pyridines) and their methiodides: • - for quinoline derivatives, × - for pyridine derivatives. C_2, C_8, C_9 atoms correspond to points on line I, the remaining carbon atoms are on line II.

The ^1H CS measured in NMR spectra are presented in Table 8. Contemporary measurements of ^1H CS for methiodides **2** are given in Table 9. The comparison of ^1H CS in **1** and in **2** shows that they vary almost proportionally. The scatter of the values can be explained by local differences in charge.

We also studied the possibility of N → Si geminal effect in trimethylsilyl-substituted pyridines **4**.

Table 9

^1H chemical shifts of trimethylsilylquinoline methiodides [a]

Substituent location	$\delta(^1H)$ ppm								
	H_2	H_3	H_4	H_5	H_6	H_7	H_8	$\overset{+}{N}Me$	$SiMe_3$
2	–	8.22	9.14	8.46	8.27	8.05	8.61	4.66	0.64
3	9.06	–	8.95	8.50	8.39	8.06	8.51	4.68	0.48
4	9.43	8.21	–	8.57	8.29	8.11	8.53	4.66	0.57
5	9.54	8.20	9.32	–	8.17	8.26	8.57	4.67	0.52
6	9.56	8.19	9.33	8.48	–	8.39	8.67	4.66	0.39
7	9.54	8.18	9.28	8.47	8.19	–	8.48	4.22	0.43

[a] Assignment was done using the long-range SSCC $^5J(H_4-H_8) \sim 0.6$ Hz and the double resonance as well.

The ^{13}C, ^{15}N (^{14}N) and ^{29}Si CS for these derivatives are summarized in Table 10, with data for methiodides of trimethylsilylpyridines **4**. Generally, CS (as well as SSCC) exhibit the same trends as those found for the quinoline derivatives. For example, ^{29}Si and ^{13}C CS fit well the lines depicted in Fig. 4 and 7.

Summing up the results obtained for **4** and **5**, one can assume that the influence of the unpaired electron pair of nitrogen on NMR parameters is approximately the same for pyridines and quinolines. This is not surprising, as the sp^2-electron pair of electrons is not involved in the interaction with the π-system of the heterocycle and, consequently, depends only slightly on its properties.

Experimental

NMR spectra were recorded on a Bruker WM-360 under impulse regime. The duration of 30 ° C impulses for ^1H was 5 μs, for ^{13}C, 10 μs, ^{15}N 15 μs, ^{14}N 20 μs, ^{29}Si 10 μs. Substances were studied as 20% solutions in $CDCl_3$ (**1**) and in DMSO-d_6 (**2**) at 30 ° C.

Tetramethylsilane was used as internal standard for ^1H, ^{13}C and ^{29}Si CS measurements and nitromethane as external standard for ^{14}N and ^{15}N CS. Accuracy of measurements was ±0.01 ppm for ^1H, ±0.03 ppm for ^{13}C, ±0.4 ppm for ^{14}N, ±0.1 ppm for ^{15}N, ±0.05 ppm for ^{29}Si.

Quantum-chemical calculations of quinoline electron structure and compounds **1** were carried out by means of MO LCAO SCF in valent approximation CNDO/2 (*spd*-base) [16]. The structural data obtained in Ref. 17 for quinoline were used as geometrical parameters.

*2-Trimethylsilylquinoline (**1a**)*

2-Bromoquinoline (15.2 g, 0.073 mol) in dry ether (50 ml) was added dropwise to 15 ml 4.875 *N* BuLi solution in hexane at −70 ° C in argon atmosphere with stirring. The stirring was continued for 10 min at the same temperature. Trimethylchlorosilane (9.2 ml, 7.9 g, 0.073 mol) in 10 ml ether was gradually added to the reaction mixture. After brief stirring at −70 ° C, cooling was stopped and stirring was continued till the temperature rose to ambient. On the next day, the precipitate was filtered, the solution evaporated and the residue distilled in vacuum at 96–97 ° C/1 mmHg. **1a** (8.6 g, 58%) with $n_D^{20} = 1.5739$, $d_4^{20} = 1.0133$ was obtained.

*3-Trimethylsilylquinoline (**1b**)*

1b was obtained using the above technique in 50% yield. B.p. 127–130 ° C/5 mmHg, $n_D^{20} = 1.5751$, $d_4^{20} = 1.0136$.

*4-Trimethylsilylquinoline (**1c**) and 4-trimethylsilylpyridine (**4c**)*

1c and **4c** were synthesized according to Ref. 12.

*5- (**1d**), 6- (**1e**), 7- (**1f**) and 8-trimethylsilylquinoline (**1g**)*

These compounds were obtained by the same method as that applied for the synthesis of **1a** using the mixture ether : THF = 1 : 1 as solvent and 1.5–2-fold excess of BuLi and Me_3SiCl in the case for **1f** and **1g**. Yield, b.p., n_D^{20}, d_4^{20} are as follows: for **1d** 57%, 106–107 ° C/2 mmHg, 1.5838, 1.0444; for **1e** 16%, 125–127 ° C/4.5 mmHg, 1.5745, 1.0060; for **1f** 30%, 124° C/5.5 mmHg, 1.5747, 1.0145; for **1g** 30%, 113–116 ° C/3 mmHg.

Table 10

^{13}C, ^{15}N (^{14}N) and ^{29}Si NMR spectral parameters for trimethylsilyl-substituted pyridines and their methiodides

Compound	Substituent	Chemical shifts, $\delta(^{13}C)$ (ppm)							$\delta(^{29}Si)$ (ppm)	$\delta(^{15}N)$ (ppm)	$\delta(^{14}N)$ (ppm)	$^1J(^{29}Si-^{13}C_\alpha)$ (Hz)	$^1J(^{29}Si-^{13}CH_3)$ (Hz)
		C_2	C_3	C_4	C_5	C_6	$SiCH_3$	$\overset{+}{N}CH_3$					
4a	2	168.23	122.58	133.80	128.55	150.06	−1.81	–	−5.46	−50.5	–	75.9	52.8
4b	3	149.87	134.88	140.87	123.13	153.84	−1.38	–	−3.75	−71.1	–	62.8	52.8
4c	4	148.83	128.12	150.22	–	–	−1.58	–	−3.39	−69.9 −63.0[21]	–	61.10	52.9
5a	2	162.00	127.84	142.80	134.63	145.47	−1.03	49.49	+1.60	–	−179.3	54.7	55.3
5b	3	145.12	140.00	149.60	126.74	148.46	−1.73	47.77	−0.57	–	−180.1	57.0	53.6
5c	4	142.78	131.70	162.48	–	–	−2.40	47.61	+0.35	–	−180.3	54.6	53.6

Table 11

Methiodides of trimethylsilylquinolines and -pyridines

Compound	M.p. (°C)	Yield (%)	Found (%)			Empirical formula	Calculated (%)		
			C	H	N		C	H	N
2a	211–212.5	15 [a]	45.59	5.12	4.06	$C_{13}H_{18}INSi$	45.48	5.28	4.08
2b	243–244.5	35	45.35	5.08	4.44	$C_{13}H_{18}INSi$	45.48	5.28	4.08
2c	152–155	22	44.09	4.70	4.51	$C_{13}H_{18}INSi$	45.48	5.28	4.08
2d	227.5–230	10	45.03	4.93	3.50	$C_{13}H_{18}INSi$	45.48	5.28	4.08
2e	148.5–151	20	45.74	5.23	4.06	$C_{13}H_{18}INSi$	45.48	5.28	4.08
2f	288.5–290	41 [a]	45.47	5.04	3.66	$C_{13}H_{18}INSi$	45.48	5.28	4.08
5a	184–185	12 [a]	36.97	5.46	4.68	$C_9H_{16}INSi$	36.85	5.50	4.78
5b	147.5–149.5	59	36.68	5.70	4.67	$C_9H_{16}INSi$	36.85	5.50	4.78
5c	135–137	40 [a]	37.15	5.50	4.65	$C_9H_{16}INSi$	36.85	5.50	4.78

[a] Yield of nonrecrystallized product.

2-Trimethylsilylquinoline methiodide (2a)

0.8 ml methyl iodide (1.8 g, 0.013 mol) was added to 1.5 g **1a** (0.0075 mol). The mixture was kept at ambient temperature till the crystalline solid appeared. The crystals were filtered off and **2a** (0.4 g, 15%) was isolated and recrystallized from a mixture of absolute alcohol and a small amount of ether. The m.p. of **2a** was equal to 211–212.5 °C.

Methiodides **2b–f** and **5a–c** were obtained using the analogous technique in ether. The mixture was heated for 2–3 h and kept for approximately 20 h at ambient temperature. The compounds were recrystallized from a mixture of absolute alcohol and ether.

Yields, m.p. and elemental analysis data for methiodides are presented in Table 11.

2-Trimethylsilylmethylquinoline (3a)

75 ml BuCl (66.5 g, 0.72 mol) in ether (75 ml) was gradually added to 10 g lithium (1.44 g/atom) in ether (450 ml) in argon atmosphere at −20 to −25 °C. The obtained BuLi solution was cooled to −50 °C, and then for approximately 40 min quinaldine (86 g, 0.6 mol) in 85 ml of ether was poured in and stirring was continued for another 30 min at the same temperature. After that 85 ml Me_3SiCl (73 g, 0.67 mol) were added over a period of 35–40 min, the mixture was stirred (keeping the temperature constant) for another 20 min, then the temperature was allowed to rise to ambient. On the next day, the precipitate was filtered, the filtrate was evaporated and the residue was distilled in vacuum at 96–98 °C/1.5 mmHg. Thus, **3a** (105 g, 81%) was obtained with $n_D^{20} = 1.5696$, $d_4^{20} = 0.9872$. ^{1}H NMR (δ, ppm): 0.08 ($Si-CH_3$), 2.48 ($Ar-CH_2-Si$), 6.80–8.09 (C_9H_6N); ^{29}Si: 2.82; ^{15}N: −79.1.

2-Dimethylsilylmethylquinoline (3b)

3b was synthesized according to the above method with only slight variations. Lithium (2.8 g, 0.4 mol), 21 ml of BuCl (18.5 g, 0.2 mol), 5.7 ml of ether were taken for BuLi preparation, then 22.9 g of quinaldine (0.16 mol) in 100 ml ether was added to the mixture. Silane was added at −70 °C. **3b** (17.7 g, 57%) was obtained;

b.p. 95–96 °C/0.6 mmHg, $n_D^{20} = 1.5778$, $d_4^{20} = 1.0053$. IR: ν(Si–H) = 2120 cm^{-1}. ^1H NMR (δ, ppm): 0.14 (Si–CH_3), 2.63 (Ar–CH_2–Si), 4.09 (Si–H), 7.01–8.21 (C_9H_6N); ^{29}Si: −11.78; ^{15}N: −77.65.

2-(β-Trimethylsilylethyl)quinoline (3c)

3c was prepared in an analogous way to **3a**. Chloromethyltrimethylsilane was added gradually at ~ −30 to −10 °C, then the reaction mixture was boiled for 2.5 h. **3c** (14.2 g, 39%) was obtained from 21.5 g quinaldine (0.15 mol); b.p. 127–129 °C/3 mmHg, $n_D^{20} = 1.5556$, $d_4^{20} = 0.9761$. ^1H NMR (δ, ppm): 0.06 (Si–CH_3), 1.03 (CH_2–Si), 2.92 (Ar–CH_2), 7.01–8.11 (C_9H_5N); ^{29}Si: 2.10; ^{15}N: −75.9.

*2- (**4a**) and 3-Trimethylsilylpyridine (**4b**)*

4a,b were synthesized according to the technique described for **1a** at −45 to −50 °C in ether 56 and 49% yield, respectively.

References

1 E. Lukevics and O.A. Pudova, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1981) 131.
2 D.G. Anderson, J.R. Chipperfield and D.E. Webster, J. Organomet. Chem., 12 (1968) 323.
3 M.A. Weiner and P. Schwartz, J. Organomet. Chem., 35 (1972) 285.
4 E. Heilbronner, V. Hornung, F.H. Pinkerton and S.F. Thames, Helv. Chim. Acta, 55 (1972) 289.
5 E. Heilbronner, V. Hornung, M. Bock and H. Alt, Angew. Chem., 81 (1969) 537.
6 E. Lukevics and R.Ya Sturkovich, Latv. PSR Zinat. Akad. Vestis, (1977) N 9, 29.
7 E. Lukevics, Heterocycles, 9 (1978) 1479.
8 E. Lukevics, E. Liepiņš, E.P. Popova, V.D. Shats and V.A. Belikov, Zh. Obshch. Khim., 50 (1980) 388.
9 H.F. Fischer and H. Kollmar, Theor. Chim. Acta, 16 (1970) 165.
10 E. Lukevics, I.D. Segal and T.V. Lapina, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1978) 371.
11 A. Fischer, M.W. Morgan and C. Eaborn, J. Organomet. Chem., 136 (1977) 323.
12 R.A. Sulzbach and A.F.M. Igbal, US Patent 3781291 (1973), C.A. 80 (1974) 60030w.
13 H. Marsmann, ^{29}Si NMR Spectroscopic Results, in: P. Diehl, E. Fluck and R. Kosfeld (Eds.), Oxygen-17 and Silicon-29, Springer-Verlag, Berlin, Heidelberg, New York, 1981, p. 65.
14 V.M.S. Gil and W. Philipsborn, Magn. Reson. Chem., 27 (1989) 409.
15 S.R. Johns, R.J. Willing, P.A. Claret and A.G. Osborne, Aust. J. Chem., 32 (1979) 761.
16 J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory, McGraw–Hill, New York, 1970, p. 236.
17 S.C. Wait, Jr. and C. McNerney, J. Mol. Spectrosc., 54 (1970) 168.
18 L. Paolillo and E.D. Becker, J. Magn. Reson., 2 (1970) 168.
19 M. Grignon-Dubois, M. Fialeix and M. Laguerre, Spectrochim. Acta, Ser. A, 44 (1988) 1327.
20 S.R. Johns and R.I. Willing, Aust. J. Chem., 29 (1976) 1617.
21 W. Städeli and W. Philipsborn, Helv. Chim. Acta, 63 (1980) 504.
22 M. Charton, Applications of Linear Free Energy Relationships to Polycyclic Arenes and to Heterocyclic Compounds, in: B. Chapman and J. Shorter (Eds.), Correlation Analysis in Chemistry, Recent Advances, Plenum Press, New York, London; 1978, p. 236.