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^{13}C, ^{15}N and ^{29}Si NMR spectra of triazasilatranes

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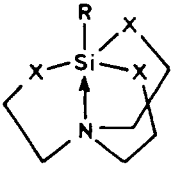
Abstract

^{13}C, ^{15}N and ^{29}Si chemical shifts and ^{29}Si–^{1}H, ^{29}Si–^{13}C and ^{29}Si–^{15}N coupling constants as well as Si–H bond stretching frequencies in the triazasilatranes (I) (2,5,8,9-tetraaza-1-silatricyclo[3.3.3.0^{1,5}]undecanes) and model compounds, tris(alkylamino)silanes with R_{Si} = H, Me, CH_2=CH (Vi) and C_6H_5 (Ph) were measured. A stronger intramolecular N→Si bonding was revealed in I compared with their oxygen analogues, silatranes (II). This was assumed to be caused by the higher polarity of the equatorial Si–X bonds in I (X = NH) in comparison with II (X = O).

Introduction

Triazasilatranes (I) were first synthesized only about 10 years ago [1]. Structural studies of I are not as numerous as those of the oxygen analogues, silatranes (II) [2] possibly owing to the enhanced susceptibility of the former to moisture.

The silatranes II are characterized by an intramolecular donor–acceptor (DA) bond N→Si resulting in a pentacoordinate silicon atom. Preliminary ^{1}H and ^{29}Si NMR studies [1,3] suggest a stronger DA N→Si bond in I compared with II. However, the reverse would have been expected because oxygen is more electronegative than nitrogen. There is no satisfactory explanation of this phenomenon in [1,3]. In order to gain a more detailed insight into the structure of triazasilatranes we have studied ^{13}C, ^{15}N and ^{29}Si NMR spectra of the most stable derivatives of I and the model compounds, III and V, the results obtained have been compared with the literature data for II [4,5].



(I, X = NH;
II, X = O)

$RSiY_3$
(III, Y = NHEt (a), NHPr (b), NMe_2 (c);
IV, Y = OEt)

$N(CH_2CH_2NHR')_3$
(V)

(R = H, Me, Vi, Ph;
R' = H, $SiMe_3$)

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We also measured Si–H bond stretching frequencies (ν(SiH)) for I, IIIb, c (R = H), as it is known that ν(SiH) depend on the strength of the N → Si bond in II [6,7].

Discussion

^{13}C, ^{15}N and ^{29}Si chemical shifts (δ) for I are summarized in Table 1. The $\delta(^{1}H)$ have been published earlier [1].

The ^{29}Si NMR spectra are very sensitive to changes in silicon coordination [8–10]. The existence of a DA N → Si bond in II increases the shielding of ^{29}Si nuclei by 12–22 ppm as compared with triethoxysilanes [4]. In the case of I the coordination shift is almost twice as large and is close to 45 ppm (Tables 1 and 2). This confirms the existence of a stronger N → Si interaction in II.

The ^{15}N NMR signals for the apical nitrogen in I are shifted downfield with respect to the model compounds (Table 1 and 2). This difference tends to increase with an increase in acceptor properties of the silicon atom. An analogous dependence has been found earlier for silatranes and reflects the growing strength of the DA N → Si bond [5]. It is known [5,11,12] that the sensitivity of $\delta(^{15}N)$ of the apical nitrogen atom to substituents at the silicon atom decreases with the N → Si bond strength. In this respect, I resembles the silatran-3-ones which also are characterized by a stronger N → Si bond than II [12].

$\delta(^{15}N)$ of equatorial nitrogens in I is only slightly different from the values of IIIb. The same has been found previously for the ^{17}O spectra of II and IV [13]. However, this may be just coincidence. The data presented in Table 3 demonstrate what a profound influence is exerted by cyclization and the substituent in the γ-position on $\delta(^{15}N)$ (cf. also $\delta(^{15}N)$ for IIIa and IIIb, R = H, Tables 1 and 2) [14] and $\delta(^{17}O)$ [15].

A downfield shift of α-carbon signals of substituents at the silicon atom with respect to the values found for the model compounds is a characteristic feature of the ^{13}C NMR spectra of I (Tables 1 and 2). This is also indicative of a DA N → Si bond in I. These shifts for I and II are approximately equal in value. It is worth

Table 1

^{13}C, ^{15}N and ^{29}Si NMR data for triazasilatranes I in CDCl$_3$ at 303 K

R	$\delta(^{13}C)$ [a]			$\delta(^{29}Si)$ [a]	$\delta(^{15}N)$ [a]		^{1}J(NSi) [b]	^{1}J(SiC) [b]
	α-C	β-C	SiR		NH	N(CH$_2$)$_3$		
Me	50.82	37.17	3.05	−68.3	−352.8	−354.5	25.3	66.2
Vi	50.88	36.97	149.14(α) 126.66(β)	−79.2	−354.0	−352.8	25.8	77.6
Ph	50.99	37.22	149.55(α) 133.57(o) 127.67(m) 127.47(p)	−77.2	−354.1	−352.2	26.5	76.0
H	51.44	36.54	–	−82.3	−350.1	−346.8	–	–

[a] In ppm (±0.1). [b] In Hz (±0.1).

Table 2

^{13}C, ^{15}N and ^{29}Si NMR data for the model compounds in $CDCl_3$ at 303 K

Compound	R	$\delta(^{13}C)$ [a] (SiR)	$\delta(^{29}Si)$ [a]	$\delta(^{15}N)$ [a] NH	N$(CH_2)_3$	$^1J(NSi)$ [b]	$^1J(SiC)$ [b]
IIIa	H	–	−32.7	−343.9	–	–	–
IIIb	H	–	−34.8	−350.3	–	–	–
	Me	−2.71	−23.3	−351.6	–	25.8	75.3
	Vi	137.50(α) 132.41(β)	−34.6	−353.6	–	–	92.3
	Ph	139.18(α) 134.64(*o*) 129.31(*p*) 128.02(*m*)	−33.0	−353.5	–	27.4	92.9
IIIc	H	–	−25.4	–	–	–	–
	Me	−6.18	−16.3	–	–	–	79.6
	Vi	139.22(α) 132.89(β)	−26.9	–	–	–	97.7
	Ph	136.82(α) 135.69(*o*) 129.22(*p*) 127.88(*m*)	−25.3	–	–	–	–
V	$SiMe_3$	–	–	−364.1	−354.4	–	–
	H	–	–	−364.4	−360.9		

[a] In ppm ±0.01 (^{13}C), ±0.1 (^{15}N, ^{29}Si). [b] In Hz (±0.1).

noting that the same phenomenon in II was explained [4] by lengthening of the apical Si–C bond as a result of DA N→Si bond formation. The $\delta(^{13}C)$ of the N$(CH_2\text{-})_3$ carbons in I and II are virtually the same.

Reactivity constants (σ*) can be calculated for Ph derivatives using $\delta(^{13}C)$ of the SiPh group [16]. The σ* values obtained for the Ph derivatives I (−0.38), IIIb

Table 3

^{15}N and ^{17}O NMR chemical shifts for the model compounds

Compound	$\delta(^{15}N)$ (ppm) X = NH [14]	$\delta(^{17}O)$ (ppm) X = O [15]
X(Et)$_2$	−333.7	+6.5
	−343.2	+5
	−346.4	−6

Table 4

^{29}Si–^{1}H coupling constants (Hz) and Si–H bond stretching frequencies (cm^{-1}) in silatranes (I, II) and model compounds (III, IV) in $CDCl_3$ at 303 K

R	Solvent	^nJ(SiH)	ν(SiH)	^nJ(SiH)	ν(SiH)
		N derivatives		O derivatives	
		I		II	
H	$CDCl_3$	176.6	1995	280.1 [a]	2135 [a]
	cyclo-hexane-d_{12}	178.4	1995	–	–
	acetone-d_6	175.1	1988	275.9 [a]	2130 [a]
	DMSO-d_6	171.6	1980	268.8 [a]	2111 [a]
	Nujol	–	1980	–	2090 [a]
CH_3	$CDCl_3$	5.87	–	8.06	–
Vi	$CDCl_3$	6.46(A) 13.5(B) 4.60(C)	– – –	9.06 (A) 18.17 (B) 5.79 (C)	– – –
		IIIb		IV	
H	$CDCl_3$	227.0	2115	287.4 [c]	2197 [d]
[b]	$CDCl_3$	226.9	2114		
Me	$CDCl_3$	7.12	–	8.21	–
Vi	$CDCl_3$	8.55 (A) 16.68 (B) 6.92 (C)	– – –	9.63 (A) 19.39 (B) 7.79 (C)	– – –

[a] Ref. 7. [b] Compound IIIa. [c] Ref. 18. [d] Ref. 6.

(−0.03) and IIIc (−0.13) indicate enhanced donating properties of I compared with IIIb and IIIc which is due to N→Si bond formation.

Spin–spin coupling constants

One-bond spin–spin coupling constants (^1J) permit one to obtain valuable information on the nature of chemical bonds in structurally related compounds [17]. It is known that spin coupling through the axial Si–R bond essentially depends on the strength of the DA N→M bond in metallatranes [18,19]. The ^{29}Si–^{13}C and ^{29}Si–^{1}H couplings in I are considerably smaller than in the model compounds IIIa–c (Tables 1,2 and 4). This indicates a reduction in Si-R bond s-character in I due to N→Si bonding. The appropriate changes in II are less pronounced (Table 4), which supports the existence of a weaker N→Si bond in II compared with the corresponding derivatives of I. Solvent effect on ^{29}Si–^{1}H coupling and, consequently, on the N→Si bond in I is less expressed than in II (R = H).

It has been found previously [19] that the value of ^{29}Si–^{13}C coupling in the 1-methylsilatrane (II, R = Me) is larger than in the corresponding model compound (IV, R = Me). This is apparently connected with the existence of some kind of anomaly in II, since no such phenomenon has been observed in I. Two- and three-bond ^{29}Si–^{1}H couplings through the Si–R bond also decline on going from III to I (Table 4). The difference between I and II is less pronounced in this case.

We studied coupling constants in the Si-vinyl group, as has been found previ-

Table 5

^1H NMR data and $^{13}C-^{13}C$ coupling constants in Si-vinyl systems of silatranes and model compounds at 303 K

Compound	$\delta(^1H)$ (ppm)			Coupling constants (Hz)			
	A	B	C	$^2J_{A,B}$	$^3J_{B,C}$	$^3J_{A,C}$	$^1J(^{13}C-^{13}C)$
$ViSi(NMe_2)_3$	5.678	5.955	6.037	4.38	14.75	20.42	58.0
$ViSi(NHPr)_3$	5.797	5.921	6.000	4.16	14.79	20.49	57.7
$ViSi(NHCH_2CH_2)_3N$	5.512	5.605	5.986	4.05	14.93	20.60	56.2
$ViSi(OEt)_3$ [a]	6.002	6.107	5.888	3.87	14.97	20.70	58.2
$ViSi(OCH_2CH_2)_3N$	5.775	5.730	5.959	4.82	14.54	20.28	58.2

[a] ^1H chemical shifts and $^1H-^1H$ coupling constants are taken from Ref. 4.

ously [4] that N→Si bonding reduces the value of geminal $^1H-^1H$ coupling (see Table 5). However, in our case these changes were negligible.

Investigation of IR spectra of I and III (R = H) shows that (a) $\nu(SiH)$ decreases on going from III to I, (b) these changes are more pronounced in I compared with II, (c) solvent effect on $\nu(SiH)$ in I is weaker than in II. We have shown that there is a linear correlation (eq. 1) between $^1J(^{29}Si-^1H)$ and $\nu(SiH)$ for the N derivatives. No such relationship was found for the O derivatives II and IV (R = H) possibly due to the anomalous values of $^{29}Si-^1H$ couplings in II.

$$^1J(^{29}Si-^1H) = 0.4224\ \nu(SiH) - 664.9 \quad (r = 0.999) \tag{1}$$

The existence of this relationship (eq. 1) suggests that the values of both $\nu(SiH)$ and $^1J(^{29}Si-^1H)$ are controlled by the same factor, viz. Si–H bond *s*-character. A decrease in Si–H bond stretching frequency and a decrease in $^{29}Si-^1H$ coupling constant values indicate a lengthening of the Si–H bond with increasing strength of the DA N→Si bond.

Investigation of the influence of N→Si bond formation on the nature of equatorial bonds merits attention. A certain reduction of $^1J(^{29}Si-^{15}N)$ in I compared with IIIb points to diminished *s*-character (increased polarity) of the equatorial bonds [10,21]. It is noteworthy that the absence of $^1J(^{15}N,^1H)$ and $^3J(^{15}N,^1H)$ indicates fast inter- or intramolecular NH-proton exchange (on the NMR time scale) in solution.

The data presented above are consistent with the notion that a stronger DA N→Si bond exists in I as compared with II. This is difficult to reconcile with the fact that the strength of the DA N→Si bond diminishes upon substitution of equatorial oxygen atoms by less electronegative nitrogen atoms. The existence of a stronger N→Si bond in I per se suggests that the equatorial bonds in I are more polar than in II [22,23].

This anomaly as well as the anomalous values of spin–spin couplings to ^{29}Si in II may be possibly ascribed to the stereoelectronic effect of the oxygen lone pairs [24,25].

Experimental

^1H, ^{13}C, ^{15}N and ^{29}Si NMR spectra of the title compounds were obtained using a

Bruker WM-360 spectrometer operating at 360.13, 90.56, 36.48 and 71.55 MHz, respectively.

The ^1H NMR spectra were recorded in 5-mm NMR sample tubes. Iterative analysis of the Si-vinyl systems ABC and ABCX ($X = {}^{29}Si$) was carried out by use of Bruker Instruments PANIC 85 NMR simulation program. The agreement between simulated and experimental spectra was excellent with rms error within 0.05 Hz. Two- and three-bond $^{29}Si-^{1}H$ coupling constants were measured in ^1H NMR spectra using multiquantum technique as described earlier [26].

The ^{13}C and ^{29}Si spectra were recorded using 10-mm sample tubes. The ^{13}C and ^{29}Si chemical shifts were measured with respect to cyclohexane (27.42 ppm) and TMS (0.0 ppm), respectively. The ^{13}C spectra were obtained using broad-band proton decoupling. The ^{29}Si spectra were recorded using the polarization transfer (INEPT) [27] technique. $^{29}Si-^{13}C$ coupling constants were measured in ^{13}C spectra by the ^{29}Si satellites at the natural abundance of the isotopes. $^{13}C-^{13}C$ coupling constants were measured using INADEQUAT pulse sequence [28].

^{15}N spectra were taken using broad-band proton decoupling in 15-mm sample tubes. The ^{15}N chemical shifts were measured with respect to CH_3NO_2 (0.0 ppm) used as internal standard. $^{15}N-^{29}Si$ coupling constants were measured in ^{15}N spectra by the ^{29}Si satellites at the natural abundance of the isotopes as described earlier [20]. Required sensitivity was provided by the almost maximum nuclear Overhauser effect.

All spectra were recorded at 303 K. The solvents $CDCl_3$, cyclohexane-d_{12}, acetone-d_6 and dimethylsulphoxide-d_6 were dried over 4 Å molecular sieves.

The triazasilatranes (I) used in the present work were synthesized according to ref. 1 by the reaction of organotris(dimethylamino)silanes (IIIc) and tris(aminoethyl)amine (Va).

The starting compounds IIIc were prepared by the commonly used procedures [29,30] from organotrichlorosilanes and dimethylamine. The model compound tris(ethylamino)silane (IIIa) was obtained according to [31] in the reaction of trichlorosilane and ethylamine. The methyl- and phenyltris(propylamino)silanes (IIIb) described earlier were synthesized analogously. By using the same method we obtained tris(propylamino)silane (it was used without distillation in order to avoid decomposition) and vinyltris(propylamino)silane with b.p. 84°C/4 mmHg, n_{20}^{D} 1.4475 unknown from the literature.

Tris(trimethylsilylaminoethyl)amine (Vb) was prepared by silylating Va with hexamethyldisilazane in the presence of trimethylchlorosilane. The silyl derivative, Vb, is a viscous liquid with b.p. 140°C/4 mmHg.

Appendix

Recently the crystal structure of 1-phenyl-3,7,10-triazasilatrane became known [33]. The length of transannular N→Si bond (2.13 Å) is comparable with the shortest N,Si distance of three 1-phenyl-silatrane modifications: 2.19 (α), 2.15 (β), 2.13 (γ) [2]. This does not contradict our results. However, as with our earlier investigations on silatranones [12], we may conclude here, that the negligible changes in N→Si distances observed by X-ray diffraction do not completely reflect the changes in electronic structure of these compounds observed by multinuclear NMR.

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