

CORRELATION OF ONE-BOND ^{15}N - ^{13}C , ^{15}N - M , ^{29}Si - X ($\text{M} = ^{11}\text{B}$, ^{29}Si , ^{119}Sn , $\text{X} = ^1\text{H}$, ^{13}C) NUCLEAR SPIN-SPIN COUPLING CONSTANTS WITH THE STRUCTURE OF METALLATRANES IN SOLUTION

E. KUPČE, E. LIEPIŅŠ, A. LAPSIŅA, I. URTĀNE, G. ZELČĀNS and E. LUKEVICS*

Institute of Organic Synthesis, Latvian SSR Academy of Sciences, Riga (U.S.S.R.)

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Summary

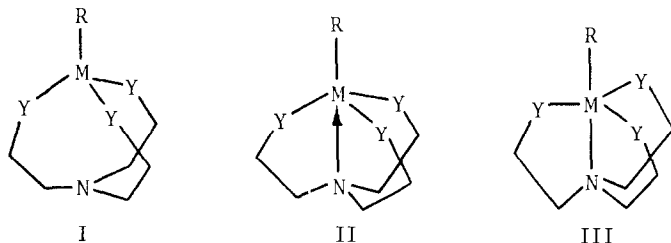
The ^{15}N - ^{13}C , ^{15}N - ^{11}B , ^{15}N - ^{29}Si , ^{29}Si - ^1H and ^{29}Si - ^{13}C one-bond coupling constants in ^{15}N -labelled boratranes, silatranes and germatranes were measured and considered together with the literature data on ^{15}N - ^{119}Sn and ^{119}Sn - ^{13}C couplings in stannatranes. The quantitative pattern of structural variations in metallatranes revealed by analysis of X-ray data was used for the interpretation of the results. $^1J(^{15}\text{N}$ - $^{13}\text{C})$ coupling constants quantitatively describe the increase in nitrogen pyramidalicity with the strengthening of the donor-acceptor (DA) bond $\text{N} \rightarrow \text{M}$ in solution. The coupling constants of the DA bond $\text{N} \rightarrow \text{M}$ were interpreted in terms of the Fermi contact interaction. $^1J(^{15}\text{N}$ - $^{29}\text{Si})$ values were used to predict the bond order and the length of the $\text{N} \rightarrow \text{Si}$ bond in silatranes. In silocanes, bicyclic analogues of silatranes, a linear correlation was found between the $^1J(^{15}\text{N}$ - $^{29}\text{Si})$ values and the free activation energy for DA bond cleavage in solution. The latter was used to estimate the energy of the DA bond $\text{N} \rightarrow \text{Si}$ in silatranes (50–70 kJ/mol).

The coupling constant $^2J(^{15}\text{N}$ - Si - $^1\text{H})$ depends greatly on the size of the corresponding valence angle, whose increase from 90 to 180° results in a sharp reduction of the coupling constant $^2J(^{15}\text{N}$ - Si - $^1\text{H})$ from ~8 to 0 Hz. The effect of the substituents' electronegativity on the coupling constant through the covalent and DA bonds was found to be the opposite.

Introduction

Experimental evidence available on the X-ray analysis [1–24] of metallatranes [25] demonstrates that the structures of these compounds can be represented by two bordering structures, I and III. The actual structure generally corresponds to the intermediate state II due to the fact that the properties of the donor-acceptor (DA) bond $\text{N} \rightarrow \text{M}$ are essentially dominated by the nature of the metal atom (M), the

acceptor properties of substituents Y and R, and environmental influences (state of aggregation, temperature, solvent polarity).



(M = B, C, Si, Ge, Sn, P etc; Y = O, S, NH, CH₂)

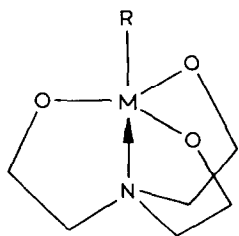
NMR spectroscopy has been extensively applied to measure the chemical shifts (CS) of metallatranes on ¹H [25], ¹¹B [26], ¹³C [27,28], ¹⁵N [29–34], ¹⁷O [35], ²⁹Si [27,36,37], ³¹P [28], ⁷³Ge [38,39] and ¹¹⁹Sn [33,34] nuclei. This allowed mainly the character of the alterations in the electronic and, to some extent, three-dimensional structures of these compounds in solution to be evaluated qualitatively. Quantitative characteristics of the structural variation in metallatranes were obtained by interpretation of X-ray analysis data [10,13]. The scalar spin–spin coupling directly reflects the nature of the chemical bonding between the interacting nuclei; it may also be related to different structural parameters of hybridization [40].

Individual coupling constants have been reported for metallatranes only by some investigators [30,33,34,41,42] without systematic examination. In order to gain new insight into the relationship between spin–spin coupling and metallatranes structure in solution, as well as into the nature of the DA bond N → M in metallatranes, we examined the ¹⁵N–¹³C, ¹⁵N–M and ²⁹Si–X (M = ¹¹B, ²⁹Si; X = ¹H, ¹³C) coupling constants in ¹⁵N-enriched boratranes, silatranes and germatranes and in some related compounds.

Results

The structures of metallatranes in the crystalline state

In the crystalline state, by far the best-studied metallatranes are the silatranes IVb [1–13]. The structures of some germatranes (IVc) [14–19], phosphatranes (IVd) [20–22] and boratranes [23,24] have also been investigated. It has been found that N and M hybridization in IV is mainly determined by the DA bond length *l*(N,M) [10,13]. In the type I structure, found for some phosphatranes [20,22] and for the Pt-complex of silatrane, where the N → M bond is absent, the M atom has a tetrahedral structure, whereas the nitrogen atom is trigonal-planar. As proposed for l-aza-manxane [43], the carbon analogue of I (Y = CH₂, RM = CH), the planarity of the nitrogen atom results from steric constraints imposed by the hydrogen atoms in the N(CH₂)₃ moiety. With increasing strength of the DA bond N → M, the nitrogen becomes more pyramidal, while the M atom configuration approaches that of a trigonal-bipyramid (TBP) (tetrahedron in the case of IVa).



(a, M = B ; b, M = Si ; c, M = Ge ;
d, M = P ; e, M = Sn)

(IV)

The ^{15}N - ^{13}C spin-spin coupling

In solution the pyramidity of the nitrogen atom can be estimated from $^1J(^{15}\text{N}-^{13}\text{C})$, using the well-known equation proposed by Binsch et al. [44]:

$$^1J(^{15}\text{N}-^{13}\text{C}) = 80^{-1} s_{\text{N}}\% s_{\text{C}}\% \quad (1)$$

where s_{N} and s_{C} are the contributions of the $2s$ orbitals of N and C atoms, respectively, to N-C bond formation. Unfortunately, eq. 1 is not strictly quantitative [45,46], since the $^1J(^{15}\text{N}-^{13}\text{C})$ term is largely dependent on the electronegativity (EN) of the substituents at the N and C atoms. However, as demonstrated by aniline derivatives [47,48], $^1J(^{15}\text{N}-^{13}\text{C})$ in the case of closely related structures is a good measure of the changes in the nitrogen atom pyramidity. Therefore, in the case of metallatranes, the rise in $^1J(^{15}\text{N}-^{13}\text{C})$ with increasing $l(\text{N},\text{M})$ in crystals reflects the appropriate decrease in the pyramidity of the nitrogen atom in solutions (see Table 1). It can be demonstrated for silatranes that the dependence of $^1J(^{15}\text{N}-^{13}\text{C})$ on $l(\text{N},\text{Si})$ in crystals is not linear and is affected by the nature of the solvent (see Fig. 1). The decrease of $^1J(^{15}\text{N}-^{13}\text{C})$ in metallatranes upon transition from less polar (CDCl_3) to more polar ($\text{DMSO}-d_6$) solvents (see Table 1) is indicative of increased

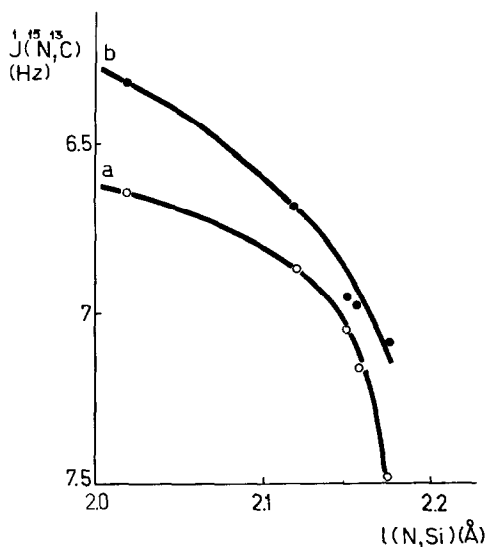


Fig. 1. Variation of the spin-spin coupling constant $^1J(^{15}\text{N}-^{13}\text{C})$ in CDCl_3 (a) and $\text{DMSO}-d_6$ (b) vs. the $\text{N} \rightarrow \text{Si}$ bond length in crystals.

nitrogen pyramidity and hence decreased $l(N,M)$, which is consistent with the results obtained during ^{15}N and ^{29}Si CS analysis [32].

The ^{15}N -M spin-spin coupling

One may assume that spin-spin interaction over the DA bond $\text{N} \rightarrow \text{M}$ must be directly influenced by the properties of this bond. It follows from Table 1 that $^1J(^{15}\text{N}-\text{M})$ reflecting the s -character of the $\text{N} \rightarrow \text{M}$ bond increases with decreasing $l(\text{N},\text{M})$ in crystals and with increasing solvent polarity, which in compliance with ^{15}N NMR spectroscopic data [29-32] indicates a gain in the $\text{N} \rightarrow \text{M}$ bond strength. However, the influence of solvent on ^{15}N - ^{29}Si coupling increases, while that on CS of ^{15}N and ^{29}Si decreases [32,49] with shortening of the $\text{N} \rightarrow \text{Si}$ bond in silatranes. This may possibly be explained by a corresponding decrease in the contribution of valent p - and d -orbitals of N and Si atoms to the $\text{N} \rightarrow \text{Si}$ bond formation with decreasing $l(\text{N},\text{Si})$. It may also be concluded that the dependence of ^{15}N and ^{29}Si CS as well as of ^{15}N - ^{29}Si coupling constants on $l(\text{N},\text{Si})$ cannot be linear. As can be seen

TABLE 1
SPIN-SPIN COUPLING CONSTANTS IN ^{15}N -ENRICHED METALLATRANES (IV)

Compound	M	R	$l(\text{N},\text{M})$ in crystals (Å)	Solvent	$^1J(^{15}\text{N}-\text{M})$ (Hz)±0.07	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)±0.07	$^1J(\text{M}-\text{X})$ (Hz)±0.1 (X = ^{13}C , ^1H)	$\nu(\text{SiH})$ (cm^{-1})
1	^{11}B	-	1.647 ^a	CDCl_3	(5.2) ^b	6.82	-	-
2	^{29}Si	Me	2.175 ^c	$\text{DMSO}-d_6$	(11.8) ^b	6.75	-	-
				CDCl_3	≤0.2	7.48	107.0	-
3	^{29}Si	Vi	2.15 ^d	$\text{DMSO}-d_6$	0.70	7.08	106.5	-
				CDCl_3	0.55	7.04	-	-
4	^{29}Si	Ph	2.156 ^e	$\text{DMSO}-d_6$	1.47	6.94	-	-
				CDCl_3	0.66	7.15	-	-
5	^{29}Si	MeO	-	$\text{DMSO}-d_6$	1.43	6.97	-	-
				CDCl_3	1.17	7.04	-	-
6	^{29}Si	H	-	$\text{DMSO}-d_6$	1.65	6.82	-	-
				CDCl_3	1.10	7.04	(280.1)	2135
				$(\text{CD}_3)_2\text{CO}$	1.17	6.97	(275.9)	2130
				CD_3CN	1.76	6.75	(270.7)	2119
7	^{29}Si	CH_2Cl	2.12 ^g	$\text{DMSO}-d_6$	2.05	6.75	(268.8)	2111
				CDCl_3	(2.97) ^f	-	-	2090
				$\text{DMSO}-d_6$	1.54	6.86	115.7	-
				CDCl_3	2.57	6.68	114.0	-
8	^{29}Si	Cl	2.02 ^h	$\text{DMSO}-d_6$	1.98	6.64	-	-
				CDCl_3	3.37	6.31	-	-
9	^{73}Ge	Et	2.26 ⁱ	$\text{DMSO}-d_6$	-	7.23	-	-
				CDCl_3	-	7.04	-	-
10	^{73}Ge	Me	-	$\text{DMSO}-d_6$	-	7.12	-	-
				CDCl_3	-	7.04	-	-
11	^{73}Ge	PhO	-	$\text{DMSO}-d_6$	-	6.82	-	-
12	^{73}Ge	Cl	-	$\text{DMSO}-d_6$	-	6.68	-	-
13	^{119}Sn	$t\text{-Bu}$ ^j	-	CDCl_3	69.9	-	-	-
14	^{119}Sn	Me(a) ^k	-	CDCl_3	75.6	-	1275	-
		(b,c) ^k	-	CDCl_3	110.0	-	1090	-

^a Ref. 23. ^b Half-height width of ^{15}N signal (Hz±0.2). ^c Ref. 6. ^d Ref. 11. ^e β -modification, ref. 3.

^f Obtained by extrapolation using eq. 3. ^g Ref. 9. ^h Ref. 10. ⁱ Ref. 14. ^j Ref. 34. ^k Ref. 33

from Fig. 2 the plots of $^1J(^{15}\text{N}-^{29}\text{Si})$ in CDCl_3 and $\text{DMSO}-d_6$ against $l(\text{N},\text{Si})$ in crystals actually are not linear and depend on the solvent nature. However, these curves, as in the case of $^1J(^{15}\text{N}-^{13}\text{C})$, fail to depict the actual relationship between $^{15}\text{N}-^{29}\text{Si}$ coupling and the $\text{N} \rightarrow \text{Si}$ bond length because the latter becomes weakened in solution [32,49]. Nevertheless, the curves mentioned above can be used to predict the length of the DA bond, $l(\text{N},\text{Si})$, in crystals when the coupling constant $^1J(^{15}\text{N}-^{29}\text{Si})$ is known. For instance, it has been estimated that the $\text{N} \rightarrow \text{Si}$ bond length in crystalline 1-methoxysilatrane approaches 2.15 Å, whereas in 1-hydrosilatrane it is 2.14 Å. The latter value agrees better with the value 2.146 Å reported in [50] for 3,7,10-trimethyl-1-hydrosilatrane than that calculated from ^{15}N CS (2.11 Å) [49].

We found a linear relationship between $^1J(^{15}\text{N}-^{29}\text{Si})$ and $^1J(^{15}\text{N}-^{13}\text{C})$:

$$^1J(^{15}\text{N}-^{13}\text{C}) = 7.30 - 0.28 \ ^1J(^{15}\text{N}-^{29}\text{Si}) \quad (2)$$

$$r = -0.96$$

The certain dispersion of points (see Fig. 3) may possibly be explained by the effect of the electronegativity of substituent R on $^1J(^{15}\text{N}-^{29}\text{Si})$. Bearing in mind that $^1J(^{15}\text{N}-^{29}\text{Si})$ reflects the variation in $l(\text{N},\text{Si})$ while $^1J(^{15}\text{N}-^{13}\text{C})$ reflects the variation in nitrogen atom pyramidity, one may suggest that eq. 2 is actually analogous to the relationships describing the dependence of nitrogen pyramidity on $\text{N} \rightarrow \text{Si}$ bond length deduced from X-ray analysis data [10,13].

It was found earlier [51] that the stretching frequency of the Si-H bond ($\nu(\text{SiH})$) in the IR spectra of 1-hydrosilatrane and its derivatives diminishes with increasing $\text{N} \rightarrow \text{Si}$ bond strength. We observed a linear relation (eq. 3) and by extrapolating this

$$\nu(\text{SiH}) = 2159 - 23.23 \ ^1J(^{15}\text{N}-^{29}\text{Si}) \quad r = -0.99 \quad (3)$$

equation to the $\nu(\text{Si-H})$ value in Nujol, we obtained $^1J(^{15}\text{N}-^{29}\text{Si}) = 2.97$ Hz for 1-hydrosilatrane in the solid state (see Fig. 4).

Large $^1J(^{15}\text{N}-^{119}\text{Sn})$ values have been reported for stannatranes [33,34] (see Table 1).

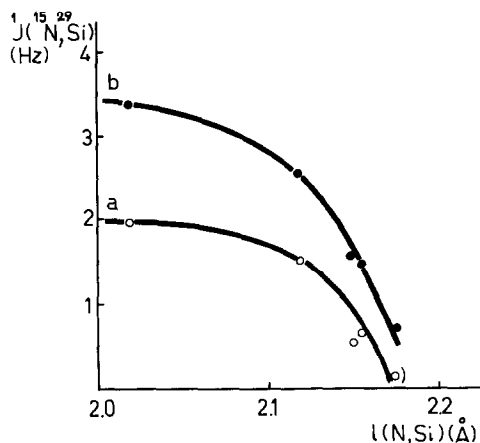


Fig. 2. Variation of the spin-spin coupling constant $^1J(^{15}\text{N}-^{29}\text{Si})$ in CDCl_3 (a) and $\text{DMSO}-d_6$ (b) vs. the $\text{N} \rightarrow \text{Si}$ bond length in crystals.

Measurement of the spin-spin coupling $^{15}\text{N}-\text{M}$ in other metallatranes is frequently prevented by the rapid quadrupole relaxation of nuclei whose spin is $I \geq 1$ (e.g., ^{11}B $I = 3/2$, ^{73}Ge $I = 9/2$). Nevertheless, in boratrane, owing to the high natural content of ^{11}B isotope (80%), the strengthening of the DA bond $\text{N} \rightarrow \text{B}$ can be judged by the increase in the ^{15}N signal half-width upon transition from CDCl_3 to $\text{DMSO}-d_6$ (see Table 1).

In germatranes direct observation of the $^{15}\text{N}-^{73}\text{Ge}$ coupling is not feasible because of the low content (10%) and high quadrupole moment of the only magnetic isotope ^{73}Ge .

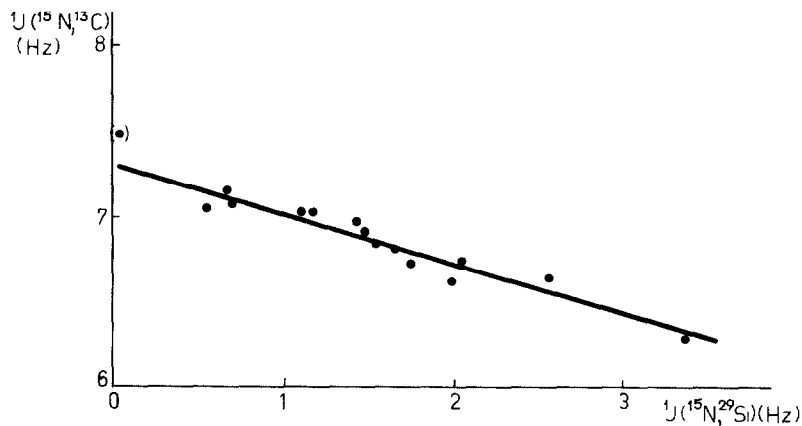


Fig. 3. Plot of $^1J(^{15}\text{N}-^{13}\text{C})$ vs. $^1J(^{15}\text{N}-^{29}\text{Si})$ for silatranes in solution

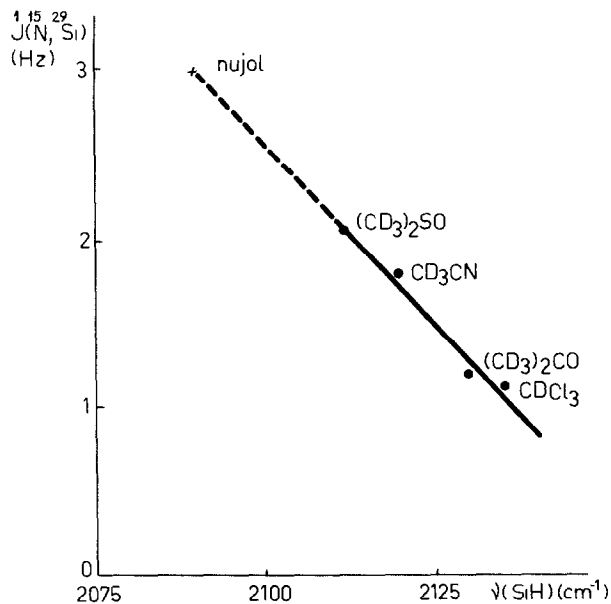


Fig. 4. Plot of $^1J(^{15}\text{N}-^{29}\text{Si})$ vs. $\nu(\text{SiH})$ for 1-hydrosilatranes

The M–X spin–spin coupling

The M–X spin–spin coupling reflects the variation in the hybridization of the M atom in metallatranes. Decreased $^1J(\text{M}–^1\text{H})$ values in the 1-hydrosilatrane [41] and 1-hydrophosphatrane [21] relative to reference compounds of the $\text{HM}(\text{OR})_3$ type are interpreted in terms of the Fermi contact (FC) interaction by the diminished *s*-character of the axial M–H bond upon extension of the coordination of atom M. In 1-hydrosilatrane, $^1J(^{29}\text{Si}–^1\text{H})$ decreases with increasing polarity of the solvent [32] (see also Table 1). This is accounted for by the Si atom configuration approaching a TBP with increasing solvent polarity. Consequently, the relationship 4 which we

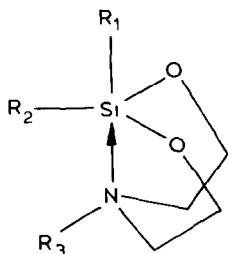
$$^1J(^{29}\text{Si}–^1\text{H}) = 290.0 - 10.63 \ ^1J(^{15}\text{N}–^{29}\text{Si}), \quad r = 0.96 \quad (4)$$

found is analogous in its meaning to another one which relates the bond structure of the silicon atom and $I(\text{N},\text{Si})$ in crystals [10,13].

The $^1J(^{29}\text{Si}–^{13}\text{C})$ in 1-methylsilatrane is greater than that in $\text{MeSi}(\text{OEt})_3$ [41]. However, our data (see Table 1) reveal that the $^1J(^{29}\text{Si}–^{13}\text{C})$ for compounds **2** and **7** decreases with increasing N → Si bond strength upon transition to more polar solvents (see Table 1). Similarly, in 1-methylstannatrane $^1J(^{119}\text{Sn}–^{13}\text{C})$ decreases at higher $^1J(^{15}\text{N}–^{119}\text{Sn})$. Hence, both $^1J(\text{M}–^{13}\text{C})$ and $^1J(\text{M}–^1\text{H})$ variations are conceivable in terms of the FC interaction suggesting that the *s*-character of the M–X bond decreases with increasing M atom coordination as its structure approaches that of type III. The smaller value of $^1J(^{29}\text{Si}–^{13}\text{C})$ in $\text{MeSi}(\text{OEt})_3$ as compared to that of **2** is apparently attributable to the differences in the structures of the compounds being compared and to the contribution of non-contact terms to $^1J(^{29}\text{Si}–^{13}\text{C})$.

The $^{15}\text{N}–\text{Si}–^1\text{H}$ spin–spin interaction

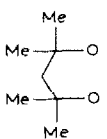
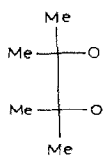
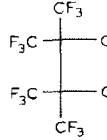
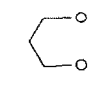
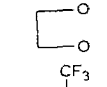
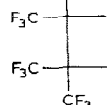
We have found that axial–axial coupling $^2J(^{15}\text{N}–\text{Si}–^1\text{H})$ in 1-hydrosilatrane is equal to zero, whereas similar axial–equatorial coupling in the bicyclic analogue **V** reaches the value ~ 8 Hz (see compound **19** in Table 2). It is known, too, that for $\text{N}(\text{SiH}_3)_3$, which contains a tetrahedral Si atom, $^2J(^{15}\text{N}–\text{Si}–^1\text{H}) = 4$ Hz [52]. This indicates that the $^2J(^{15}\text{N}–\text{Si}–^1\text{H})$ coupling is strongly influenced by the valence angle in the N–Si–H fragment. By increasing the latter from ~ 90 to 109.5° and 180° in the compounds under study, $^2J(^{15}\text{N}–\text{Si}–^1\text{H})$ decreases from ~ 8 Hz to 4 and 0 Hz, respectively. A similar situation has also been reported for compounds with a five-coordinated phosphorus atom [53].



(V)

TABLE 2

SPIN-SPIN COUPLING CONSTANTS $^1J(^{15}\text{N}-^{29}\text{Si})$ AND FREE ENERGY OF DISSOCIATION OF DONOR-ACCEPTOR BOND $\text{N} \rightarrow \text{Si}$ IN SILOCANES (V)

Compound	R ¹	R ²	R ³	<i>l</i> (N,Si) in crystals (Å)	Solvent	$^1J(^{15}\text{N}-^{29}\text{Si})$ at 303 K (Hz) ± 0.07	ΔG_c^* (kJ/mol) ± 1	<i>T</i> _c (K) ± 1
15	Me ₂ CHO	Me ₂ CHO	Me	—	(CD ₃) ₂ CO	—	40.2	206 ^u
16			Me ₂	2.247 ^b	CDCl ₃	≤ 0.2 ^f	51.0	234 ^d
17			Me	—	CCl ₄ + C ₆ D ₆ CDCl ₃ DMSO- <i>d</i> ₆	1.85 ^e 2.71 ^e 3.18 ^e	61.5 65.7 66.9	286 ^u 291 ^d 314 ^d
18			Me	2.032 ^e	DMSO- <i>d</i> ₆	8.36	~ 94	443 ^f
19	Ph	H	Me	—	(CD ₃) ₂ CO DMSO- <i>d</i> ₆	+ 3.5 ^g 4.3 ^f	(~ 50) —	(258) ^h —
20	Ph ⇌ Me		Me	—	(CD ₃) ₂ CO	1.20	—	—
	Ph Me		Me	—	(CD ₃) ₂ CO	3.96 ^k	40.6	220 ^h
	Me Ph		Me	—	(CD ₃) ₂ CO	1.47 ^k	41.4	220 ^h
21	Ph	Ph	Me	2.68 ^l	(CD ₃) ₂ CO	≤ 0.2	42.3	223 ^h
22			H	—	CDCl ₃ DMSO- <i>d</i> ₆	— 5.31	51.5 —	263 ^m —
23			H	2.004 ⁿ	DMSO- <i>d</i> ₆	6.63	72.8	348 ^m
24			H	—	DMSO- <i>d</i> ₆	10.61	~ 100	443 ^f

^u CH₃-¹³C. ^b Ref. 70. ^c At *T*_c. ^d CH₃-¹H. ^e Ref. 71. ^f NCH₂-¹H. ^g $^2J(^{15}\text{N},\text{Si},^1\text{H})$ 7.12 Hz. ^h Ref. 63. ⁱ Some broadening of NCH₃ ¹H signals at 258 K. ^j $^2J(^{15}\text{N},\text{Si},^1\text{H})$ 8.35 Hz. ^k At 193 K. ^l Ref. 72. ^m OC-¹³C. ⁿ Ref. 73.

Discussion

It has been reported earlier [54–57] that spin–spin coupling through the DA bond is dominated by the Fermi-contact term. This is supported by the correlation (eq. 3) described here which relates $^1J(^{29}\text{Si}-^1\text{H})$ and $^1J(^{15}\text{N}-^{29}\text{Si})$. The dependence of spin–spin coupling constants on DA bond length is mainly due to the decrease of

valent *s*-orbital overlap upon DA bond elongation [54,55]. The contribution of Fermi contact interaction may be represented as:

$${}^1J^{\text{FC}}({}^{15}\text{N}-\text{M}) = \frac{64\pi^2}{9} \beta^2 \gamma_{\text{N}} \gamma_{\text{M}} (\Delta E)^{-1} S_{\text{N}}^2(0) S_{\text{M}}^2(0) P_{s_{\text{N}^s\text{M}}}^2 \quad (5)$$

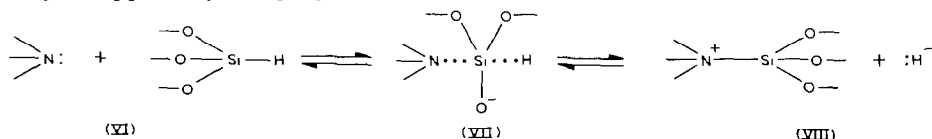
where γ_{I} is the gyromagnetic ratio for nucleus I, β is the Bohr magneton, ΔE is the mean energy of excitation, $S_{\text{I}}^2(0)$ is the valence *s*-electron density on nucleus I, and $P_{s_{\text{N}^s\text{M}}}$ is the *s*-order of the N–M bond.

If we assume that $(\Delta E)^{-1} S_{\text{N}}^2(0) S_{\text{M}}^2(0) \sim \text{const}$, eq. 5 can be reduced to eq. 6, which is widely used for interpretation of spin–spin coupling constants:

$${}^1J({}^{15}\text{N}-\text{M}) = \text{const} \cdot P_{s_{\text{N}^s\text{M}}}^2 \quad (6)$$

Quantum chemical calculations [58,59] have shown that with increasing *s*-character of the bond, its strength is increased. This signifies that ${}^1J({}^{15}\text{N}-\text{M})$ may be used to obtain information on the length and energy of the DA bond N → M in solution.

In the case of silatranes, prediction by way of the $S_{\text{N}}-2$ substitution reaction [60] may be applied by using eq. 4.



$$\begin{array}{ll} {}^1J({}^{15}\text{N}-{}^{29}\text{Si}) & 00 \text{ Hz} \\ {}^1J({}^{29}\text{Si}-{}^1\text{H}) & 290.0 \text{ Hz} \end{array}$$

$$\begin{array}{ll} {}^1J({}^{29}\text{Si}-{}^1\text{H}) & 0.0 \text{ Hz} \\ {}^1J({}^{15}\text{N}-{}^{29}\text{Si}) & 25.1 \text{ Hz} \end{array}$$

The validity of such an approach is illustrated by the fact that the value ${}^1J({}^{29}\text{Si}-{}^1\text{H})$ 290.0 Hz derived from eq. 4 for the initial state VI is in good agreement with the data for triethoxy- and trimethoxyhydrosilanes (288.8–291.6 Hz) [61]. However, the value ${}^1J({}^{15}\text{N}-{}^{29}\text{Si})$ 25.1 Hz obtained from eq. 4 for the final state VIII is considerably smaller than that observed for tetravalent silicon in triethoxysilylamines (~ 44 Hz) [62] (cf. compounds **27** and **28** in Table 3). This is, however, readily explained by the higher order of the N–Si bond in silylamines as a result of *dp*- π interaction and quaternization of the nitrogen atom in VIII. Besides, by introducing ${}^1J({}^{15}\text{N}-{}^{29}\text{Si})$ 25.1 Hz into eq. 6, we can show that a change of N atom hybridization from sp^2 in VI to sp^3 in VIII leads to a decrease in ${}^1J({}^{15}\text{N}-{}^{13}\text{C})$ by 7.03 Hz, which agrees well with the value (7.6 Hz) acquired in ref. 47 for aniline derivatives.

Alteration of the nature of the DA bond N → M can be demonstrated by means of bond order P_{NM} . By postulating sp^3 -hybridization for N and Si atoms in VIII ($P_{s_{\text{N}^s\text{Si}}}^2 = 0.25 \times 0.25 = 0.0625$), we can calculate the *s*-order of the N → Si bond in silatranes and their analogues using eq. 6. The more convenient total bond order P_{NSi} can be estimated from eq. 7, which was derived from eq. 6 assuming that $P_{\text{NSi}} = 1$ for VIII:

$$P_{\text{NSi}} = \sqrt{\frac{{}^1J({}^{15}\text{N}-{}^{29}\text{Si})}{25.1}} \quad (7)$$

The values of P_{NSi} obtained (see Table 3) clearly indicate changes in the extent of N → Si interaction in the series of compounds under study and an increase in N–Si

TABLE 3

THE LENGTH, FREE ENERGY OF DISSOCIATION AND ORDER OF DONOR ACCEPTOR BOND $N \rightarrow Si$ CALCULATED FOR SILATRANES (IV), SILOCANES (V), SILATRANONES (IX) AND SILYLAMINES (X) (COVALENT $N-Si$ BOND) IN SOLUTION

Compound No.	SiR	NR	Solvent	$l(N,Si)$ (Å)		ΔG^{*d}	ΔH^{*d}	P_{NSi}	
				eq. 8	Ref. 49	eq. 9	Ref. 64		
IV	2	Me	-	CDCl ₃	≥ 2.253	2.25	≤ 51.9	43.1	≤ 0.10
				DMSO- <i>d</i> ₆	2.221	2.20	55.2	-	0.19
	3	Vi	-	CDCl ₃	2.229	-	54.4	49.4	0.17
				DMSO- <i>d</i> ₆	2.189	-	59.0	-	0.27
	4	Ph	-	CDCl ₃	2.223	2.20	55.2	49.4	0.18
				DMSO- <i>d</i> ₆	2.190	2.16	59.0	-	0.27
	5	MeO	-	CDCl ₃	2.200	2.13	57.7	-	0.24
				DMSO- <i>d</i> ₆	2.183	2.11	60.2	-	0.29
	6	H	-	CDCl ₃	2.203	2.16	57.3	-	0.23
				(CD ₃) ₂ CO	2.200	-	57.7	-	0.24
				CD ₃ CN	2.180	-	60.7	-	0.30
				DMSO- <i>d</i> ₆	2.171	2.14	61.9	-	0.32
7	CH ₂ Cl	-	cryst. ^a	2.146	2.11	66.9	-	0.38	
			CDCl ₃	2.187	2.16	59.4	64.0	0.28	
8	Cl	-	DMSO- <i>d</i> ₆	2.156	2.13	64.9	-	0.36	
			CDCl ₃	2.173	2.06	61.9	-	0.31	
			DMSO- <i>d</i> ₆	2.139	2.05	68.6	-	0.41	
V	16	Me	Me	CCl ₄ + C ₆ D ₆	≥ 2.253	-	-	-	≤ 0.10
				CDCl ₃					
17	Me	Me	CCl ₄ + C ₆ D ₆	2.177	-	-	-	0.35	
			CDCl ₃	2.153	-	-	-	0.37	
			DMSO- <i>d</i> ₆	2.141	-	-	-	0.40	
18	Me	Me	DMSO- <i>d</i> ₆	2.048	-	-	-	0.65	
22	H	H	DMSO- <i>d</i> ₆	2.097	-	-	-	0.51	
23	H	H	DMSO- <i>d</i> ₆	2.075	-	-	-	0.57	
24	H	H	DMSO- <i>d</i> ₆	2.017	-	-	-	0.73	

TABLE 3 (continued)

Compound No.	SiR	NR	Solvent	$l(\text{N,Si})$ (Å)		ΔG_c^* ^d eq. 9	ΔH_c^* ^d Ref. 64	P_{NSi} eq. 7
				eq. 8	Ref. 49			
IX 25			DMSO- <i>d</i> ₆	2.050	–	93.3	–	0.64
26			DMSO- <i>d</i> ₆	2.014	–	106.7	–	0.74
X 27	(EtO) ₃ SiNHPh		CDCl ₃	1.734 ^b	–	–	–	1.32 ^b
28	(EtO) ₃ SiNH <i>Bu-t</i>		CDCl ₃	1.730 ^c	–	–	–	1.33 ^c

^a In Nujol. ^b $^1J(^{15}\text{N}-^{29}\text{Si})$ 43.9 Hz, ref. 62. ^c $^1J(^{15}\text{N}-^{29}\text{Si})$ 44.6 Hz, ref. 62. ^d In kJ/mol.

bond order in model silylamines (**27** and **28**) owing to $dp-\pi$ interaction. It must be stressed that $^1J(^{15}\text{N}-^{29}\text{Si})$ and the P_{NSi} values calculated so far reflect only changes in valent s -orbital overlap.

If we assume a linear relationship between the bond order and length, $^1J(^{15}\text{N}-\text{M})$ and $l(\text{N},\text{M})$ may be linked by eq. 8:

$$l(\text{N},\text{M}) = A\sqrt{^1J(^{15}\text{N}-\text{M})} + B \quad (8)$$

In the case of silatranes, coefficients A and B can be calculated using the data obtained for 1-hydrosilatranes in Nujol, $^1J(^{15}\text{N}-^{29}\text{Si})$ 2.97 Hz, $l(\text{N},\text{Si})$ 2.14 Å, and for the final state VIII, $^1J(^{15}\text{N}-^{29}\text{Si})$ 25.1 Hz, $l(\text{N},\text{Si})$ 1.87 Å (the sum of the covalent radii). A and B are found to be equal to -0.084 and 2.291 , respectively. The values of $l(\text{N},\text{Si})$ calculated for the silatranes in solution (see Table 3) are in fairly good agreement with those found by Pestunovich et al. [49] using the relationship between ^{15}N CS in the solid state and $l(\text{N},\text{Si})$ in crystals. It should be pointed out that as $^1J(^{15}\text{N}-^{29}\text{Si})$ essentially depends on the EN of substituents at N and Si [62], eq. 8 can be applied only to compounds where the EN of the substituents differs insignificantly from that in 1-hydrosilatranes.

Another intriguing issue is that concerning the energy of the DA bond $\text{N} \rightarrow \text{M}$ in metallatranes. To estimate the relation between $^1J(^{15}\text{N}-^{29}\text{Si})$ and $\text{N} \rightarrow \text{Si}$ bond energy, silocanes (V), (bicyclic analogues of silatranes) may be useful since direct measurement of the dissociation energy of the $\text{N} \rightarrow \text{Si}$ bond is possible [63]. In doing so, we chose the spirocyclic derivatives (V) **16–18**, in which the EN of the substituents practically undergoes no variation. The data obtained are summarized in Table 2. An increase in ΔG_c^* with diminishing cycle size at the Si atom effectively demonstrates the increase of acceptor properties of the latter in the case of small cycles [64]. For compounds **16–18** we established a linear relationship (eq. 9) which was used to determine the free energy of dissociation for the DA bond $\text{N} \rightarrow \text{Si}$ in silatranes (see Table 3).

$$\Delta G_c^* = 51.4 + 51.11 \ ^1J(^{15}\text{N}-^{29}\text{Si}), \quad r = 0.999 \quad (9)$$

Equation 9 apparently yields correct values only for compounds where the EN of the substituents at the N and Si atoms only departs insignificantly from the model

compounds **16–18** (as, for example, in the case of **5**). Our findings are consistent with the ΔH^\ddagger values estimated from the analysis of dipole moments [65]. Such a comparison is legitimate, since in compounds of type V $\Delta G^\ddagger \approx \Delta H^\ddagger$ [66], i.e. the influence of the entropy factor is negligible.

It can be written that ΔH^\ddagger [65] is linearly related to $^1J(^{15}\text{N}-^{29}\text{Si})$:

$$\Delta H^\ddagger = 40.0 + 15.50 \ ^1J(^{15}\text{N}-^{29}\text{Si}), \quad r = 0.997 \quad (10)$$

The coefficients in eq. 10 are somewhat different from those found in eq. 9. This is apparently due to differences between the ΔH^\ddagger and ΔG^\ddagger parameters, the effects of substituent EN on eq. 9, and to the different methods of ΔH^\ddagger and ΔG^\ddagger determination used. Nevertheless, over the range of N \rightarrow Si bond energies examined, eqs. 9 and 10 show a fairly good consistency of results.

If we assume that N \rightarrow Si bonds of equal energy have comparable lengths, it would be possible, using Table 2, to follow the pattern of $^1J(^{15}\text{N}-^{29}\text{Si})$ variation in response to changes in the EN of substituents at N and Si. In general (i.e. in the case of a covalent bond), coupling constants increase with increasing EN of the substituents [40]. This is also true for $^1J(^{15}\text{N}-^{29}\text{Si})$ [62]. Therefore, at first glance, the converse situation observed in some cases of spin–spin coupling through DA bond N \rightarrow Si seems all the more paradoxical (cf. compounds **16,19,20** and **21** in Table 2). To explain the anomalous values for compounds **19** and **20** it may be assumed that at $l(\text{N,Si}) \geq 2.3 \text{ \AA}$, $^1J(^{15}\text{N}-^{29}\text{Si})$ sign reversal occurs. However, a drop in the absolute values of $^1J(^{15}\text{N}-^{29}\text{Si})$ should be expected with decreasing $l(\text{N,Si})$ distance as a result of temperature decrease or upon transition to more polar solvents. Actually, the reverse situation is observed (see Table 2). Besides, applying the selective polarization transfer (SPT) technique [67], we found that in compound **19**

$$^1J(^{15}\text{N}-^{29}\text{Si}) > 0 \quad ({}^1K(^{15}\text{N}-^{29}\text{Si}) > 0).$$

The discrepancy between the coupling constants and DA bond length has been explained previously [57] by the increase in $S_{\text{M}}^2(0)$ and the decrease in the ΔE term in eq. 9 with increasing steric hindrance.

An alternative explanation is possible if one assumes that the effect of substituents' EN on the ΔE term is opposite in the case of DA and covalent bonds.

Consequently, eqs. 7–9 can be applied only in special cases, e.g. for compounds where the EN of substituents at N and Si differs insignificantly from that in the model compounds.

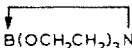
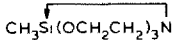
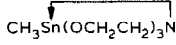
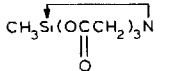
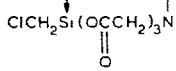
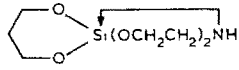
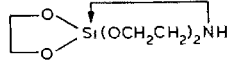
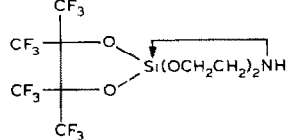
The N \rightarrow M bond strength in various metallatranes can be comparatively described if we consider a coupling constant through the DA and covalent bonds in iso-structural compounds. The results summarized in Table 4 demonstrate that the strength of the DA bond N \rightarrow M increases in the sequence: Si < B < Sn. This is evidently due to the increase of ionic character (decrease in *s*-character) of M–O bonds in the same sequence and upon transition from silatranes to silatrane-3,7,10-triones [75] as well.

According to Bent's rule [69], this leads to enhanced *s*-character of the DA bond N \rightarrow M, which is accompanied by a gain in its strength. For an alternative explanation see ref. 68.

It is generally believed that with increasing strength of the DA bond N \rightarrow M the ^{15}N signal is shifted to lower fields [29–34]. However, from Table 4 it follows that

TABLE 4

COMPARISON OF SPIN-SPIN COUPLING CONSTANTS $^1J(^{15}\text{N}-\text{M})$ THROUGH COVALENT AND DONOR-ACCEPTOR BONDS IN ISO-STRUCTURAL COMPOUNDS OF B, Si, AND Sn

No.	Compound	Solvent	$^1J(^{15}\text{N}-\text{M})$ (Hz)	$\delta(^{15}\text{N})$ (ppm)	Ref.
1		CDCl_3 $\text{DMSO}-d_6$	(5.2) ^a (11.8) ^a	-319.9 -320.9	This work This work
29	$\text{B}[\text{N}(\text{C}_2\text{H}_5)_2]_3$	neat	(30) ^a	-	45
2		CDCl_3 $\text{DMSO}-d_6$	≤ 0.2 0.7	-360.0 -356.3	This work This work
28	$\text{CH}_3\text{Si}(\text{NHPh})_3$	CDCl_3	25.4	-313.1	62
14		(a) CDCl_3 (b,c) CDCl_3	75.6 110.0	-353.5 -360.1	33 33
30	$\text{CH}_3\text{Sn}[\text{N}(\text{CH}_3)\text{Ph}]_3$	C_6D_6	+175.0	+17.4	74
25		$\text{DMSO}-d_6$	8.2	-319.9	75
26		$\text{DMSO}-d_6$	10.9	-320.6	75
22		$\text{DMSO}-d_6$	5.31	-347.0	This work
23		$\text{DMSO}-d_6$	6.63	-348.2	This work
24		$\text{DMSO}-d_6$	10.61	-347.2	This work

^a Half-height width of ^{15}N signal (Hz).

^{15}N CS does not allow the relative strength of the $\text{N} \rightarrow \text{M}$ bond for various M to be compared. Moreover, the data for compounds 22–24 suggest that even for identical M, caution must be exercised when analysing ^{15}N CS. This is apparently due to unequal contributions of the mean energy of excitation to the paramagnetic component of the nitrogen atom screening at different M.

Experimental

The ^1H , ^{11}B , ^{13}C , ^{15}N and ^{29}Si NMR spectra were recorded with Bruker WH-90 and WM-360 spectrometers, using 5 mm sample-tubes. The solvents (CDCl_3 , CCl_4 , acetone- d_6 , CD_3CN and $\text{DMSO}-d_6$) were dried over molecular sieves (4 Å). The INEPT method was used to record ^{13}C , ^{15}N and ^{29}Si spectra [67]. The ^{15}N – ^{11}B spin–spin coupling was studied by means of ^{15}N spectra, since the signal width in

^{11}B NMR spectra was ca. 35 Hz for compounds **1** and no splitting was observed. The ^{15}N - ^{29}Si coupling constants for compounds **22**-**24** were measured from ^{29}Si satellites in ^{15}N spectra for samples with a natural abundance of ^{15}N . The experimental details have been described elsewhere [62]. The sign of $^1J(^{15}\text{N}-^{29}\text{Si})$ for compound **19** was determined by means of the SPT experiment [67] assuming that $^1J(^{29}\text{Si}-^1\text{H}) < 0$ and $^2J(^{15}\text{N}-\text{Si}-^1\text{H}) < 0$ [45]. The free energies of activation, ΔG_c^\ddagger , at coalescence temperature were calculated as described in [76].

^{15}N -Triethanolamine employed in the synthesis of labelled metallatranes was prepared from commercial $^{15}\text{NH}_4\text{OH}$ as described in [30].

^{15}N -Boratrane was obtained according to [77] by treating ^{15}N -triethanolamine with boric acid. The synthesis of ^{15}N -silatranes (**2**-**5,7**) has been described earlier [30]. ^{15}N -1-Hydrosilatane (**6**) was prepared by re-etherification of ^{15}N -boratrane with triethoxysilane following the technique of [78]. To obtain ^{15}N -1-chlorosilatane we applied our procedure for the synthesis of atrane systems [38,75,79] using triethanolamine trimethylsilyl ester. The latter technique [38] was also used to synthesize all labelled ^{15}N -germatranes (**9**-**12**).

The synthesis of ^{15}N -methyl-diethanolamine and its organosilicon esters (**19**-**21**) has been described elsewhere [80,81]. Spirocyclic esters (**16**-**18**) were obtained by treating ^{15}N -methyl-diethanolamine with tetramethoxysilane and the corresponding diol.

Two examples of unpublished syntheses are given below.

*^{15}N -1-Chlorosilatane (**8**)*

A solution containing SiCl_4 (0.17 g, 0.001 *M*) and ^{15}N - $[\text{CH}_2\text{CH}_2\text{OSi}(\text{CH}_3)_3]_3$ (0.37 g, 0.001 *M*) in 10 ml chloroform was heated for 3 h under reflux. Following distillation of the $(\text{CH}_3)_3\text{SiCl}$ formed and of the solvent, compound **8** was obtained (0.17 g; yield 81%) as a white solid, which decomposed at $> 200^\circ\text{C}$ without melting.

*^{15}N -2,2,3,3,9-Pentamethyl-1,4,6,12-tetraoxa-9-aza-5-silaspiro[4,7]-dodecane (**17**)*

A mixture of ^{15}N -methyl-diethanolamine (0.60 g, 0.005 *M*), pinacol (0.59 g, 0.005 *M*) and tetramethoxysilane (0.76 g, 0.005 *M*), with a catalytic amount of sodium methoxide added, was heated in a distillation flask under reflux until complete methanol distillation had been attained. The residue in the flask was extracted twice with hot heptane to afford crystals of compound **17** (0.6 g; yield 46%; m.p. 154°C) upon cooling.

Some other labelled (**16,18**) and unlabelled (**22**-**24**) compounds were obtained in a similar way.

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