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^{29}Si–^{15}N Spin–spin coupling constants; a novel probe for structural studies of nitrogen-containing organosilicon compounds *

Ē. Kupče and E. Lukevics *
Institute of Organic Synthesis, Latvian S.S.R., Academy of Sciences, 226006, Riga (U.S.S.R.)

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Abstract

Results of recent investigations concerning the relation between scalar one-bond ^{29}Si–^{15}N spin–spin coupling constants (^1J(SiN)) and the structure of nitrogen-containing organosilicon compounds are summarized. The ^1J(SiN) show marked sensitivity to hybridization of the N and Si atoms, the length of the N–Si bond, its polarity, and the extent of d_π–p_π bonding. A quantitative relationship between ^1J(SiN) and the *s*-character of the N–Si bond reveals atypical cases of pyramidal nitrogen atoms in aminosilanes and allows the characterization of the reactivity of compounds having a N–Si bond. ^{29}Si–^{15}N couplings via the coordinate N → Si bond provide quantitative data as to the length, free energy of dissociation and the order of this bond in solution.

Introduction

Scalar one-bond nuclear spin–spin coupling constants (^1J) are a valuable source of information on the nature of chemical bonding and the structure of molecules in the solution [1]. The sign and magnitude of ^1J(^{29}Si–^{15}N) coupling constant were first reported for ^{15}N-enriched $(H_3Si)_3N$ in 1973 by Rankin and colaborators [2]. Only three more values of ^1J(SiN) were reported during the next decade [3–5] which presented theoretical rather than practical interest. This can presumably be explained by the need for isotope-enriched compounds because of the low natural content of either the ^{15}N (0.36%) or ^{29}Si (4.7%) isotopes. Nevertheless, the closest

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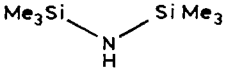
* Based on a report at the Eight International Symposium on Organosilicon Chemistry, St. Louis, USA, 1987.

analogues of the ^1J(SiN), the $^{15}N-^{13}C$ couplings, have been widely used in structural studies [6] despite the fact that the natural abundance of the ^{13}C isotope (1.1%) is four times lower.

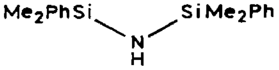
The situation improved dramatically after the development of polarization transfer techniques [7], which permitted measurement of the ^1J(Si–N) at natural abundance levels of the isotopes [8–10]. Since 1983, systematic investigation of these coupling constants in relation to the structure of organosilicon compounds has been carried out in our laboratory. Here we survey recent advances in this field, with only representative ^1J(SiN) values are given for each type of compound. A more complete compilation of published ^1J(SiN) values, together with ^{15}N couplings to nuclei of the group 14 metals is in preparation.

Silazanes

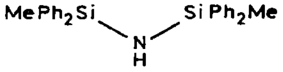
The ^1J(SiN) values in silazanes rise monotonously with increasing electronegativity (*EN*) of substituents at the silicon atom [11,12]:



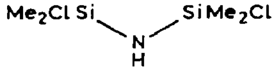
13.5 Hz



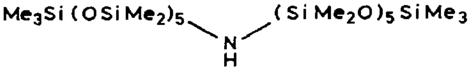
13.8 Hz



14.2 Hz

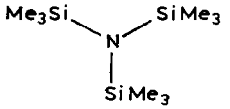


14.4 Hz

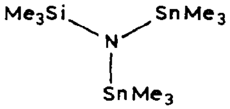


17.4 Hz

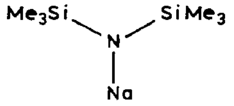
Since the reduced couplings [13*] are positive (^1K(SiN) > 0) [9] this increase in ^1J(SiN) reflects the growing *s*-character of the N–Si bond. Irregular changes in ^1J(SiN) are observed upon variation of the EN substituent at the nitrogen atom:



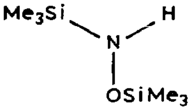
7.6 Hz [14]



6.8 Hz [14]



7.8 Hz [12]



6.5 Hz [15]

This is due to the existence of a lone pair of electrons (lp) at the nitrogen atom. Consequently, approximation of the mean excitation energy (ΔE) frequently applied to obtain quantitative relationships between ^1J and hybridization is invalid if the *N*-substituent *EN* is subject to variation.

The effect of ring size on ^1J(SiN) in systems with constant *EN* of substituents at the Si and N atoms reveals that there is a relation between ^1J(SiN) and geometric parameters such as valence angles and N–Si bond length. The data obtained [11,12] suggest that an increase in ring size and transition to acyclic derivatives results in greater ^1J(SiN) values:

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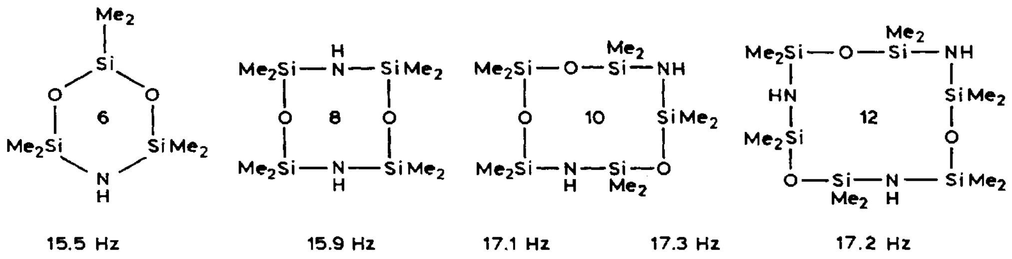
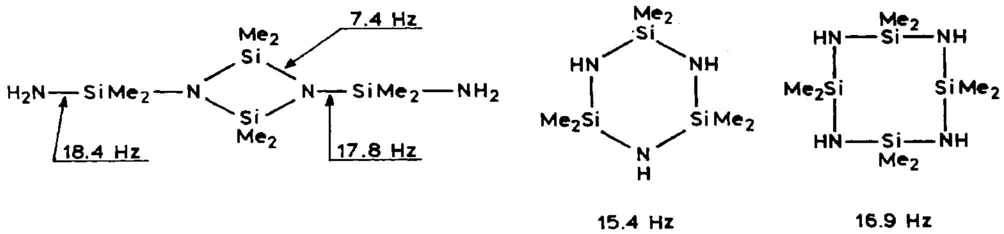
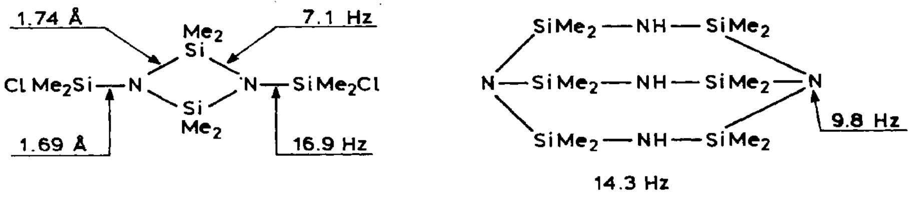
* Reference number with asterisk indicates a note in the list of references.



This increase in ${}^1J$(SiN) reflects a decrease in Si–N bond polarity (rise in the extent of d_π–p_π bonding) with diminishing ring strain. More dramatic changes were observed for cyclodisilazanes:





However, such a comparison is not completely valid because of the slight variation in the *EN* of substituents at the nitrogen atoms. Proper comparison, however, is possible for the ${}^1J$(SiN) values for the intracyclic and exocyclic N–Si bonds in 1,3-bis(dimethylaminosilyl)-2,2,4,4-tetramethylcyclodisilazane (7.4 and 17.8 Hz, respectively). Substantial discrepancy between these couplings indicates that the respective bonds differ in their electronic structure. As judged from the ${}^1J$(SiN) values the intracyclic nitrogen *s*-electrons are generally involved in bonding with the exocyclic silicon atoms, while the intracyclic N–Si bonds are formed mainly because of the participation of the N atom 2*p*-orbitals. The extent of redistribution of the valence *s*-electrons in the N–Si bonds may also be inferred from comparison of ${}^1J$(SiN) values in the cyclodisilazane mentioned above and 2,2,4,4,6,6,8,8,9,9,11,11-dodecamethylbicyclo[3.3.0]hexasilazane (9.8 Hz). This variation in the electronic structure of N–Si bonds has associated with it variations in the lengths of these bonds (as demonstrated by X-ray data in the case of 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane [16]) and in their reactions (the intracyclic N–Si bonds are less stable).

Aminosilanes

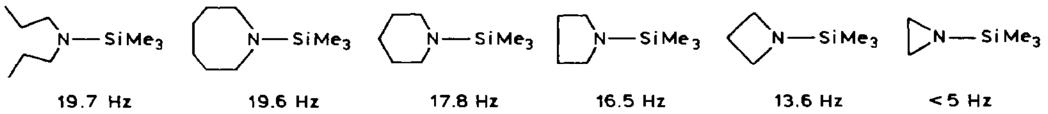
The ^{1}J(SiN) values presently available for aminosilanes cover the range 13.6 to 47.6 Hz and their tend to increase with increasing *EN* of substituents at the silicon atom [9,17]. However, there is a slight deviation from linearity in the relation between ^{1}J(SiN) and the sum of *EN* of the Si-substituents (see Fig. 1). It has been assumed that the ^{29}Si–^{15}N couplings are positive (^{1}K(SiN) > 0) and that their values are dominated by Fermi-contact interaction [9]. The latter has been recently confirmed by ab initio calculations of ^{1}J(SiN) [18] thus providing a firm theoretical base for the relationship between ^{1}J(SiN) and *s*-character of the N–Si bond [17]:

$$25\ {}^{1}J({}^{29}\mathrm{Si}-{}^{15}\mathrm{N}) = S_{\mathrm{Si}}(\%)S_{\mathrm{N}}(\%) \qquad (1)$$

where S_x is the *s*-character of the hybrid used by X in the N–Si bond.

The nitrogen atom usually adopts a planar configuration in compounds with covalent N–Si bonds. Similar ^{1}J(^{15}N–^{1}H) values, observed for NHPh-derivatives and their NHAlk-analogous (76–79 and 73–75 Hz, respectively [9,17]), confirm this observation. However, in several cases the ^{1}J(SiN) values provide evidence in favour of an unusual pyramidal structure of the nitrogen atom in aminosilanes.

^{1}J(SiN) decreases significantly with diminishing ring size in the Me$_3$Si derivatives of cyclic amines [10,17]:



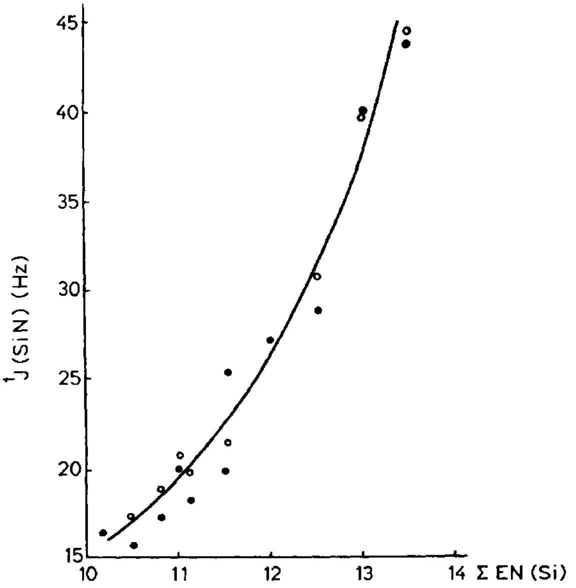
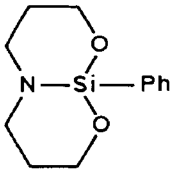


Fig. 1. Relationship between scalar one-bond ^{29}Si–^{15}N spin–spin coupling constants (^{1}J(SiN)) and the sum of electronegativities of Si substituents in aminosilanes; ○, NHBu^{t} derivatives, ●, NHPh derivatives.

According to eq. 1, this indicates an increase in nitrogen pyramidality demonstrating that $^1J(\mathrm{SiN})$ is sensitive to nitrogen hybridization.

$^1J(\mathrm{SiN})$ has been used to prove the existence of a N–Si bond in 1-phenyl-2,10-dioxa-6-aza-1-silabicyclo[4.4.0^{1,6}]decane [19].



$\mathrm{Bu^tHNSi(OEt)_2Me}$

27.7 Hz 29.0 Hz

A low value of $^1J(\mathrm{SiN})$, as compared to that observed in the acyclic analogue, suggests increased pyramidality of the nitrogen atom in the bicyclic derivative, probably due to existence of steric constraints.

The $^1J(\mathrm{SiN})$ values for the NPh-derivatives are slightly smaller than in their NAlk-analogues ($\mathrm{Me_3SiNHBu^t}$, 17.2 Hz; $\mathrm{Me_3SiNHPh}$, 15.7 Hz) indicating that $^1J(\mathrm{SiN})$ is dependent on the degree of d_π–p_π interaction between the nitrogen lp and the vacant *d*-orbitals of the silicon atom. For NPh-compounds there is competitive conjugation of the nitrogen lp with the phenyl ring, which weakens the d_π–p_π bonding, leading to elongation of the N–Si bond and a decrease in the N–Si *s*-overlap integral ($\beta(\mathrm{SiN})$) [9].

Silylamides

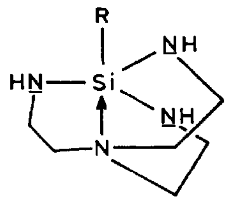
Silylamides have lower $^1J(\mathrm{SiN})$ values than the corresponding NPh-silylamines ($\mathrm{Me_3SiN(H)COCH_3}$, 13.4 Hz; $\mathrm{Me_3SiN(Me)COH}$, 12.7 Hz) [17]. This results from stronger conjugation between nitrogen lp and carbonyl group which increases N–Si bond polarity (decreased d_π–p_π bonding). In several cases the $^{29}\mathrm{Si}$–$^{15}\mathrm{N}$ coupling has not been observed at all. This may be because of rapid (on the NMR time scale) intermolecular exchange with the $\mathrm{Me_3Si}$ groups. It has been suggested [17] that $^1J(\mathrm{SiN})$ can be used to predict the reactivity of compounds having a N–Si bond.

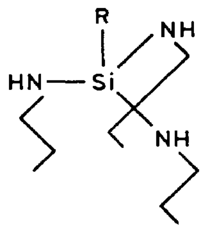
Other compounds

The relatively small $^1J(\mathrm{SiN})$ values found in compounds containing a C=N bond may be attributed to the greater length of the Si–N bond in these compounds [10] ($\mathrm{Me_3Si{-}N{=}C{=}O}$, 14.5 Hz; $\mathrm{Me_3Si{-}N{=}C{=}S}$, 12.2 Hz; $\mathrm{Si(NCS)_4 \cdot 2Py}$, 32.5 Hz [20*]).

The value measured for $\mathrm{Si(NCS)_4}$ in pyridine [17] must be attributed to the adduct $\mathrm{Si(NCS) \cdot 2Py}$ (Py = pyridine), because its formation has been described previously [21]. This is the only value of $^1J(\mathrm{SiN})$ for a hexacoordinated silicon known to date.

Smaller $^1J(\mathrm{SiN})$ values were observed for the equatorial N–Si bonds in azasilatranes, as compared to the corresponding model compounds [22]. This





R = Me	25.3 Hz	25.8 Hz
R = CH_2 = CH	25.8 Hz	27.0 Hz
R = Ph	26.5 Hz	27.4 Hz

indicates only slight variation in the electronic structure of the equatorial N–Si bonds as a result of N → Si bond formation.

Couplings via the coordinate N → Si bond

The ^{29}Si–^{15}N coupling via the coordinate N → Si bond depends on the nature of substituents at the Si and N atoms in a complex manner. ^1J(SiN) increases with the growing N → Si bond strength, as indicated by greater ^1J(SiN) values in the silatranes with a shorter N → Si bond, as well as in solvents of greater polarity (see

Table 1

^{29}Si–^{15}N spin–spin coupling constants (^1J) the bond length (l) and order (P) of the coordinate N → Si bonds in silatranes

SiR	Solvent	^1J(SiN)(Hz)	l(NSi)(Å)	P(NSi)
Me	$CDCl_3$	$\leqslant 0.2$	$\geqslant 2.253$	$\leqslant 0.09$
	$(CD_3)_2SO)$	0.70	2.221	0.17
	cryst.	–	2.175	–
CH_2=CH	$CDCl_3$	0.55	2.229	0.15
	$(CD_3)_2SO$	1.47	2.189	0.24
	cryst.	–	2.15	–
Ph	$CDCl_3$	0.66	2.223	0.16
	$(CD_3)_2SO$	1.43	2.190	0.24
	cryst.	–	2.15	–
MeO	$CDCl_3$	1.17	2.159 ^{a,b}	0.31 ^{a,b}
	$(CD_3)_2SO$	1.65	2.147 ^{a,b}	0.24 ^{a,b}
H	$CDCl_3$	1.10	2.203	0.21
	$(CD_3)_2CO$ (303 K)	1.17	2.200	0.22
	$(CD_3)_2CO$ (183 K)	2.20	2.166	0.30
	$CD_3C{\equiv}N$	1.76	2.180	0.26
	$(CD_3)_2SO$	2.05	2.171	0.29
CH_2Cl	$CDCl_3$	1.54	2.187	0.25
	$(CD_3)_2SO$	2.57	2.156	0.32
	cryst.	–	2.12	–
Cl	$CDCl_3$	1.98	2.090^{a,c}	0.48^{a,c}
	$(CD_3)_2SO$	3.37	2.067^{a,c}	0.53^{a,c}
	cryst.	–	2.02	–

[a] Corrected to the *EN* of Si-substituent. [b] Δ^1J(SiN) 1.28 Hz. [c] Δ^1J(SiN) 3.74 Hz.

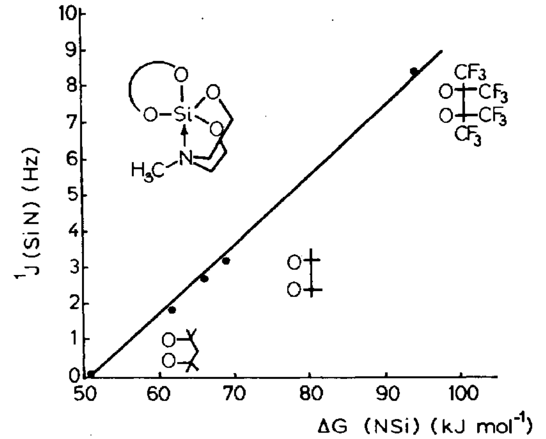


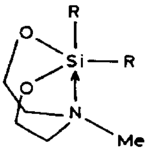
Fig. 2. Correlation between ^{29}Si–^{15}N spin–spin coupling constants via the coordinate N → Si bond and the free energy of dissociation of this bond in spirocyclic derivatives of 1,3-dioxa-6-aza-2-silacyclooctanes [23].

Table 1). ${}^1J$(SiN) rises as the free energy of dissociation of the N → Si bond ($\Delta G^{\neq}$) increases, observed for the spirocyclic derivatives of 1,3-dioxa-6-aza-2-silacyclooctanes (silocanes, see Fig. 2). A linear relationship (2) found

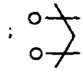
$$\Delta G^{\neq}_{\mathrm{NSi}}(\mathrm{kJ/mol}) = 51.4 + 51.1\ {}^1J(\mathrm{SiN}) \qquad (2)$$

for the NMe-derivatives was used to estimate the N → Si bond energy in silatranes [23].

On the other hand, the data obtained for silocanes (R(Si) = Ph, H; Ph, Me; Ph, MeO; RO, RO) [23,24] indicate that, in contrast to the derivatives with a covalent



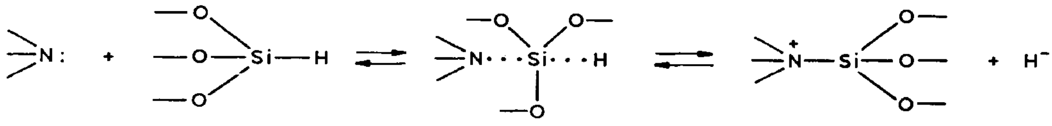
(R$_2$ = Ph, H, +3.5 Hz ; Ph, Me (+) 1.2 Hz ; Ph, MeO (+) 1.9 Hz [24] ;



0 Hz)

N–Si bond, ${}^1J$(SiN) of a coordinate N → Si bond may increase as the EN of substituents at Si decreases. This can be attributed to the inverse pattern of variation of ΔE with EN of Si-substituents in compounds containing covalent and coordinate bonds. Hence, the analysis of ${}^1J$(SiN) data in the case of the coordinate N → Si bond must be carried out with caution.

A prediction by way of the S_N2 substitution reaction was applied to obtain relationships for the estimation of the bond length



${}^1J$(SiN) = 0.0 Hz

${}^1J$(SiH) = 290.0 Hz

${}^1J$(SiN) = 25.1 Hz

${}^1J$(SiH) = 0.0 Hz

$$l(\mathrm{NSi})(\text{Å}) = 2.291 - 0.084(^{1}J(\mathrm{SiN}))^{1/2} \qquad (3)$$

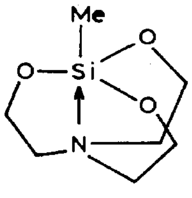
$$P^{2}_{(\mathrm{NSi})} = {}^{1}J(\mathrm{SiN})/25.1$$

(l(NSi)) and order (P(NSi)) of the N → Si bond in silatranes in solution (see Table 1). In light of the above, eq. 3 and 4 are true only for those compounds with Si-substituents whose *EN* differ very little from those in the 1-hydrosilatrane used as a model compound, e.g., for silatranes with R_{Si} = H, Alk, CH_2=CH, Ph etc. A nonlinear correlation between ^1J(SiN) and the ^{15}N chemical shift (δ(N)) has been found recently for the last case [25]:

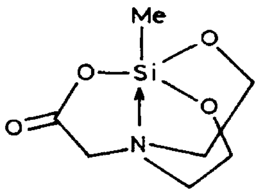
$$^{1}J(\mathrm{SiN}) = (\delta^{3} - 46.5\ \delta) \times 10^{-3} \qquad (4)$$

where $\delta = 367.7 + \delta(\mathrm{N})$. It was assumed that this relationship could be used to take into account the effect of the *EN* of the Si-substituent on ^1J(SiN) thus enabling the use of eq. 3 and 4 in the case of silatranes with different *EN* of the Si-substituents (e.g., R_{Si} = MeO and Cl, see Table 1).

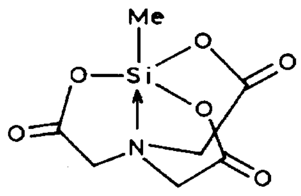
^1J(SiN) have also been used to show that the strength of the N → Si bond grows with increase in the number of carbonyl groups in silatranones [26]. The gain in N → Si bond strength was explained in terms of the greater polarity of the equatorial Si–OC(O) bonds, compared with Si–OCH_2.



0.7 Hz



0.9 Hz [24]



8.2 Hz

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20 The value $^1J(^{29}\mathrm{Si}-^{15}\mathrm{N})$ was calculated by multiplying $^1J(^{29}\mathrm{Si}-^{14}\mathrm{N})$ with $\gamma(^{15}\mathrm{N})/\gamma(^{14}\mathrm{N}) \approx 1.4$, $^1J(^{29}\mathrm{Si}-^{14}\mathrm{N})$ 23.2 Hz [17].

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