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The use of $^{15}N-X$ (X = ^{29}Si, ^{73}Ge, $^{117/119}Sn$, ^{207}Pb) spin–spin coupling constants in structural studies on Group IV organoelement compounds

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ABSTRACT. Data for the $^{15}N-X$ spin–spin coupling constants and their relation with the structure of Group IV organoelement compounds are surveyed. The ^{15}N and X chemical shifts are quoted. The experimental and theoretical aspects of the spin–spin coupling are briefly considered. It is shown that the possibility of measuring the given constants for the natural abundance of the isotopes and also of their sensitivity to the nature of the N–X chemical bond and various aspects of the electronic and steric structures of the molecules, which has arisen recently, has given rise to new prospects in strucural research on nitrogen-containing Group IV organoelement compounds.

The bibliography includes 80 references.

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I. Introduction

The spin–spin coupling constants (SSCC) are a valuable source of information about the steric and electronic structures of molecules.[1–4] Almost all Group IV elements (with the exception of germanium) have natural isotopes with spin $I = 1/2$ (Table 1). This creates favourable conditions for the investigation of SSCC with participation of these nuclei X and provides a unique possibility for tracing the periodicity in the variation of SSCC for Group IV elements.

Until recently, the $^{15}N-X$ (X = ^{29}Si, $^{117/119}Sn$, ^{207}Pb) SSCC were measured only for individual compounds. One of the causes of this is the extremely low natural abundance of molecules with two magnetically active isotopes—^{15}N and X. Therefore all the data were obtained in the early stages of this research for isotopically enriched specimens, which required a considerable expenditure of time and resources for the synthesis of the labelled compounds. Nevertheless, the first investigations already showed that the $^{15}N-X$ SSCC (J_{NX}) can be used successfully in structural research.

Table 1. The NMR parameters of the nuclei of nitrogen and Group IVA elements.[16]

Nucleus	Natural abundance, %	Spin	$\gamma \cdot 10^{-7}$	$\lvert\psi_{ns}(0)\rvert^2$, a.u. (Ref.66)	Sensitivity* $\times 10^3$
^{13}C	1.10	$^1/_2$	6.7263	2.772	15.90
^{14}N	99.63	1	1.9331	4.775	1.01
^{15}N	0.37	$^1/_2$	−2.7116	4.775	1.04
^{29}Si	4.70	$^1/_2$	−5.3146	3.811	7.84
^{73}Ge	7.76	$^9/_2$	−0.9331	9.543	1.40
^{117}Sn	7.61	$^1/_2$	−9.5319	12.680	45.20
^{119}Sn	8.58	$^1/_2$	−9.9756	12.680	51.80
^{207}Pb	22.60	$^1/_2$	5.5797	20.53	9.13

* Relative to protons for the same number of nuclei and in a constant field B_0.

The $^{15}N-^{13}C$ spin–spin coupling constants were investigated in much greater detail than the constants involving other elements of this Group, which is undoubtedly due to the important role which the N–C bond plays in bioorganic chemistry. The $^{15}N-^{13}C$ spin–spin coupling constants have been examined in other reviews[5–7] and therefore will not be considered here. Furthermore, the chemistry of the remaining Group IV elements differs significantly from the chemistry of carbon. For example, such compounds are characterised by a greater tendency towards the formation of coordinate bonds and by a lower stability in the case of unsaturated compounds. The fields involving research into the SSCC differ correspondingly and their comparison is not always possible. Nevertheless, the principal conclusions and regularities observed in the study of the $^{15}N-^{13}C$ SSCC indicate the most promising aspects of such research. Thus the popularity and success of the empirical relations between the $^{15}N-^{13}C$ SSCC ($^1J_{NC}$) and different structural parameters, such as the hybridisation of the N and C atoms (the Binsch relation[8]), i.e.

$$80\,{}^1J(^{15}N-^{13}C) = \alpha_N^2\alpha_C^2 \qquad (1)$$

(where α is the amount of *s* character of the localised hybrid bond

expressed as a percentage), the pyramidality of the nitrogen atom,[7,9] the atomic charges, etc., demonstrates the usefulness of studies of this kind.

After superconducting magnets had been devised and a method had been developed for increasing the sensitivity of the NMR of heavy nuclei via polarisation transfer from protons, the measurement of the $^{15}N-X$ SSCC became possible for the natural abundance of isotopes. The amount of experimental data which have become available hitherto is so large that their systematic arrangement and survey are required. This communication is the first attempt on these lines. Together with the SSCC, we quote also the chemical shifts (CS) of the ^{15}N nuclei (relative to $MeNO_2$) and X (relative to XMe_4), since this usually makes it possible to achieve a more reliable interpretation of SSCC which have been little investigated hitherto. We hope that this review will promote the expansion of the field of research into $^{15}N-X$ SSCC and will facilitate the interpretation of new data.

II. Fundamentals of the theory

According to Ramsey's theory,[10] the spin–spin coupling in a liquid can be regarded as a result of the contribution of three components: spin–orbital (SO), spin–dipole (SD), and Fermi-contact (FC). The spin–orbital coupling can also be subdivided into two components—diamagnetic (OD) and paramagnetic (OP). The contributions of the SO and SD components are relatively small and tend to diminish with increase in the degree of π-bonding between the atoms of the interacting nuclei.[11] If the interacting nuclei are linked by a multiple chemical bond, then the SSCC is as a rule determined by the FC interaction. This simplifies significantly the interpretation of the experimental data within the framework of the analytical relations obtained from the quantum-chemical theory of spin–spin coupling.

The observed SSCC $^1J_{NX}$ depend significantly on the gyromagnetic ratio γ of the N and X nuclei. In order to exclude from consideration the individual properties of the nuclei, the concept of the reduced SSCC ^1K, which depends only on the electronic environment of the nuclei, has been introduced:

$$^1K_{NX} = 4\pi^2\, {}^1J_{NX}/h\gamma_N\gamma_X. \quad (2)$$

According to Pople and Santry,[12] in terms of the approximation of the LCAO-MO theory, the contribution of the FC interaction is described by the equation

$$^1K_{NX}^{FC} = -\frac{16e^2h^2}{9M_p^2c^2} |\psi_N(0)|^2 |\psi_X(0)|^2 \cdot \sum_i^{occ} \sum_j^{unocc} (^3\Delta E_{i\to j})^{-1} \cdot c_{is_N} c_{js_N} c_{is_X} c_{js_X}, \quad (3)$$

where $|\psi_N(0)|^2$ and $|\psi_X(0)|^2$ are the valence s electron densities at the N and X nuclei, $^3\Delta E_{i\to j}$ the energy of the excitation of the electronic transitions, and c_{is} and c_{js} are the LCAO coefficients of the s orbitals of the N and X atoms, while the remaining constants have the usual significance. In the extended Hückel method, $^3\Delta E_{i\to j} = e_j - e_i$ (e_i and e_j are the energies of the occupied and unoccupied orbitals respectively), which makes it possible to simplify Eqn. (3):

$$^1K_{NX}^{FC} = \frac{4e^2h^2}{9M_p^2c^2} |\psi_N(0)|^2 |\psi_X(0)|^2 \pi_{NX}, \quad (4)$$

$$\pi_{NX} = 4 \sum_i^{occ} \sum_j^{unocc} (e_i - e_j)^{-1} c_{is_N} c_{js_N} c_{is_X} c_{js_X}, \quad (5)$$

where π_{NX} is the mutual polarisability of the s orbitals of the N and X atoms.

In terms of the average excitation energy (ΔE) approximation, the contribution of the FC interaction can be represented by Eqn. (6), which reflects the relation between $^1K_{NX}$ and the s order of the N–X bond ($P_{s_Ns_X}$):

$$^1K_{NX}^{FC} = \frac{4e^2h^2}{9M_p^2c^2} |\psi_N(0)|^2 |\psi_X(0)|^2 P_{s_Ns_X}^2/\Delta E. \quad (6)$$

A modification of this equation within the framework of the valence bond theory [Eqn. (7)], using the concept of the s character of the localised hybrid bonds [see, for example, Eqn. (11)], is also frequently employed:

$$^1K_{NX}^{FC} = \frac{4e^2h^2}{9M_p^2c^2} \alpha_N^2\alpha_X^2 |\psi_N(0)|^2 |\psi_X(0)|^2/\Delta E. \quad (7)$$

In the interpretation of the SSCC, it is usually assumed that the quantities $|\psi_X(0)|^2$ and $|\psi_N(0)|^2$ are constant (in reality they depend on the atomic charge). This makes it possible to explain the observed changes in the SSCC by the differences in the nature of the chemical bond.

Eqns. (6) and (7), based on the ΔE approximation, presuppose that the FC interaction makes a positive contribution to the SSCC. In fact, negative contributions to the ^1K are frequently observed, especially for Group V–VII nuclei. This arises from the fact that the ΔE approximation is not always valid.

Jameson and Gutowsky[11] showed that the quantities ^1K obey periodicity laws and proposed a model for the prediction of the sign of ^1K for the nuclei of any elements in the Periodic System. According to this model, the nuclei involved in spin–spin coupling can be divided into three types.

A. Elements having an open s shell in the ground configuration. The s orbitals participate directly in the formation of the chemical bond (Group I in the Periodic System).

B. Elements having open s shells in an accessible configuration. The involvement of valence s orbitals in the formation of a chemical bond is possible as a result of the mixing of these configurations with the ground configurations (Groups II–VI).

C. Elements which do not have open s shells. In this case, the s electrons do not participate in the formation of a chemical bond (Groups VI and VII) and spin–spin coupling occurs mainly via the mechanism involving the polarisation of outer s shells, which leads to a negative sign of the FC interaction.

For Group IV elements, the valence s and p electrons have fairly close energies, so that, as a result of their mixing, the s electrons become available for the formation of a chemical bond. For this reason, the elements X should be assigned to type B. However, with increase in the radius of the atoms X their polarisability increases greatly. This can lead to an increase in the negative contribution of the polarisation of the inner s shells and hence to more negative values of $^1K_{NX}$.

For compounds of divalent X, mainly the p electrons participate in the formation of a chemical bond and the properties of the valence s electrons resemble those of closed s shells, which makes it possible to assign them to type C.

Jameson and Gutowsky assigned the Group V elements to a type intermediate between types B and C. The nitrogen(III) atom has a lone electron pair (LEP) and the difference between the energies of the valence $2s$ and $2p$ electrons is relatively large. For this reason, the use of the ΔE approximation is in general unreliable. Nevertheless, the observed correlation between $^1J_{NC}$ and the s character of the N–C bond in carbon compounds shows that in this instance the ΔE approximation is valid.

Equations describing the spin–spin coupling in liquids have been derived for a non-polar covalent bond. At the present time, there are no analogous equations describing the SSCC for coupling via a coordinate bond. Therefore in the interpretation of such SSCC, it is usually assumed that the equations obtained for the FC interactions are valid for the covalent component of the coordinate bond. Here we have in mind Eqn. (8), describing the nature of the coordinate bond within the framework of the valence bond theory:[13]

$$\psi_{N\to X} = \psi_{NX} + \lambda\psi_{N^+X^-}, \qquad (8)$$

where λ is a coefficient. However, the question how this interaction takes place and how to predict the sign of ^1K is not entirely clear. The coordinate bond has also been examined in Jameson and Gutowsky's model.[11] Certain considerations concerning this topic can be deduced from the study of the ionic bond by the above workers. In particular, it has been shown[11] that for ionic bonds there is a possibility of a small positive contribution to the FC coupling component. The overlap of the occupied *s* and *p* orbitals with the unoccupied *d* orbitals of the metal and also any kind of their mixing (covalence) give rise to a positive contribution to the spin density on the X nuclei. Consequently, in the case of a coordinate bond (at least in σ-bonding) the FC interaction should make a positive contribution to the SSCC.

III. Experimental aspects

1. The ^{14}N–X spin–spin coupling

The ^{14}N–X spin–spin coupling constants can be observed directly relatively rarely because of the effective relaxation of the ^{14}N nuclei via a quadrupolar mechanism. The merging of the components of the multiplet is then observed in the spectra of the X nuclei as a consequence of the scalar relaxation of the second kind.[14,15]

In principle, the ^{14}N–X SSCC can be determined by analysing the line form in the spectra of the X nuclei. Neglecting the natural width of the signal, the line form can be described analytically with the aid of the equation

$$I(x) = \frac{2\eta}{\pi J}\,\frac{45+\eta^2(5x^2+1)}{225x^2+\eta^2(34x^4-2x^2+4)+\eta^3(x^6-2x^4+x^2)}. \qquad (9)$$

Here $x = \Delta\nu/J$, where $\Delta\nu = \Delta\omega/2\pi$; $\eta = 10\pi T_{qN}J$, T_{qN} being the quadrupolar relaxation time. The description of the line form taking into account the natural width of the signal is more difficult. This problem has been described in detail.[15] It follows from Eqn. (9) that the line form in the spectra of the nuclei X is determined by the dimensionless parameter η. The quadrupolar relaxation time of the ^{14}N nuclei can be determined from the ^{14}N spectrum using the relations $T_2 \simeq 1/\pi\Delta\nu_{1/2}$ and $T_{qN} \simeq T_2$, where $\Delta\nu_{1/2}$ is the width of the signal at half its height.

The ^{14}N–X SSCC can be obtained directly in this case if $\eta \geqslant 10$. A clearer criterion is the relation $J \geqslant \Delta\nu_{1/2}(^{14}\mathrm{N})$, provided that the line half-width in the ^{14}N spectra does not exceed the ^{14}N–X SSCC. Consequently, the probability of finding directly these SSCC increases with increase in $^1J_{NX}$ (Fig. 1). For this reason, the ^{14}N–X SSCC for the heavy nuclei ^{117,119}Sn and ^{207}Pb are observed more frequently than for the ^{29}Si nuclei.

On the other hand, $\Delta\nu_{1/2}(^{14}\mathrm{N})$ diminishes (T_{qN} and ν increase) with increase in the symmetry of the charge distribution around the ^{14}N nuclei. Molecules with a tetrahedral or linear configuration of the nitrogen atom as well as quasi-linear molecules (isocyanates, isothiocyanates) usually have relatively long times T_{qN} because of the rapid (on the NMR time scale) exchange. In certain cases, this makes it possible to determine the ^{14}N–X SSCC from the satellites of the X nuclei in the ^{14}N spectra.

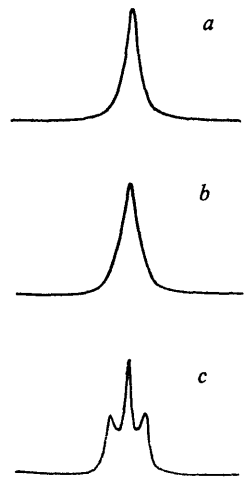


Figure 1. Dependence of the line form in the spectra of the X nuclei on the SSCC $^1J(^{14}\mathrm{N}-\mathrm{X})$ for a constant relaxation time of the ^{14}N nuclei (T_{qN} = 1.6 ms). The spectra were calculated by Eqn. (9): *a*, J = 50 Hz; *b*, J = 100 Hz; *c*, J = 200 Hz.

However, the ^{14}N–X SSCC can be found directly relatively rarely. Furthermore, the accuracy of the ^{14}N–X SSCC determined directly depends significantly on η, since the distance between the components of the multiplet in the spectra of the X nuclei (but not the ^{14}N nuclei) diminishes with decrease in η. For these reasons, preference is usually given to the study of the ^{15}N–X SSCC.

2. The ^{15}N–X spin–spin coupling

As a consequence of the extremely low natural abundance of the ^{15}N isotope, the ^{15}N–X spin–spin coupling constants were initially measured for enriched specimens. In this case, an accurate measurement of the ^{15}N–X SSCC presents no problems, provided that the ^{15}N and X nuclei form a first order spectrum. Furthermore, there is a possibility of determining the sign of ^1K.

The high sensitivity of modern NMR spectrometers makes it possible to measure ^{15}N–X SSCC for the natural abundance of the isotopes. This can be achieved in two ways: on the basis of the satellites of the X nuclei in the ^{15}N spectra and on the basis of the satellites of the ^{15}N nuclei in the spectra of X nuclei. In most studies, the ^{15}N–X SSCC have been determined from the ^{15}N spectra because the satellites are in this case more intense. It is noteworthy that the sensitivity of the measurements is in this case limited by the low natural abundances of both isotopes. However, from the standpoint of the limitations associated with the dynamic range of the spectrometer,[16] the use of ^{15}N NMR is preferable (see the reviews on ^{15}N NMR [5,7,17,18]).

The intensity of the useful signal in the measurement of the ^{15}N–X SSCC depends in the first place on the NMR sensitivity of

the observed nuclei (Table 1). A number of other factors are also significant—the Overhauser nuclear effect and the increase in signal intensity when methods involving the transfer of polarisation from protons are used (INEPT, DEPT, etc.[19,20]). Since the NMR sensitivity of the X nuclei is in all cases appreciably higher than that of the ^{15}N nculei, in principle the $^{15}N-X$ SSCC can be more conveniently determined from the spectra of the X nuclei.

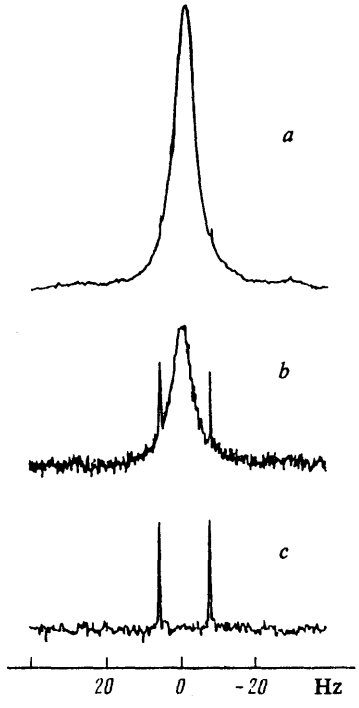


Figure 2. The ^{15}N satellites in the ^{29}Si NMR spectra of hexamethyldisilazane. The spectra were obtained by the INEPT (*a*), DEPT (*b*), and INEPT + Hahn's spin-echo (*c*) methods. Working frequency 71.55 MHz, temperature 303 K, number of accumulations 16 (*a* and *b*) and 64 (*c*).[22]

We have shown that[21] the detection of the ^{15}N satellites in the ^{29}Si NMR spectra facilitates significantly the broadening of the central line and of the ^{13}C satellites as a result of the $^{14}N-X$ spin–spin coupling and relaxation of the second kind (Fig. 2*a*). Using polarisation transfer from protons, it is usually possible to measure the $^{15}N-^{29}Si$ SSCC in the ^{29}Si NMR spectra after only a few accumulations. It has been shown[22] that the DEPT method is preferable to INEPT, since it decreases appreciably the intensity of the central line and of the ^{13}C satellites (Fig. 2*b*). The difference between the relaxation times of the central signal and of the ^{15}N satellites can be used to suppress completely the central line[22] (Fig. 2*c*). If several nitrogen atoms are attached to the silicon atom, then the ^{15}N satellites are also broadened as a result of the quadrupolar relaxation in the $^{14}N-^{29}Si-^{15}N$ fragments. In this case, the $^{15}N-^{29}Si$ SSCC can be more usefully determined from the ^{15}N spectra.

The observation of the ^{15}N satellites in the $^{117/119}Sn$ and ^{207}Pb NMR spectra is difficult.[23] This is apparently associated with the fact that the above nuclei have relatively short relaxation times.[24,25] For this reason, the difference between the widths of the central line and of the ^{15}N satellite is less pronounced, which leads to their merging as a consequence of the low intensity of the latter.

In the case of the protonated nitrogen atom, the satellites of the X nuclei in the ^{15}N NMR spectra can be observed after accumulation for 1–2 h [23,26] using the usual polarisation transfer methods (INEPT, DEPT, etc.),[19,20] provided that there is no rapid intramolecular or intermolecular exchange of NH protons. It has been shown[23,27] that, for a non-protonated nitrogen atom, it is also possible to employ the INEPT method, assuming that the long-range $^{15}N-^{1}H$ SSCC are 1–2.5 Hz. The best results have been achieved on the assumption that J_{NH} = 2.5 Hz for the NR (R = alkyl) group, 1.5 or 2 Hz for the Me_3SnN group, and 1 or 1.5 Hz for the Me_3SiN group.[23] In this case, the measurement of the $^{15}N-X$ (X = ^{29}Si, $^{117/119}Sn$) SSCC required accumulation for 6–12 h. It has been observed that[27] the main INEPT sequence (without the suppression of the spin–spin coupling with protons) is most suitable, since the use of refocussing (of the longer DEPT sequence) for such low values of the $^{15}N-^{1}H$ SSCC diminishes appreciably the signal intensity due to relaxation effects.

Table 2. The $^{15}N-^{29}Si$ SSCC for the silazanes (I)–(XVIII) (solvent—$CDCl_3$).[31]

Compound	$^{1}J_{SiN}$, Hz	$\delta(^{15}N)$, p.p.m.	$\delta(^{29}Si)$, p.p.m.
(I)	6 [28]	—	−39.9
(II)	12* [29]	—	−64.3 (SiH_2), −41.4 (SiH_3)
(III)	7.6 [23]	−342.0	—
(IV)	13.4	−354.2	2.1
(V)	14.4	−334.3	13.3
(VI)	17.4	−335.7	−11.9
(VII)	14.3 (NSi_2), 9.8 (NSi_3) [47]	—	−6.8 [47]
(VIII)	15.4	−347.3	−4.6
(IX)	15.8	−345.4	−4.0 (NSiN)
	15.8	—	−4.3 (NSiO)
(X)	15.5	−342.9	−3.4
(XI)	15.7	−341.9	−1.2
(XII)	16.9	−341.7	−8.2
(XIII)	17.4 [47]	−345.8 [47]	−15.5 [47]
(XIV)	15.9	−334.9	−11.3
(XV)	15.9	−334.9	−10.9
(XVI)	17.1	−335.1	−12.6
	17.3	—	−13.2
(XVII)	17.7	−336.7	−8.3 (NSiN)
	17.7	—	−12.6 (NSiO)
(XVIII)	17.2	−334.8	−12.3

* It is not indicated to which of the non-equivalent silicon atoms the SSCC amounting to 12 Hz corresponds.

Note. Here and in other tables the numerals in square brackets denote references (Ed. of Translation).

IV. Silicon-29

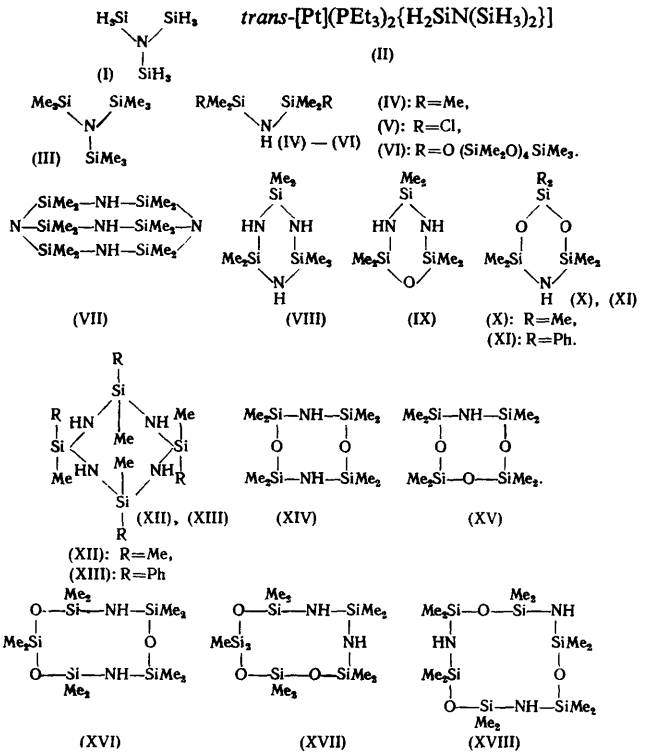
1. Coupling across a covalent bond

(a) Silazanes

Historically the $^{15}N-^{29}Si$ SSCC were first measured for compounds (I) and (II) enriched in the ^{15}N isotope.[28,29] It was established that $^{1}K_{NSi} > 0$. During the next 10 years, these SSCC

were scarcely measured. Systematic studies on the $^{15}N-^{29}Si$ SSCC began in 1983 [30] after polarisation transfer methods, permitting measurements for the natural abundance of the isotopes, became available.

It has been found that the $^{15}N-^{29}Si$ SSCC for the silazanes (I)–(XVIII) increase with increasing electronegativity (EO) of the substituents at the Si atom in the sequence H < Me < Cl < NR, OR (Table 2).[31] A similar trend has been observed also for substituents at the nitrogen atom. Thus, when the silyl group is replaced by the more electronegative hydrogen atom, the $^{15}N-^{29}Si$ SSCC increase. On this basis, it has been suggested that $^1K_{NSi} > 0$ for the silazanes (I)–(XVIII). However, in the presence of only electropositive substituents at the nitrogen atom (for example, Li), negative values of $^1K_{NSi}$ may be expected.[22]



The cyclosilazane and cyclosiloxazane $^{15}N-^{29}Si$ SSCC are virtually the same for the N–Si–N and N–Si–O fragments, whereas the $^{29}Si-^{13}C$ SSCC differ significantly (63 ± 1 Hz and 69 ± 1 Hz respectively). This was explained on the basis of Bent's rules[32] by the more significant change in the *s* character of the bonds involving the Si atom with the most electropositive substituents, i.e. Si–C.

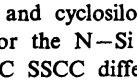
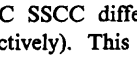
The tendency towards a decrease in the $^1J_{NSi}$ on passing to smaller rings has been explained by the increased polarity of the N–Si bonds (decrease in $d_\pi-p_\pi$ conjugation), which agrees well with the conclusions reached for the ^{15}N and ^{29}Si chemical shifts. A decrease in the Si–N–Si valence angle in smaller rings reduces the *s* character of the N–Si bonds and hence reduces $^1J_{NSi}$.

(b) Silylamines

Higher values of $^{15}N-^{29}Si$ SSCC have been observed for silylamines (Table 3) compared with silazanes (Table 2). This is associated with the increase in the electronegativities of the substituents at the nitrogen atom in the sequence $SiMe_3$ < H < alkyl.

The $^{15}N-^{29}Si$ SSCC increase systematically with increase in the electronegativities of the substituents at the Si atom in the sequence Me < Ph < NR < OR.[22,26] Consequently $^1K_{NSi} > 0$ in the given sequence. A similar conclusion was reached from a comparison of the SSCC $^1J_{NSi}$ and $^1J_{PSi}$ for isostructural nitrogen(III) and phosphorus(III) compounds,[22] which revealed the opposite dependences of these SSCC on the electronegativities of the substituents. Since it is known that $^1K_{PSi} < 0$,[33,34] it follows from the foregoing that $^1K_{NSi} > 0$.

Table 3. The $^{15}N-^{29}Si$ SSCC for silylamines, silylamides, azasilatranes, and other compounds with a covalent N–Si bond (solvent—$CDCl_3$).[21,22,26,42,43]

Compound	Chemical formula	$^1J_{NSi}$, Hz	δ(^{15}N), p.p.m.	δ(^{29}Si), p.p.m.
(XX)	$Pr^nHNSiMe_3$	17.1	—	2.6
(XXI)	$Pr^iHNSiMe_3$	17.0	—	0.9
(XXII)	$Bu^tHNSiMe_3$	17.2	−323.9	−2.3
(XXIII)	$PhHNSiMe_3$	15.7	−314.9	1.7
(XXIV)	Et_2NSiMe_3	19.2	—	3.8
(XXV)	$Pr_2^nNSiMe_3$	19.7	—	3.9
(XXVI)	$(CH_2)_6NSiMe_3$	19.6	—	3.5
(XXVII)	$(CH_2)_5NSiMe_3$	17.8	—	3.9
(XXVIII)	$(CH_2)_4NSiMe_3$	16.5	—	2.5
(XXIX)	$(CH_2)_3NSiMe_3$	13.6	—	1.8
(XXX)	$(CH_2)_2NSiMe_3$	<5	—	14.1
(XXXI)	$PhHNSiHMe_2$	16.4	−320.4	—
(XXXII)	$Bu^tHNSiMe_2Ph$	18.8	−325.7	−9.6
(XXXIII)	$PhHNSiMe_2Ph$	17.3	−317.7	−5.8
(XXXIV)	$Bu^tHNSiMePh_2$	19.8	−327.3	−15.4
(XXXV)	$PhHNSiMePh_2$	18.3	−319.5	−11.8
(XXXVI)	$(PrHN)_2SiMe_2$	21.5	−351.0	−8.1
(XXXVII)	$(Bu^tHN)_2SiMe_2$	20.8	−317.4	−16.9
(XXXVIII)	$(PhHN)_2SiMe_2$	19.9	−312.7	−12.8
(XXXIX)	$PrHNSi(OEt)Me_2$	21.8	−348.9	−4.8
(XL)	$Bu^tHNSi(OEt)Me_2$	21.5	−317.6	—
(XLI)	$PhHNSi(OEt)Me_2$	19.9	−310.8	−5.1
(XLII)	$Pr_2^nNSi(OEt)Me_2$	23.8	—	−3.4
(XLIII)	$(PrHN)_3SiMe$	25.8	−351.6	−23.3
(XLIV)	$(PrHN)_3SiCH{=}CH_2$	27.0	−353.6	−36.4
(XLV)	$(PrHN)_3SiPh$	27.4	−353.5	−33.0
(XLVI)	$(PhHN)_3SiMe$	25.4	−313.1	−29.5
(XLVII)	$(PhHN)_3Si(OEt)Me$	27.3	−313.5	−30.1
(XLVIII)	$Bu^tHNSi(OEt)_2Me$	30.9	−321.5	—
(XLIX)	$PhHNSi(OEt)_2Me$	29.0	−314.4	−34.2
(L)	$PhSi(OCH_2CH_2CH_2)_3N$	27.7	—	−48.9
(LI)	$Si(NHPr)_4$	31.7	−354.4	−40.6
(LII)	$(Bu^tHN)_2Si(OEt)_2$	39.8	−324.9	—
(LIII)	$(PhHN)_2Si(OEt)_2$	40.1	−319.2	−63.0
(LIV)	$Bu^tHNSi(OEt)_3$	44.6	−330.4	—
(LV)	$PhHNSi(OEt)_2$	43.9	−322.3	−71.6
		43.7*1	−321.5*1	—
		43.2*2	−320.7*2	—
(LVI)	$Et_2NSi(OEt)_3$	47.6	−349.9	−69.2
(LVII)	$HC(O)NMeSiMe_3$	12.7	—	—
(LVIII)	$MeC(O)NHSiMe_3$	13.4	—	5.3
(LIX)	 R=H	12.0	−281.3	7.1
(LX)	 R=$SiMe_3$	12.8	−280.1	6.4
(LXI)	$(p\text{-}MeC_6H_4SO_2)NHSiMe_3$	*3	−283.1	9.7
(LXII)	$(Me_3SiNH)_2CO$	*3	—	1.8
(LXIII)	$Me_2SiN{=}C{=}O$	14.5	—	3.9
(LXIV)	$Me_2SiN{=}C{=}S$	12.2*4	−265.3	5.3
(LXV)	$Si(N{=}C{=}S)_4$	(32.5)*5	(−237.2)*6	—
(LXVI)	$Me_2SiN{=}N{\equiv}N$	<5	—	15.8
(LXVII)	$N(CH_2CH_2NH)_3SiMe$	25.3	−352.8	−68.3
(LXVIII)	$N(CH_2CH_2NH)_3SiCH{=}CH_2$	25.8	−354.0	−79.2
(LXIX)	$N(CH_2CH_2NH)_3SiPh$	26.5	−354.1	−77.2

*1 Solvent—C_6D_{12}.

*2 Solvent—$(CD_3)_2SO$.

*3 $^1J_{NSi}$ is not observed because of the rapid intermolecular exchange of the $SiMe_3$ groups.

*4 $^1J(^{14}N-^{29}Si)$ = 8.4 Hz.

*5 Calculated from $^1J(^{14}N-^{29}Si)$ = 23.2 Hz by multiplying it by $\gamma(^{15}N)/\gamma(^{14}N)$.

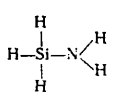
*6 The δ(^{14}N) chemical shift is quoted.

The parallel variation of the $^{15}N-^{29}Si$ and $^{29}Si-^{13}C$ (for the $Si-CH_3$ bond) SSCC has been observed in silylamines.[22] A linear correlation has been discovered for aniline derivatives:

$$^1J(^{15}N-^{29}Si) = 0.41\ ^1J(^{29}Si-^{13}C) - 7.3 \quad (r = 0.97,\ n = 7). \qquad (10)$$

Bearing in mind that $^1K_{SiC} > 0$ [35] and that this SSCC is determined by the contribution of the FC interaction,[36] it has been postulated that a similar equation is valid also for $^1K_{NSi}$.

The first calculation of the $^{15}N-^{29}Si$ SSCC for the silylamine (XIX) was carried out recently by the *ab initio* method:[37]



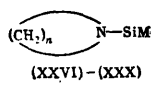
(XIX)

PC = 25.97 Hz
OD = 0.02 Hz
OP = −1.00 Hz
SD = 0.29 Hz
$^1J_{theor}$ = 25.26 Hz.

The theoretical quantity (25.26 Hz) reflects correctly the sign of $^1K_{NSi}$ and has a reasonable value. An important result of these calculations has been the conclusion that the $^{15}N-^{29}Si$ SSCC is determined by the sign of the FC interaction.

Bearing in mind that the $^{15}N-^{29}Si$ SSCC for silylamines have large and positive values, it has been suggested that they can be interpreted within the framework of the ΔE approximation, i.e. in conformity with Eqns. (6) and (7). Consequently the application of the $^{15}N-^{29}Si$ SSCC in structural studies in no less promising than the application of $^1J_{NC}$. The higher value of $^1J_{NSi}$ and the possibility of measuring them for the natural isotope abundances make them actually preferable.

An example in illustrating the sensitivity of $^1J_{NSi}$ to the hybridisation of the nitrogen atom is the significant decrease of the $^{15}N-^{29}Si$ SSCC on passing to smaller rings which has been observed for the trimethylsilyl (TMS) derivatives of the cyclic amines (XXVI)–(XXX) [21] and has been explained by the enhancement of the pyramidal configuration of the nitrogen atom.



(XXVI)–(XXX)

(XXVI): $n = 6$, (XXIX): $n = 3$,
(XXVII): $n = 5$, (XXX): $n = 2$.
(XXVIII): $n = 4$,

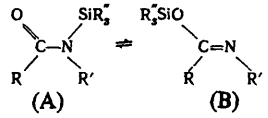
The similar phenomenon observed for silazanes is also associated with the decrease in the valence angle at the nitrogen atom in smaller rings.[31]

The anomalous decrease in $^1J_{NSi}$ on passing from the NBu^t derivatives to the NPh derivatives of silylamines has been explained by the weakening of the $d_\pi-p_\pi$ conjugation via the N–Si bond as a result of the stronger competing conjugation of the LEP of the nitrogen atom with the phenyl group.[26] It has been suggested that this leads to lengthening of the N–Si bond, as a result of which the degree of overlap of the valence *s* orbitals diminishes and $^1J_{NSi}$ also decreases.

(c) Silylamides

Fairly low $^{15}N-^{29}Si$ SSCC have been observed for trimethylsilylamides [compounds (LVII)–(LXII)]. It has been suggested that this is a consequence of the stronger competing conjugation of the LEP of the nitrogen atom with the carbonyl group.

The high polarity of the N–Si bond in trimethylsilylamide increases the rate of the intramolecular and intermolecular exchange of the Me_3Si groups. The question which of the structures (A) or (B) predominates in solution has been most frequently discussed for these compounds.[38–40]



(A) (B)

The ^{29}Si chemical shifts do not always make it possible to solve unambiguously this problem, whereas the $^{15}N-^{29}Si$ SSCC can be used as significant evidence in support of structure (A).

The ^{15}N and ^{29}Si chemical shifts also failed to permit the observation of the intermolecular exchange of the $SiMe_3$ groups. On the other hand, using the $^{15}N-^{29}Si$ SSCC it is possible, in principle, not only to observe the process but also to determine the activation parameter by means of dynamic NMR methods.[41] For a detailed investigation of this process, specimens enriched in the ^{15}N isotope are apparently essential. However, it has been demonstrated by simulating the ^{29}Si line form that the observation of the ^{15}N satellites in the ^{29}Si NMR spectrum is difficult or impossible if the free energy of activation for the intermolecular exchange of $SiMe_3$ group ($\Delta G^{\neq}$) is smaller than 80 kJ mol^{-1}.[22]

(d) Silicon isocyanates

The relatively long relaxation times of the ^{14}N nuclei in these compounds frequently make it possible to find the $^{14}N-^{29}Si$ SSCC directly. Thus a relatively well resolved triplet with a splitting of 8.4 Hz has been observed in the ^{29}Si NMR spectrum of trimethylsilyl isothiocyanate (LXIV) (Fig. 3). The low solubility and long relaxation time of the ^{29}Si nuclei of the compound (LXV) precluded the measurement of the ^{29}Si NMR spectrum of this compound. However, it has been possible to observe the ^{29}Si satellites in the ^{14}N NMR spectrum and to measure the $^{14}N-^{29}Si$ SSCC.[22]

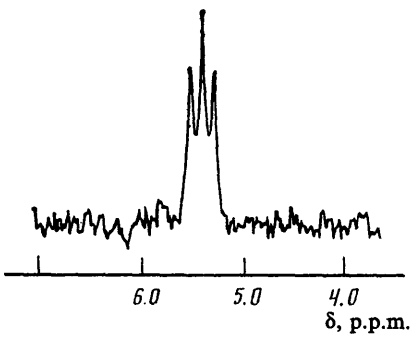


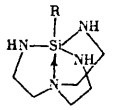
Figure 3. The splitting of the signal in the ^{29}Si NMR spectra of the compound $Me_3SiN=C=S$ as a result of the $^{14}N-^{29}Si$ spin–spin coupling. The spectrum was obtained using the INEPT pulse train for a 50% solution in $CDCl_3$ at a frequency of 71.55 MHz.[22]

The constants $^1J_{NSi}$ for the isocyanates (LXIII)–(LXV) are relatively small, which has been explained tentatively by the increase in the length of the N–Si bond in trimethylsilyl isocyanate (1.76 Å) and trimethylsilyl isothiocyanate (1.78 Å) compared with trimethylsilyl-amine (cf. the value 1.72 Å).

The $^{15}N-^{29}Si$ SSCC could not be found for trimethylsilyl azide (LXVI) with the natural isotope abundances.[22] The ^{29}Si line width (0.4 Hz) shows that $^1J_{NSi}$ is apparently not high (< 10 Hz). The difficulties in the measurement of the $^{15}N-^{29}Si$ SSCC were in this case associated with the fact that the ^{15}N satellites in the ^{29}Si spectra are apparently broadened as a result of the long-range $^{14}N-^{29}Si$ coupling; the lines in the ^{15}N spectra are also broadened as a result of the $^{14}N-^{15}N$ coupling; furthermore, there is a possibility of the intermolecular exchange of the $SiMe_3$ groups.

(e) Other compounds

The $^{15}N-^{29}Si$ SSCC can be used to investigate the influence of the transannular N → Si interaction on the properties of equatorial bonds in the triazasilatranes (LXVII)–(LXIX).[42]

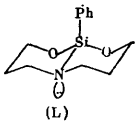


(LXVII): R=Me,
(LXVIII): R=CH=CH$_2$,
(LXIX): R=CH$_2$Cl.

(LXVII)–(LXIX)

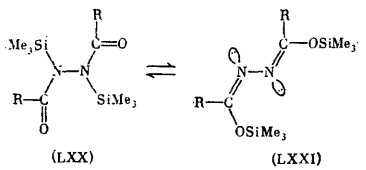
The decrease in the SSCC for these compounds relative to the corresponding aminosilanes [compounds (XLIII)–(XLV)] has been explained by the diminution of the $d_\pi-p_\pi$ interaction in the equatorial N–Si bond in compounds (LXVII)–(LXIX) with increase in the N → Si bond strength.

The $^{15}N-^{29}Si$ SSCC for compound (L) is much lower than the SSCC for compound (XLVIII) (Table 3),[43] indicating a pyramidal structure of the nitrogen atom in the given compound, which is fairly unusual, since in silylamines the nitrogen atom has a planar structure. The phenomenon is apparently caused by ring strain.



(L)

The study of compounds of type (LXX) and (LXXI) enriched in the ^{15}N isotope is an example of the use of the $^{15}N-^{29}Si$ SSCC for the investigation of tautomeric processes and for demonstrating the presence of the N–Si bond:[44]



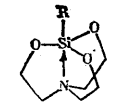
(LXX) (LXXI)

Although the quantity $^1J_{NSi}$ could not be measured accurately, since second order effects were observed in the ^{29}Si NMR spectra, nevertheless the very fact of this $^{15}N-^{29}Si$ spin–spin coupling is evidence in support of the structure (LXX).

2. Interaction across a coordinate bond

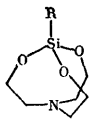
(a) Silatranes

The $^{15}N-^{29}Si$ SSCC for the silatranes (LXXII)–(LXXIX) have been measured using specimens enriched in the ^{15}N isotope (Table 4).[45–47] The structures of the silatranes (LXXII)–(LXXIX) have been studied in detail by X-ray diffraction of crystals (see the review of Voronkov et al.[49]), which made it possible to study in detail the dependence of the $^{15}N-^{29}Si$ SSCC on the N → Si bond length [l(N–Si)]. The structures of compounds (LXXII)–(LXXIX) in crystals depend significantly on the N → Si bond strength.

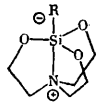


(LXXII)–(LXXIX)

(LXXII): R=Me,
(LXXIII): R=CH=CH$_2$,
(LXXIV): R=Ph,
(LXXV): R=OMe,
(LXXVI): R=H,
(LXXVII): R=CH$_2$Cl,
(LXXVIII): R=CHCl$_2$,
(LXXIX): R=Cl



(A)



(B)

If the N → Si bond is absent [structure (A)], the nitrogen atom is planar and the silicon atom is tetrahedral. With increase in the strength of the N → Si bond, the pyramidal configuration of the nitrogen atom is enhanced, whilst the configuration of the silicon atom approaches the trigonal-bipyramidal configuration [structure (B)]. The majority of silatranes have a structure intermediate between (A) and (B). In solutions, the $^{15}N-^{29}Si$ SSCC increase with decrease in the length of the N → Si bond found in crystals and also with increase in solvent polarity[45] and with decrease in temperature.[47] This indicates the corresponding increase in the mutual polarisability of the valence s orbitals of the N and Si atoms (π_{NSi}). The dependence of $^1J_{NSi}$ on l(N–Si) is non-linear and its character varies as a function of the nature of the solvent (Fig. 4). One of the causes of this behaviour of $^1J_{NSi}$ is the weakening of the N → Si bond on passing from crystals to solutions and also on passing to solvents with a lower polarity. Simultaneously with increase in $^1J_{NSi}$, the constant $^1J_{NC}$ diminishes, which clearly reflects the redistribution of the s character of the bond with increase in strength of the 1,5-transannular N → Si interaction in silatranes. A linear dependence of $^1J(^{15}N-^{13}C)$ on $^1J(^{15}N-^{29}Si)$ was then observed:

$$^1J(^{15}N-^{13}C) = 7.30-0.28\,^1J(^{15}N-^{29}Si) \quad (r = -0.96,\ n = 16). \tag{11}$$

The decrease in the $^{15}N-^{13}C$ SSCC with increase in strength of the N → Si bond was explained by the increasingly pyramidal configuration of the nitrogen atom. This shows that the relation between the structure and the N → Si bond strength, observed in crystals, persists also in solutions.

In the case of 1-hydrosilatrane, a linear correlation was observed between $^1J_{NSi}$ and the stretching vibration frequency, ν_{SiH}, of the Si–H bond in the IR spectra (for different solvents):

$$\nu_{SiH} = 2159-23.23\,^1J(^{15}N-^{29}Si) \quad (r = 0.99,\ n = 4). \tag{12}$$

Extrapolation of this relation to ν_{SiH} in nujol yielded the value of $^1J_{NSi}$ for solid 1-hydrosilatrane, which proved to be 2.97 Hz.

A similar reaction has also been observed for $^1J(^{15}N-^{29}Si)$ and $^1J(^{29}Si-^1H)$:

$$^1J(^{29}Si-^1H) = 290.0-10.63\,^1J(^{15}N-^{29}Si) \quad (r = 0.96,\ n = 4). \tag{13}$$

Relation (13) also indicates a redistribution of the s character of the bonds, i.e. the involvement of the valence s orbitals of the Si atom in the formation of the Si–H bond diminishes with increasing s character of the N → Si bond.

Since the $^{29}Si-^{1}H$ and $^{15}N-^{13}C$ SSCC reflect the *s* character of the corresponding bonds and the ΔE approximation is applicable to them [Eqns. (6) and (7)], the existence of the correlations between $^{1}J_{SiH}$ and $^{1}J_{NC}$, on the one hand, and $^{1}J_{NSi}$, on the other, indicates that the ΔE approximation is valid also for the quantitative interpretation of the constants for the $^{15}N-^{29}Si$ spin–spin coupling across a N → Si bond. Using the model of a S_N2 substitution reaction, this made it possible to obtain equations for the calculation of the length *l* and order *P* of the N → Si bond in solutions:[45]

$$l(\text{N—Si}) = 2.291 - 0.084\ ^{1}J(^{15}\text{N—}^{29}\text{Si}), \quad (14)$$

$$P(\text{N—Si}) = \sqrt{^{1}J(^{15}\text{N—}^{29}\text{Si})/25.1}. \quad (15)$$

We may note that Eqns. (14) and (15) are valid provided that the electronegativity of the substituent R at the Si atom is close to the electronegativity of the H atom. With increase in the electronegativity of the substituent (for example, in the case of R = OMe and Cl), the $^{15}N-^{29}Si$ SSCC acquire values smaller than expected. This has been explained by the tendency of ΔE to increase with increase in the electronegativity of the substituent.

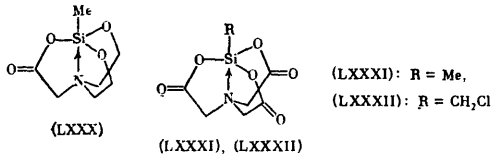
Table 4. The $^{15}N-^{29}Si$ SSCC for the silatranes (LXXII)–(LXXIX) and the silatranones (LXXX)–(LXXXII) at 303 K.[45,47,51]

Compound	Solvent	$^{1}J_{NSi}$, Hz	$\delta(^{15}N)$, p.p.m.	$\delta(^{29}Si)$, p.p.m.
(LXXII)	$CDCl_3$	<0.2	−360.0	−65.4
	DMSO-d_6	0.70	−357.0	−69.8
(LXXIII)	$CDCl_3$	0.55	−357.9	−81.1
	DMSO-d_6	1.47	−355.3	−85.3
(LXXIV)	$CDCl_3$	0.66	−357.2	−80.4
	DMSO-d_6	1.43	−355.0	−83.9
(LXXV)	$CDCl_3$	1.17	−353.1	—
	DMSO-d_6	1.65	−352.3	−95.8
(LXXVI)	$CDCl_3$	1.10	−355.9	−83.5
	acetone-d_6	1.17	−355.1	—
	acetone-d_6 (183 K)	2.20	—	−86.3
	CD_3CN	1.76	—	—
	DMSO-d_6	2.05	−353.9	−86.0
(LXXVII)	$CDCl_3$	1.54	−355.2	−80.2
	DMSO-d_6	2.57	−353.2	−83.1
	CD_3CN	2.4 [48]	—	—
(LXXVIII)	CD_3CN	3.3 [48]	—	—
(LXXIX)	$CDCl_3$	1.98	−348.8 [48]	−85.8
	DMSO-d_6	3.37	−347.8 [48]	−87.0
(LXXX)	DMSO-d_6	0.9	−344.3	−73.0
(LXXXI)	DMSO-d_6	8.2	−319.9	−135.8
(LXXXII)	DMSO-d_6	10.9	−320.6	−144.7

A non-linear dependence of the $^{15}N-^{29}Si$ SSCC on the ^{15}N chemical shift has been observed (Fig. 5). Here too low values of $^{15}N-^{29}Si$ SSCC are observed for R = OMe and Cl. The correlation between $\delta(^{15}N)$ and $^{1}J(^{15}N-^{29}Si)$ can be used to introduce a correction for the electronegativity of the substituent at the Si atom. In particular, this makes it possible to obtain a better agreement between the quantities *l*(N–Si) calculated from the chemical shifts of the ^{15}N atom[50] and $^{1}J_{NSi}$.[45]

(b) Silatronones

The $^{15}N-^{29}Si$ SSCC for the silatronones (LXXX)–(LXXXII)[45,47,51] increase with increase in the number of CO groups in the molecule (Table 4), which can be explained by the increase in strength of the N–Si bond as a consequence of the increase in the polarity of the equatorial Si–O(CO) bonds in silatronones. A pronounced temperature dependence of the $^{15}N-^{29}Si$ and $^{15}N-^{13}C$ SSCC for silatrane-3,7,10-triones has been observed.[47]



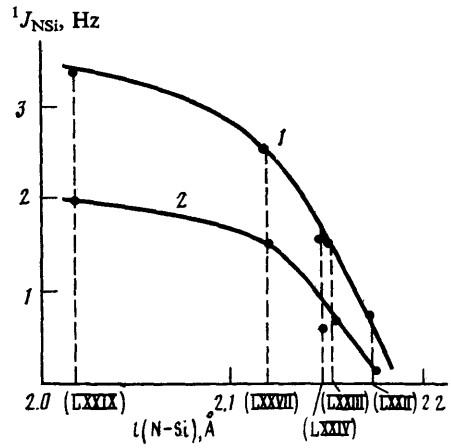


Figure 4. Dependence of the $^{15}N-^{29}Si$ SSCC on the N → Si bond length in the crystals of the silatranes (LXXII)–(LXXIV), (LXXVII), and (LXXIX) in DMSO-d_6 (*1*) and $CDCl_3$ (*2*).[45]

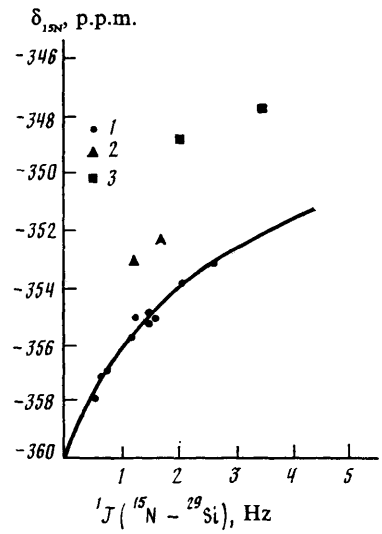


Figure 5. Relation between the ^{15}N chemical shifts and the $^{15}N-^{29}Si$ SSCC for the silatranes (LXXII)–(LXXIX): *1*, R = alkyl, Ph, or CH_2 = CH; *2*, R = OMe; *3*, R = Cl.

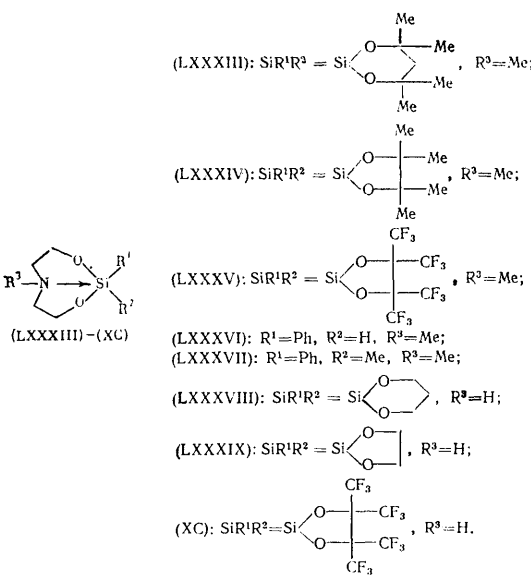
(c) Silocans

The $^{15}N-^{29}Si$ SSCC for the silocans (1,3-dioxa-6-aza-2-silacyclooctanes) (LXXXIII)–(XC) have been measured both for specimens enriched in the ^{15}N isotopes and for specimens with the natural abundances of the isotopes (Table 5). The range of variation of the constant $^1J_{NSi}$ for silocans is much greater than for silatranes, which can be explained by the smaller rigidity and greater variation of the substituents at the nitrogen and silicon atoms in silocans. The sign of $^1K_{NSi}$ for compound (LXXXVI) (Table 5) has been determined. Assuming that $^1J(^{29}Si-^1H) < 0$ and $^2J(^{15}N-Si-^1H) < 0$, it was noted that $^1J(^{15}N-^{29}Si)$ and $^1K_{NSi}$ are positive.

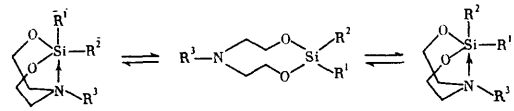
Table 5. The $^{15}N-^{29}Si$ SSCC for the silocans (LXXXIII)–(XC).

Compound	Solvent	*T*, K	$^1J_{NSi}$, Hz (Ref.45)	$\delta(^{15}N)$, p.p.m. (Ref.45)	$\delta(^{29}Si)$, p.p.m. (Ref.47)
(LXXXIII)	$CDCl_3$	238	<0.2	—	−81.1
(LXXXIV)	$CCl_4+C_6D_6$	286	1.85	—	—
	$CDCl_3$	298	2.71	—	−91.5
	DMSO-d_6	314	3.18	—	−92.2
	DMSO-d_6	298	3.30	—	−92.5
(LXXXV)	DMSO-d_6	303	8.36	—	−95.1
(LXXXVI)	acetone-d_6	303	+3.5	—	−57.3
	DMSO-d_6	303	4.3	—	−61.5
(LXXXVII)	acetone-d_6	303	1.2	—	−28.0
Ph (*a*), Me (*e*)	acetone-d_6	193	3.96	—	−30.7
Me (*a*), Ph (*e*)	acetone-d_6	193	1.47	—	−30.2
(LXXXVIII)	DMSO-d_6	303	5.31	−347.0	−106.3
(LXXXIX)	DMSO-d_6	303	6.63	−348.2	−90.2
(XC)	DMSO-d_6	303	10.61	−347.2	−92.4

The characteristic features of the variation of the $^{15}N-^{29}Si$ SSCC for silocans and silatranes are similar. A tendency towards a decrease in $^1J_{NSi}$ with increase in the [strength?] of the N → Si bond in the crystals, with decrease in solvent polarity, and with increase in temperature has also been noted for silocans.[45]



By virtue of the smaller rigidity of silocans in solutions, the dissociation of the N → Si bond, accompanied by the inversion of the eight-membered ring and the positional exchange of substituents at the Si atom, has been observed in these compounds.



Using the dynamic NMR method, this fact makes it possible to determine the free energy of dissociation of the N → Si bond.[45,52] A linear relation between $^1J_{NSi}$ and $\Delta G^{\neq}$ has been observed for compounds (LXXXIII)–(LXXXV) (Table 5):

$$\Delta G^{\neq} = 51.4 + 51.11^1J(^{15}N-^{29}Si) \quad (r = 0.999,\ n = 5). \tag{16}$$

Using Eqn. (16) and assuming that $\Delta G^{\neq} \simeq \Delta H^{\neq}$, the dissociation energy of the N → Si bond in silatranes was determined. The measurement of this characteristic for silatranes by NMR is impossible.[45] A satisfactory agreement was noted between the energies calculated by Eqn. (16) and the values obtained by other methods.

In the general case, the dependence of the $^{15}N-^{29}Si$ SSCC on the nature of the substituents at the N and Si atoms is complex. On the one hand, the strength and *s* character of the N → Si bond increase with increasing electronegativity of the substituents at the Si atom [52] and the $^{15}N-^{29}Si$ SSCC tends to increase. On the other hand, as a result of the increase under these conditions of the electron density on the Si atom and of its decrease on the nitrogen atom, the difference between the energies of the occupied and unoccupied MO rises (ΔE increases), which leads in its turn to some decrease in the $^{15}N-^{29}Si$ SSCC. Thus, one can explain, for example, the higher values of $^1J_{NSi}$ for compounds (LXXXVI) and (LXXXVII) compared with (LXXXIII) and (LXXXIV) (Table 5).

V. Germanium-73

The ^{73}Ge nucleus is exceptionally "unsuitable" for the observation of scalar spin–spin coupling. The presence of a relatively large quadrupole moment and the low frequency of the observation greatly complicate the recording of the ^{73}Ge NMR spectra. As a consequence of the effective relaxation via the quadrupolar mechanism, the direct observation of the SSCC is possible only for highly symmetrical compounds. As a result of the low value of $\delta(^{73}Ge)$ (Table 1) the observed SSCC involving the ^{73}Ge nuclei have low values.[53] The expected values of the $^{14}N-^{73}Ge$ and $^{15}N-^{73}Ge$ SSCC range from 0 to 11 and 15 Hz respectively.

VI. Tin-117 and tin-119

1. Coupling across a covalent bond

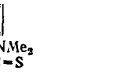
(a) Amines

The first studies on the $^{15}N-^{119}Sn$ SSCC showed[54–56] that the constants $^1K_{NSn}$ can be both positive and negative. This is associated with the relatively large atomic radius and polarisability of Sn, which leads to more negative values of π_{NSn} compared with π_{NSi}. The decrease in the degree of overlap of the valence *s* orbitals of the N and Sn atoms (β_{NSn}) compared with β_{NSi} leads to a more pronounced dependence of the sign and absolute value of $^1K_{NSn}$ on

the properties of the substituents at the N and Sn atom. For this reason, the ΔE approximation is inapplicable to the $^{15}N-^{119}Sn$ SSCC and they must be interpreted on the basis of Eqn. (4).

Subsequent systematic studies of the $^{15}N-^{119}Sn$ SSCC showed[57-60] that the quantity $^1K_{NSn}$ depends in a complex manner on the properties of the substituents at the N and Sn atoms. It has been suggested that β_{NSn} increases with the increasing electronegativity of the substituent. As a result, π_{NSn} becomes more positive and the observed values of $^1J_{NSn}$ become positive, having passed through zero. Thus Eqn. (4) makes it possible to describe at least qualitatively the trend in the variation of $^1K_{NSn}$, in particular the change in the sign of the $^1K_{NSn}$ when H or $SnMe_3$ is substituted by the more electronegative Me or PMe_2 group (Table 6).

Table 6. The $^{15}N-^{119}Sn$ SSCC for tin derivatives.[55-62,66-71]

Compound	Chemical formula	Solvent	$^1J^*_{NSn}$, Hz	$\delta(^{15}N)$, p.p.m.	$\delta(^{119}Sn)$, p.p.m.
(XCI)	$(Me_3Sn)_3N$	C_6D_6	(—) 82.5	−392.2	—
			(—) 79.6	—	86.3
(XCII)	$(Me_3Sn)_3NGeMe_3$	C_6D_6	(—) 68.4	—	73.3
(XCIII)	$(Me_3Sn)_2NBu^t$	C_6D_6	(—) 38.0	−326.7	40.7
(XCIV)	$(Me_3Sn)_2NPh$	C_6D_6	−41.4	−333.9*2	61.0
(XCV)	$Me_3SnNHPh$	C_6D_6	−26.5	−327.9*2	46.4
(XCVI)	Me_3SnNEt_2	C_6D_6	<1	—	60.0
(XCVII)	$Me_3SnNMePh$	C_6D_6	+2.2	−331.1*2	73.0
(XCVIII)	$Me_2Sn(NMePh)_2$	C_6D_6	+24.0	−323.9*2	30.5
(XCIX)	$MeSn(NMePh)_3$	C_6D_6	+87.0	−321.6*2	−66.0
(C)	$Sn(NMePh)_4$	C_6D_6	+175.0	−319.9*2	−175.6
(CI)	$Me_2SnN[P(S)Me_2]Ph$	C_6D_6	−21.0	−307.8*2	66.0
(CII)	$Me_2SnN(PMe_2)Ph$	C_6D_6	+9.5	−332.8*2	63.5
(CIII)		C_6D_6	6.4	−216.2	72.9
(CIV)	$(Me_3Sn)_2N-NMe_2$	C_6D_6	46.0	—	49.0
(CV)	$(Bu^n)_3SnN=C=S$	C_6D_6	(—) 307.0	—	—
(CVI)	$(C_6H_{11})_3SnN=C=S$	C_6D_6	(—) 190*3	−264.2(¹⁴N)	−3.2
(CVII)	$Sn(N=C=S)_6^{2-}$	CH_3OH	(+) 210*3	−227(¹⁴N)	−842.0
(CVIII)	$Sn[N(SiMe_3)_2]_2$	C_6D_6	(—) 344*3	−239.2	776
(CIX)	$Et_3P-Pt(Cl)(SnCl_3)-NH_2C_6H_4Cl\text{-}n$	C_6D_6	9 ($^2J_{NSn}$)	−344.1	−243
(CX)	$Et_3P-Pt(Cl)(SnCl_3)-NH_2C_6H_4Me\text{-}p$	C_6D_6	10 ($^2J_{NSn}$)	344.7	−248
(CXI)	$Bu^tSn(OCH_2CH_2)_3N$	$CDCl_3$	64.9	—	−245.5
		(263K)	69.9	−365.3	−246
(CXII)	$MeSn(OCH_2CH_2)_3N$*4 (A), (B), and (C)	$CDCl_3$	75.6	−354	−537
		(263K)	110.0	−360	−353
(CXIII)	$Bu^t_2Sn(OCH_2CH_2)NH$	C_6D_6	37.1	—	—
(CXIV)	$Sn(OCH_2CH_2)_2NMe$	$CDCl_3$	109.0	—	−303
		DMSO-d_6	117.5	—	—
(CXV)	$(CO)_5CrSn(OCH_2CH_2)_2NMe$	$CDCl_3$	173.3	−340.3	−27.0
(CXVI)	$(CO)_5MoSn(OCH_2CH_2)_2NMe$	$CDCl_3$	167.8	−345.7	−88.3
(CXVII)	$(CO)_5WSn(OCH_2CH_2)_2NMe$	$CDCl_3$	161.1	−346.3	−208.2

*1 The postulated sign is indicated in brackets (if the sign is not indicated, this means that it is unkown; in other cases, the sign has been established experimentally).

*2 The literature data relative to $NMe_4^+I^-$ have been recalculated in terms of the $MeNO_2$ scale in accordance with the relation $\delta[^{15}N(MeNO_2)] = \delta[^{15}N(NMe_4^+I^-)] - 337.3$.

*3 The constants were calculated by multiplying $^1J(^{14}N-^{119}Sn)$ by $\gamma(^{15}N)/\gamma(^{14}N)$.

*4 Data for the three isomers (A), (B), and (C) are presented.

It has been suggested that, for low values of $^1K_{NSn}$, the latter may be influenced significantly by steric factors, which in the general case complicates the determination of quantitative relations. This explains the more negative value of $^1K_{NSn}$ for $Me_3SnN[P(S)Me_2]Ph$ compared with $Me_3SnN(PMe_2)Ph$,[57] although the first substituent has a higher electronegativity. However, one cannot rule out in this instance also the influence by the LEP of the P^{III} atom on the $^{15}N-^{119}Sn$ SSCC.

The $^{15}N-^{119}Sn$ and $^{31}P-^{119}Sn$ SSCC have been compared qualitatively.[57] It has been shown that, on the whole, the constants $^1K_{PSn}$ have more negative values than the constants $^1K_{NSn}$, since the LEP of the P^{III} atom has a greater amount of *s* character.

(b) Isothiocyanates

Direct observation of the $^{14}N-^{119}Sn$ SSCC is possible for the isothiocyanates (CVI) and (CVII) (Table 6) [61,62] because of the relatively slow relaxation of the ^{14}N nuclei as a result of the high symmetry of the charge distribution around the nitrogen atom.

A multiplet made up of 11 lines (13 have been predicted theoretically), with the relative intensities 6:14:36:67:90:100:90:67:36:14:6 and a splitting of 150 Hz as a result of the $^{14}N-^{119}Sn$ spin–spin coupling, has been observed[62] in the ^{119}Sn NMR spectrum of compound (CVII). The ratios of the line intensities of the multiplet, the high value of the $^{14}N-^{119}Sn$ SSCC, and the chemical shifts of the ^{14}N and ^{119}Sn nuclei confirm the hexacoordinate structure of the ion, demonstrating that the Sn atom is linked to the nitrogen and not the sulphur atom and showing that the intermolecular exchange of the NCS groups is slow (on the NMR time scale). All this demonstrates that the SSCC $^1J_{NSn}$ have a high information content.

$^{14}N-^{119}Sn$ spin–spin coupling has also been observed in the ^{119}Sn NMR spectrum of compound (CVI). In this case the ^{119}Sn signal was observed in the form of a well resolved triplet with a splitting of 136 Hz.

The $^{14}N-^{119}Sn$ SSCC cannot be observed directly for compound (CV),[62] which is extremely unexpected. It has been noted that this is associated with the rapid quadrupolar relaxation of the nitrogen atom in compound (CV) (T_{qN} = 0.15 ms) compared with compounds (CVI) and (CVII) (T_{qN} = 35 and 50 ms respectively). Only the $^{15}N-^{119}Sn$ SSCC has been measured for compound (CV).

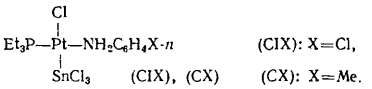
It is noteworthy that the $^1K_{NSn}$ for the isothiocyanates investigated have comparable values. Since the sign of these SSCC has not been established, in order to account for this phenomenon it is reasonable to assume that $^1K_{NSn} > 0$ for compound (CVII) and $^1K_{NSn} < 0$ for compounds (CV) and (CVI) (Table 6).

(c) Sn^{II} derivatives

Hitherto only one $^1J_{NSn}$ SSCC has been determined for Sn^{II} compounds. A signal in the form of a poorly resolved quintet as a consequence of the $^{14}N-^{119}Sn$ spin–spin coupling with J = 245 ± 10 Hz has been observed[58] in the ^{119}Sn spectrum of compound (CVIII) at 80 °C. This SSCC represents at the present time the highest absolute value of $^1K_{NSn}$. It is reasonable to assume that $^1K_{NSn} < 0$ [$^1J(^{14}N-^{119}Sn) > 0$]. Such a negative value of $^1K_{NSn}$ can be accounted for by the high amount of *s* character of the LEP of the Sn(II) atom, which is indicated also by structural data.[63] In particular, the $N-Sn^{II}$ bonds are on average longer than the $N-Sn^{IV}$ bonds and the values of β_{NSn} are therefore smaller for Sn^{II}. This leads to more negative values of π_{NSn} and ultimately to negative values of $^1K_{NSn}$ for Sn^{II} derivatives. It is noteworthy that a similar phenomenon is known also for phosphorus derivatives, i.e. $^1K_{NP} > 0$ for P^V and $^1K_{NP} < 0$ for P^{III}.[64]

(d) Long range SSCC

Long range SSCC has so far been little studied. Using specimens enriched in the ^{15}N isotope, it has been observed[65] that the constants $^2J(^{15}N-^{119}Sn)$ are 9–10 Hz for the platinum complexes (CIX) and (CX).



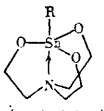
(CIX), (CX) (CIX): X=Cl, (CX): X=Me.

Presumably these SSCC can be used to determine the *cis*- and *trans*-configurations of the ligands in similar complexes, by analogy with the widely known variation of the $^2J(^{31}P-^{119}Sn)$ SSCC.[66]

2. Coupling across the coordinate bond

(a) Sn^{IV} derivatives

The $^{15}N-^{117}Sn$ and $^{15}N-^{119}Sn$ SSCC have been measured for ^{15}N-enriched specimens and have been used mainly to demonstrate the existence of the N → Sn bond in solutions of the test compounds (Table 6). The first constants for the $^{15}N-^{117/119}Sn$ across a coordinate bond were measured for the stannatranes (CXI) and (CXII):

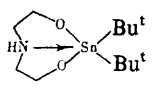


(CXI): R = Bu^t
(CXII): R = Me.

(CXI), (CXII)

Three sets of signals have been observed in the ^{15}N and ^{119}Sn NMR spectra of 1-methylstannatrane (CXII), which was explained by the formation of trimers in solution. The observed SSCC indicates the existence of the N → Sn bond in all the isomers and reflects quantitatively its strength. It has been noted that, in conformity with Bent's rules, the smallest $^{15}N-^{117/119}Sn$ SSCC are characteristic of the largest $^{119}Sn-^{13}C$ and $^{119}Sn-C-^1H$ SSCC [isomer (A)]. This indicates a redistribution of the *s* character of the bonds in the axial fragment of the molecule. A significant temperature dependence of the $^{15}N-^{117/119}Sn$ SSCC for the given compounds has not been observed.

Lower values of the $^{15}N-^{117/119}Sn$ SSCC have been noted for the stannocan (CXIII), which probably indicates a weaker N → Sn bond.[69]

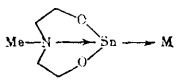


(CXIII)

It has been noted that the $^{15}N-^{117/119}Sn$ SSCC decrease as the temperature is raised. This has been explained by the dissociation of the N → Sn bond at higher temperatures.

(b) Derivatives of Sn^{II}

The $^{15}N-^{117/119}Sn$ SSCC for the Sn^{II} stannocans (CXIV)–(CXVII) greatly exceed the values observed for the analogous Sn^{IV} derivative (CXIII).



(CXIV)–(CXVII)

M = LEP(CXIV), $Cr(CO_5)$(CXV), $Mo(CO)_5$(CXVI), $W(CO)_5$(CXVII).

This is partly associated with the greater strength of the N → Sn bond in Sn^{II} derivatives.[70,71] However, one should note that compounds (CXIII) and (CXIV) have comparable N → Sn bond dissociation energies, whereas the corresponding SSCC differ significantly.

It has been noted that the $^{15}N-^{117/119}Sn$ SSCC increase on passing to more polar solvents.[70]

VII. Lead-207

The $^{15/14}N-^{207}Pb$ SSCC have been investigated in less detail than the constants involving ^{29}Si and $^{117/119}Sn$. It is of interest to note that almost all compounds with the exception of compound (CXX) (Table 7) have been investigated for the natural abundances of the isotopes, which was facilitated by the high natural abundance of the ^{207}Pb isotope (22.6%). In certain cases the $^{14}N-^{207}Pb$ SSCC were measured directly in the ^{207}Pb spectra.[57,58]

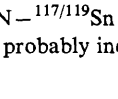
Table 7. The $^{14}N-^{207}Pb$ and $^{15}N-^{207}Pb$ SSCC.[57–59,72–75]

Compound	Chemical formula	Solvent	$^1J(^{14}N-^{207}Pb)/^1J(^{15}N-^{207}Pb)$, Hz	δ(^{15}N), p.p.m.	δ(^{207}Pb) p.p.m.
(CXVIII)	$Me_3PbN(SnMe_3)_2$	C_6D_6	(—) 170/238*1	—	242.0
(CXIX)	$(Me_3Pb)_2NSnMe_3$	C_6D_6	(—) 170/238*1	—	268.0
(CXX)	$Me_3PbNMePh$	C_6D_6	—/+261 (5)	—321.8*2	226.5
(CXXI)	Me_3PbN 	C_6D_6	—/(+) 290	—206.7	204.0
(CXXII)	$Pb[N(SiMe_3)_2]_2$	C_6D_6	(—) 300/(421) *1	—209.1	4916
(CXXIII)	$Pb(Cydta)]^{2-}$ *3	H_2O/D_2O	—/187.5	—312.3	—
		H_2O/D_2O	—/188.3	—	—
(CXXIV)	$[Pb(L)][NO_3]_2$ *4	DMSO-d_6	—/207.5	—318.8	—
		DMSO-d_6	—/19.8	—325.5	—

*1 Calculated by multiplying $^1J(^{14}N-^{207}Pb)$ by $\gamma(^{15}N)/\gamma(^{14}N)$.

*2 The literature data relative to $NMe_4^+I^-$ have been recalculated in terms of the $MeNO_2$ scale in accordance with the relation $\delta[^{15}N(MeNO_2)] = \delta[^{15}N(NMe_4^+I^-)] - 337.3$.[7]

*3 Cydta = *trans*-1,2-diaminocyclohexane-*NNNN'*-tetraacetate.

*4 L = 

It has been established[72] that the SSCC $^1K_{NPb}$ have high negative values. This is associated with the high polarisability of the Pb atom and the weak overlap of the valence *s* orbitals of the N and Pb atoms. The values of $^1K_{NPb}$ for Pb^{IV} derivatives are comparable in magnitude despite the significant variation of the nature of the substituents at the nitrogen atom. This has been explained by the fact that the high and negative values of π_{NPB} are less sensitive to the variation of the character of the chemical bond than the quantity π_{NSn}.

The highest absolute value of $^1K_{NPb}$, which is probably negative, has been observed for a Pb^{II} derivative [compound (CXXII) in Table 7]. As for the Sn analogue, this can be explained by the low value of β_{NPb} and the large amount of *s* character of the LEP of the Pb^{II} atom.

The $^{15}N-^{207}Pb$ SSCC have been measured for two Pb coordination compounds, namely (CXXIII) and (CXXIV). The marked difference between the $^{15}N-^{207}Pb$ SSCC for the equatorial and axial bonds in compound (CXXIV) led to some misunderstanding,[73-75] since in crystals the lengths of these bonds differ little (2.43 and 2.47 Å for the equatorial bonds and 2.47 and 2.48 Å for the axial bonds[73,74]). It has been suggested that the frequency 207.5 Hz corresponds to the normal equatorial bonds and 19.8 Hz corresponds to bonds in the highly distorted axial fragment.

In our view, the SSCC data reflect the real bonding situation in the given compound in solution, i.e. the nature of the equatorial and axial bonds (length and strength) in solutions is significantly different in contrast to their apparent equivalence in crystals. In particular, this is indicated by the valence isomerisation process observed in solutions of compound (CXXIV),[73-75] which has an extremely high activation energy ($\Delta H^{\neq} = 100 \pm 10$ kJ mol^{-1}, $\Delta S^{\neq} = 105 \pm 20$ J mol^{-1} K^{-1}) at 298 K, probably leading to the averaging of the ^{15}N chemical shifts and SSCC. Some increase in the $^{15}N-^{207}Pb$ SSCC in the case of equatorial bonds in compound (CXXIV) compared with the analogous SSCC observed for the complex (CXXIII) agrees well with the shorter $Pb-N_e$ distance in the crystals of compound (CXXIV) compared with (CXXIII) (Table 7).

VIII. Conclusion

The $^{15}N-X$ (X = ^{29}Si, $^{117/119}Sn$, ^{207}Pb) SSCC make it possible to obtain information about the electronic and steric structures of nitrogen-containing Group IV organoelement compounds. A dependence of the $^{15}N-X$ SSCC on the hybridisation of the N and X atoms, their geometry, the *s* character of the N–X bond, its polarity and length, and the degree of $d_\pi-p_\pi$ conjugation between the N and X atoms has been observed for compounds with a covalent N–X bond. At the same time, these constants must be interpreted taking into account the position of the element X in the Periodic System. With increase in the atomic number of X, the constant $^1K_{NX}$ becomes more negative, which is associated with the increasing polarisability of the X atom. Thus all the $^1K(^{15}N-^{29}Si)$ SSCC known hitherto are positive, the constants $^1K(^{15}N-^{117/119}Sn)$ have both positive and negative values, while the constants $^1K(^{15}N-^{207}Pb)$ have only negative values. The highest absolute values of $^1J(^{15}N-X)$ increase in the same sequence: 47.6 Hz (X = ^{29}Si, 344 Hz for ^{119}Sn, and 421 Hz for ^{207}Pb. The constants $^1K(^{15}N-X)$ for the X(II) derivatives are as a rule more negative than the constant ^1K for X(IV). This is associated with the fact that the valence *s* shells in X(II) are less accessible compared with the *s* shells in X(IV), i.e. are less involved in the formation of chemical bonds with the nitrogen atom. With increase in the number of electro-negative substituents at the X atom, the constants $^1K(^{15}N-X)$ become more positive, since the polarisability of the X atom then diminishes and the amount of *s* character of the N–X bond increases. Hitherto the long-range $^{15}N-X$ SSCC have been hardly investigated.

The $^{15}N-X$ SSCC for the coordinate N → X bond make it possible to obtain very valuable information about the nature of the bond in solutions. In many instances, these SSCC have been used as direct evidence for the existence of the N → X bond in solutions. Quantitative relations have been obtained between the $^{15}N-^{29}Si$ SSCC and the length, dissociation energy, and the order of the N → Si bond. However these relations are valid only for related compounds. A correspondence between the change in $^1J(^{15}N-X)$ and the properties of the N → X bond have been observed also for X = $^{117/119}Sn$ and ^{207}Pb. The $^{15}N-X$ SSCC then as a rule increase with increase in the strength of the N → X bond. This is one of the reasons why we have suggested in the present review that all the constants $^1K(^{15}N-X)$ for spin–spin coupling across a N → X coordinate bond are positive. However, in order to justify this hypothesis, it is essential to carry out additional studies (in the first place theoretical studies), since the mechanism of the spin–spin coupling across a coordinate bond remains obscure.

At the present time the measurement of the $^1J(^{15}N-X)$ SSCC for the natural abundances of isotopes presents no difficulties in most cases. The recently developed ultrahigh resolution NMR method[76-78] has led to the possibility of measuring the long-range $^{15}N-X$ SSCC for the natural abundances of the isotopes.[79,80] Hence one may expect that the study of these constants and their employment in structural research will expand.

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