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Indirect Nuclear Spin–Spin Coupling Constants of Nitrogen-15 to Silicon-29 in Silylamines

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The ^{15}N–^{29}Si spin–spin coupling constants in silylamines have been measured from ^{29}Si satellites in their natural abundance ^{15}N n.m.r. spectra in an INEPT sequence for accumulation of signals and interpreted in terms of Fermi-contact interaction; the sensitivity of $^1J(^{15}N\text{–}^{29}Si)$ to d_π–p_π bonding was noted.

Spin–spin coupling is a valuable source of information on the nature of chemical bonds in and the structure of compounds in solutions.[1] To investigate ^{15}N–X spin-spin coupling (where X is a group 4A element), ^{15}N-enriched samples are generally used. For instance, ^{15}N–^{13}C coupling has been studied in detail in this manner.[2] Recently, $^1J(^{15}N\text{–}^{119}Sn)$ and $^1J(^{15}N\text{–}^{209}Pb)$ have been measured and their properties studied in several compounds.[3] $^1J(^{15}N\text{–}^{29}Si)$ has not been examined systematically until recently. The present communication reports a study of ^{15}N–^{29}Si coupling in silylamines at the natural abundance level of the ^{15}N isotope. $^1J(^{15}N\text{–}^{29}Si)$ values were measured from ^{29}Si satellites in ^{15}N n.m.r. spectra (Figure 1) using the INEPT sequence for accumulation of signals.[4]

^{15}N–X Spin-spin coupling constants are generally interpreted by assuming a dominant Fermi-contact interaction.[2,3] This is, in part, indicated by the fact that the reduced constants $^1K(^{15}N\text{–X}) > 0$ for X = ^{13}C, ^{29}Si, or ^{119}Sn.[2,3,5] The negative $^1K(^{15}N\text{–X})$ values for X = ^{209}Pb and, in some cases, ^{119}Sn are ascribed to the small values of the N–X s-overlap integral (β_{NX}).[3] For increasing electronegativity of substituents on N and X there is an increase in β_{NX} to give more positive $^1K(^{15}N\text{–X})$ values.[3] Therefore, the systematic increase in $^1J(^{15}N\text{–}^{29}Si)$ with increasing electronegativity of substituents on N and Si within the series of silylamines in Table 1 suggests that $^1K(^{15}N\text{–}^{29}Si) > 0$ for these compounds. This also indicates that the s-character of the N–Si bond also increases in the same way in this series.[6]

The exception to this rule, *i.e.*, that $^1J(^{15}N\text{–}^{29}Si)$ values for NPh derivatives are less than those of their NBu^t analogues, suggests that the coupling constant is sensitive to d_π–p_π bonding between the lone electron pair (lp) on the nitrogen atom and the vacant d-orbitals on Si. The d_π–p_π bonding affects $^1J(^{15}N\text{–}^{29}Si)$ only to the extent that it affects β_{NSi}.[7] Therefore, the differences in $^1J(^{15}N\text{–}^{29}Si)$ of the NBu^t and NPh derivatives (where for the NPh compounds there is a stronger competitive conjugation of the nitrogen lone pair with the phenyl ring) are small.

The values for $PhHNSi(OEt)_3$ (compound 22) in different solvents (Table 1) show that the effect of these solvents on $^1J(^{15}N\text{–}^{29}Si)$ is negligible. A slight decrease in the ^{15}N–^{29}Si

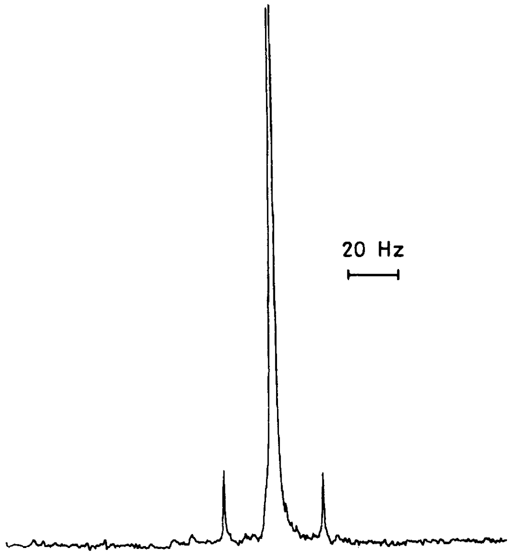

Figure 1. ^{29}Si Satellites in the ^{15}N n.m.r. spectra of a 50% solution of $(PhNH)_2Si(OEt)_2$ in $CDCl_3$ (15 mm sample tube, INEPT pulse sequence, overnight run, relaxation time 2 s).

Table 1. N.m.r.[a] parameters for 50% solutions of silylamines[b] in $CDCl_3$.

No.	Compound	$^1J(^{15}N\text{–}^{29}Si)$/ (±0.1) Hz	$\delta(^{15}N)$ (±0.1) p.p.m.	No.	Compound	$^1J(^{15}N\text{–}^{29}Si)$/ (±0.1) Hz	$\delta(^{15}N)$ (±0.1) p.p.m.
1[c]	$N(SiH_3)_3$	+6	—	13	$PhHNSiHMe_2$	16.4	−320.4
2[d]	$HN(SiMe_3)_2$	13.4	−354.2	14[d]	$PhHNSiMe_2Ph$	17.3	−317.7
3[d]	$(HNSiMe_2)_4$	16.9	−341.7	15	$PhHNSiMePh_2$	18.3	−319.5
4	$Bu^tHNSiMe_3$	17.2	−323.9	16	$(PhHN)_2SiMe_2$	19.9	−312.7
5[d]	$Bu^tHNSiMe_2Ph$	18.8	−325.7	17	$PhHNSi(OEt)Me_2$	19.9	−310.8
6[d]	$Bu^tHNSiMePh_2$	19.8	−327.3	18	$(PhHN)_3SiMe$	25.4	−313.1
7	$(Bu^tHN)_2SiMe_2$	20.8	−317.4	19	$(PhHN)_2Si(OEt)Me$	27.3	−313.5
8	$Bu^tHNSi(OEt)Me_2$	21.5	−317.6	20	$PhHNSi(OEt)_2Me$	29.0	−314.6
9	$Bu^tHNSi(OEt)_2Me$	30.9	−321.5	21	$(PhHN)_2Si(OEt)_2$	40.1	−319.2
10	$(Bu^tHN)_2Si(OEt)_2$	39.8	−324.9	22	$PhHNSi(OEt)_3$	43.9	−322.3
11	$Bu^tHNSi(OEt)_3$	44.6	−330.4	[e]	,,	43.7	−321.5
12	$PhHNSiMe_3$	15.7	−314.9	[f]	,,	43.2	−320.7

[a] ^{15}N N.m.r. spectra were recorded on a Bruker WM-360 spectrometer, at 36.5 MHz, INEPT pulse sequence, sweep width = 3600 Hz, 4 K data points, relaxation time 2 s, number of scans = 2000—4000, digitalization 0.11 Hz per point, temperature 303 K. [b] Silylamines 4—22 were synthesized from the reactions of excess of the amines with the corresponding chlorosilanes, compounds 2 and 3 were commercial products. [c] Taken from ref. 5. [d] In $[^2H_6]$acetone. [e] In $[^2H_{12}]$cyclohexane. [f] In $[^2H_6]$dimethyl sulphoxide.

spin–spin coupling with increasing solvent polarity may be accounted for in terms of co-ordination of the solvent to Si.

$^1J(^{15}N-^1H)$ shows little dependence on the substituent on Si, however, it is significantly increased by an increase in the electronegativity of substituents on N so that SiR_3 (67) < Bu^t (73—75) < Ph (76—79 Hz). The similarity of the values of these constants for the NPh an NBu^t derivatives suggests a similar (planar) configuration of the nitrogen atom in these compounds in solution.[2]

Changes in the shielding of ^{15}N nuclei correspond to those found earlier in silylamines.[8]

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