

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

Eriks Kupče, Edvards Liepiņš, Olga Pudova, and Edmunds Lukevics

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

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 $^1J(^{15}\text{N}-^{29}\text{Si})$ to $d_{\pi}-p_{\pi}$ 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, $^1J(^{15}\text{N}-^{119}\text{Sn})$ and $^1J(^{15}\text{N}-^{209}\text{Pb})$ have been measured and their properties studied in several compounds.³ $^1J(^{15}\text{N}-^{29}\text{Si})$ 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. $^1J(^{15}\text{N}-^{29}\text{Si})$ 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 $^1K(^{15}\text{N}-\text{X}) > 0$ for X = ^{13}C , ^{29}Si , or ^{119}Sn .^{2,3,5} The negative $^1K(^{15}\text{N}-\text{X})$ 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 $^1K(^{15}\text{N}-\text{X})$ values.³ Therefore, the systematic increase in $^1J(^{15}\text{N}-^{29}\text{Si})$ with increasing electronegativity of substituents on N and Si within the series of silylamines in Table 1 suggests that $^1K(^{15}\text{N}-^{29}\text{Si}) > 0$ 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 $^1J(^{15}\text{N}-^{29}\text{Si})$ values for NPh derivatives are less than those of their NBU^t analogues, suggests that the coupling constant is sensitive to $d_{\pi}-p_{\pi}$ bonding between the lone electron pair (lp) on the nitrogen atom and the vacant d-orbitals on Si. The $d_{\pi}-p_{\pi}$ bonding affects $^1J(^{15}\text{N}-^{29}\text{Si})$ only to the extent that it affects β_{NSi} .⁷

Therefore, the differences in $^1J(^{15}\text{N}-^{29}\text{Si})$ 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 $^1J(^{15}\text{N}-^{29}\text{Si})$ is negligible. A slight decrease in the ^{15}N - ^{29}Si

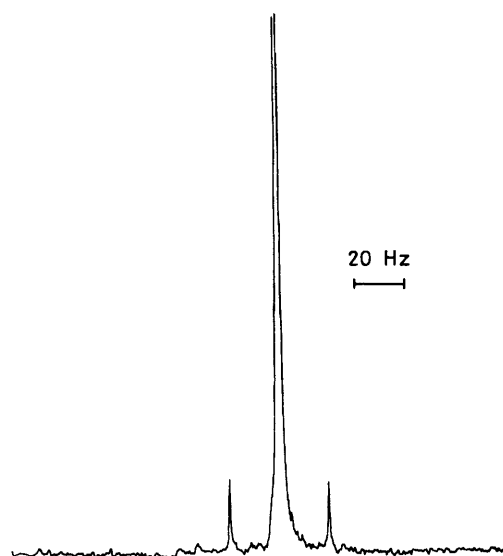


Figure 1. ^{29}Si Satellites in the ^{15}N n.m.r. spectra of a 50% solution of $(\text{PhNH})_2\text{Si}(\text{OEt})_2$ in CDCl_3 (15 mm sample tube, INEPT pulse sequence, overnight run, relaxation time 2 s).

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

No.	Compound	$^1J(^{15}\text{N}-^{29}\text{Si})/$ (± 0.1) Hz	$\delta(^{15}\text{N})$ (± 0.1) p.p.m.	No.	Compound	$^1J(^{15}\text{N}-^{29}\text{Si})/$ (± 0.1) Hz	$\delta(^{15}\text{N})$ (± 0.1) p.p.m.
1 ^c	$\text{N}(\text{SiH}_3)_3$	+6	—	13	PhHNSiHMe ₂	16.4	-320.4
2 ^d	$\text{HN}(\text{SiMe}_3)_2$	13.4	-354.2	14 ^d	PhHNSiMe ₂ Ph	17.3	-317.7
3 ^d	$(\text{HNSiMe}_2)_4$	16.9	-341.7	15	PhHNSiMePh ₂	18.3	-319.5
4	Bu ^t HNSiMe ₃	17.2	-323.9	16	$(\text{PhHN})_2\text{SiMe}_2$	19.9	-312.7
5 ^d	Bu ^t HNSiMe ₂ Ph	18.8	-325.7	17	PhHNSi(OEt)Me ₂	19.9	-310.8
6 ^d	Bu ^t HNSiMePh ₂	19.8	-327.3	18	$(\text{PhHN})_3\text{SiMe}$	25.4	-313.1
7	$(\text{Bu}^t\text{HN})_2\text{SiMe}_2$	20.8	-317.4	19	$(\text{PhHN})_2\text{Si}(\text{OEt})\text{Me}$	27.3	-313.5
8	Bu ^t HNSi(OEt)Me ₂	21.5	-317.6	20	PhHNSi(OEt) ₂ Me	29.0	-314.6
9	Bu ^t HNSi(OEt) ₂ Me	30.9	-321.5	21	$(\text{PhHN})_2\text{Si}(\text{OEt})_2$	40.1	-319.2
10	$(\text{Bu}^t\text{HN})_2\text{Si}(\text{OEt})_2$	39.8	-324.9	22	PhHNSi(OEt) ₃	43.9	-322.3
11	Bu ^t HNSi(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 $[\text{H}_6]$ acetone. ^e In $[\text{H}_{12}]$ cyclohexane. ^f In $[\text{H}_6]$ dimethyl sulphoxide.

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

$^1J(^{15}\text{N}-^1\text{H})$ 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 and 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

Received, 21st October 1983; Com. 1383

References

- 1 W. McFarlane, *Q. Rev., Chem. Soc.*, 1969, **2b**, 187.
 - 2 W. Freyer, *Z. Chem.*, 1981, **21**, 47; G. C. Levy and R. L. Lichter, 'Nitrogen-15 NMR Spectroscopy,' Wiley, New York, 1979, Ch. 4; G. J. Martin, M. L. Martin, and J. P. Gouesnard, ' ^{15}N -NMR Spectroscopy,' Springer-Verlag, Berlin, 1981, pp. 195—197.
 - 3 J. D. Kennedy, W. McFarlane, and G. S. Pyne, *J. Organomet. Chem.*, 1980, **195**, 285.
 - 4 G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, 1979, **101**, 160.
 - 5 D. W. N. Anderson, J. E. Bentham, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1973, 1215.
 - 6 H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.
 - 7 L. M. Venanzi, *Chem. Br.*, 1968, **4**, 162.
 - 8 M. L. Filleux-Blanchard and N. D. An, *Org. Magn. Reson.*, 1979, **12**, 12.
-