CORRELATION BETWEEN ^{29}Si-^{15}N SPIN-SPIN COUPLING CONSTANTS AND THE ^{15}N-NMR CHEMICAL SHIFTS IN SILATRANES

É. L. Kupche and É. Lukevits

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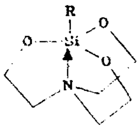
A nonlinear correlation has been found between the ^{29}Si-^{15}N spin-spin coupling constants and the ^{15}N-NMR chemical shifts in silatranes. The dependence has been used to calculate corrections to the spin-spin coupling constant for the electronegativity of a substituent on the silicon atom. This has allowed the previously obtained data on the length and order of the N → Si coordinate bond for silatranes in solutions to be refined.

It was shown earlier [1-10] that the ^{29}Si-^{15}N spin-spin coupling constants (SSCC) ${}^1J_{SiN}$ afford valuable information about the spatial and electronic structure of nitrogen-containing, organosilicon compounds in solutions. In particular, on the basis of the spin-spin coupling constant, ${}^1J_{SiN}$, through the N → Si coordinate bond, the length [Eq. (1)] and order (Eq. (2)] of this bond in silatranes I and related compounds have been determined [5, 6]. The ^{15}N chemical shifts (CS) are also used to estimate the N → Si bond length (ℓ_{NSi}) in silatranes [11] [Eq. (3)]. This assumes the existence of a specific interaction between the ^{15}N CS (^{1}N) and ${}^1J_{SiN}$.



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However, with some silatranes, the values of the N → Si coordinate bond lengths predicted from the ^{15}N CS and the ^{29}Si-^{15}N SSCC differ quite substantially. In the present work, we have studied the interaction between the ^{15}N CS and ${}^1J_{SiN}$ in compounds I and consider the reasons for the discrepancy in the ℓ_{NSi} values predicted using Eqs. (1) and (3).

$$l_{NSi} = 2{,}291 - 0{,}084\ ({}^1J_{SiN})^{1/2}; \quad (1)$$

$$P_{NSi} = ({}^1J_{SiN}/25{,}1)^{1/2}; \quad (2)$$

$$l_{NSi} = -4{,}20 - 0{,}018\ \delta_N. \quad (3)$$

The NMR data and the length of the N → Si coordinate bonds for silatranes I in solution are presented in Table 1. We have shown previously [5] that the value of ${}^1J_{SiN}$ depends not only on the distance between the N and Si atoms, but on the electronegativities (EN) of the substituents on these atoms as well. For this reason, Eq. (1) is only applicable, strictly speaking to compounds (silatranes) in which the EN of substituents on the N and Si atoms do not differ substantially from that in the 1-hydrosilatrane used in constructing the model [5].

From the dependence between ${}^1J_{SiN}$ and δ_N shown in Fig. 1, it follows that for derivatives of I with R = H, Alk, $CH_2{=}CH$, and Ph; i.e., in the case of compounds with substituents of approximately the same EN on the Si atom, there is a general, nonlinear dependence that can be approximated by Eq. (4):

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TABLE 1. ^{15}N Chemical Shifts, ^{29}Si–^{15}N Spin-Spin Coupling Constants, and Calculated N → Si Bond Lengths and Orders for Silatranes in Solutions*

R	Solvent	$^1J_{SiN}$, Hz	δ_N, ppm	l_{NSi}, Å		P_{NSi}
				by Eq. (1)	by Eq. (2)	
Me	$CDCl_3$	$\leqslant 0{,}2$	−360,0	$\geqslant 2{,}253$	2,28	$\leqslant 0{,}09$
	$(CD_3)_2SO$	0,70	−357,0	2,221	2,23	0,17
$CH_2{=}CH$	$CDCl_3$	0,55	−357,9	2,229	2,24	0,15
	$(CD_3)_2SO$	1,47	−355,3	2,189	2,19	0,24
Ph	$CDCl_3$	0,66	−357,2	2,223	2,23	0,16
	$(CD_3)_2SO$	1,43	−355,0	2,190	2,19	0,24
MeO	$CDCl_3$	1,17	−353,1	2,159†	2,16	0,31†
	$(CD_3)_2SO$	1,65	−352,3	2,147†	2,14	0,34†
H	$CDCl_3$	1,10	−355,9	2,203	2,21	0,21
	$(CD_3)_2CO$	1,17	−355,1	2,200	2,19	0,22
	$(CD_3)_2CO$ (183 K)	2,20	—	2,166	—	0,30
	CD_3CN	1,76	—	2,180	—	0,26
	$(CD_3)_2SO$	2,05	−353,9	2,171	2,17	0,29
CH_2Cl	$CDCl_3$	1,54	−355,2	2,187	2,19	0,25
	$(CD_3)_2SO$	2,57	−353,2	2,156	2,16	0,32
Cl	$CDCl_3$	1,98	−348,8	2,090‡	2,08	0,48‡
	$(CD_3)_2SO$	3,37	−347,8	2,067‡	2,06	0,53‡

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*^{15}N Chemical shifts and ^{29}Si–^{15}N spin–spin coupling constants were measured for the same solutions [5, 6] at a temperature of 303 K unless otherwise stated.

†With an electronegativity correction of ΔJ = 1.28 Hz.

‡With an electronegativity correction of ΔJ = 3.74 Hz.

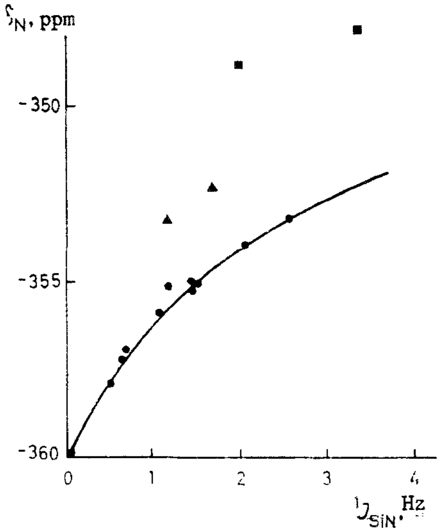

Fig. 1. Correlation of ^{15}N chemical shifts with ^{29}Si–^{15}N SSCC in silatranes. The correlation curve is described by Eq. (4). Symbols: ▲ – R=MeO, ■ – R=Cl, ● –other R.

$$^1J_{SiN} = (\delta^3 - 46{,}5\delta)\cdot 10^{-3} \quad (\sigma = 0{,}11), \tag{4}$$

where $\delta = 367.7 + \delta_N$. The deviations from this relation that can be observed for R = MeO and Cl are due to the effect of the EN of substituent R on the value of $^1J_{SiN}$. These deviations can be used to introduce a corresponding correlation (ΔJ) in the calculation of l_{NSi} by way of Eq. (5):

$$l_{NSi} = 2{,}291 - 0{,}084(^1J_{SiN} + \Delta J)^{1/2}. \tag{5}$$

Allowing for the effect of the EN of substituents on ${}^{1}J_{SiN}$ in Eq. (5), broadens the range of it applicability over that of Eq. (1). The EN effect in Eq. (2) can be compensated for in a similar manner.

LITERATURE CITED

1. E. Kupče, E. Liepinš, D. Udova, and E. Lukevics, Chem. Commun., No. 9, 581 (1984).
2. E. Kupče, E. Liepinš, and E. Lukevics, Angew. Chem. Int. Ed., 24, 568 (1985).
3. E. Kupče, E. Liepinš, E. Lukevics, and B. Astapov, J. Chem. Soc., Dalton Trans., No. 7, 1593 (1987).
4. E. Kupče, and E. Lukevics, J. Magn. Reson., 76, No. 1, 63 (1988).
5. E. Kupče, E. Liepins, A. Lapsina, I. Urtane, G. Zelčans, and E. Lukevics, J. Organomet. Chem., 279, 343 (1985).
6. E. L. Kupche (Kupče), Investigation of Intramolecular Interactions in Sil- and Germoxacyclanes by means of NMR, Author' abstract of dissertation for Candidate in Chemical Science [in Russian], Riga, 1984.
7. E. Kupče, E. Liepinš, A. Lapsina, G. Zelčans, and E. Lukevics, J. Organomet. Chem., 251, 15 (1983).
8. E. Kupče, E. Liepinš, A. Lapsina, G. Zelčans, and E. Lukevics, J. Organomet. Chem., 333, 1 (1987).
9. I. P. Urtane, G. I. Zelchan, E. E. Liepin'sh, E. L. Kupche, and E. Lukevits, Zh. Obshch. Khim., 57, 1110 (1987).
10. B. Wrackmeyer, S. Kerschl, O. Stader, and K. Horchler, Spectrochim. Acta, Pt. A, 42A, 1113 (1986).
11. V. A. Pestunovich, E. Z. Shterenberg, E. T. Lippmaa, M. Ya. Myagi, M. A. Alla, S. N. Tandura, V. P. Baryshok, L. P. Petukhov and M. G. Voronkov, Dokl. Akad. Nauk SSSR, 258, 1410 (1981).