Nitrogen-15 and Oxygen-17 Nuclear Magnetic Resonance Chemical Shifts and ^{15}N-^{29}Si, ^{13}C-^{29}Si, and ^{15}N-^{1}H Coupling Constants in Cyclosilazoxanes

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The effects of ring size on ^{15}N, ^{17}O, and ^{29}Si n.m.r. chemical shifts and ^{15}N–^{29}Si, ^{13}C–^{29}Si, ^{15}N–^{1}H, and ^{29}Si–^{29}Si coupling constants in cyclosilazoxanes have been studied. The opposite shielding sequence in $\delta(^{15}N)$ and $\delta(^{29}Si)$ and the decrease in ^{15}N–^{29}Si coupling with diminishing ring size are consistent with higher Si–N bond ionicity (reduced d_π–p_π interaction) in smaller rings. The ^{17}O chemical shift is practically independent of ring size in cyclosiloxanes. It has been proposed that the factors governing the ^{17}O chemical shift act in opposite directions and are balanced. A linear relationship between N–H bond stretching frequency and ^{15}N n.m.r. parameters (^{15}N–^{1}H coupling and ^{15}N chemical shifts) has been established.

Although a large amount of data is available on ^{1}H, ^{13}C, and ^{29}Si n.m.r. chemical shifts (δ) of cyclosiloxanes, cyclosilazanes, and cyclosilazoxanes,[1–5] data have not been reported for the ^{15}N and ^{17}O chemical shifts or the one-bond coupling constants (^{1}J) ^{15}N–^{29}Si, ^{13}C–^{29}Si, and ^{15}N–^{1}H for these types of compounds.

It has been suggested[1,2] that $\delta(^{29}Si)$ reflects variations in d_π–p_π interaction along Si–X (X = O or N). In this respect measurement of $\delta(^{15}N)$, $\delta(^{17}O)$, and especially $^{1}J(^{15}N$–$^{29}Si)$ can give a more definite result.

In this paper we report the ^{15}N and ^{17}O chemical shifts and the ^{15}N–^{29}Si, ^{13}C–^{29}Si, and ^{15}N–^{1}H coupling constants, together with some two-bond ^{29}Si–O–^{29}Si couplings, in six- to twelve-membered cyclosilazoxanes and in some acyclic derivatives, selected partly on the basis of their availability.

It has been reported[6] that a linear relationship exists between the NH stretching frequency (ν_{NH}) and the ^{15}N n.m.r. parameters [$\delta(^{15}N)$ and $^{1}J(^{15}N$–$^{1}H)$] in saturated primary amines and anilines. In order to examine the existence of the analogous relationships in cyclosilazoxanes and to compare the factors influencing i.r. and n.m.r. parameters in organic amines with those in cyclosilazoxanes, we have also measured ν_{NH}.

$(Me_3Si)_2X$

(1) X = NH

(2) X = O

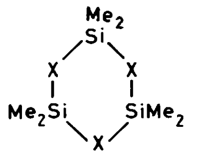
$(ClMe_2Si)_2X$

(3) X = NH

(4) X = O

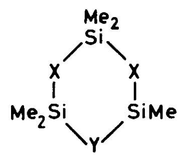
$[Me_3Si(OSiMe_2)_5]_2NH$

(5)



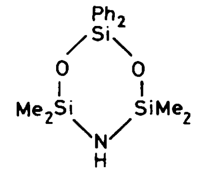
(6) X = NH

(7) X = O



(8) X = NH, Y = O

(9) X = O, Y = NH



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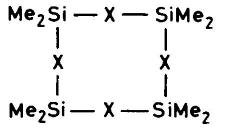
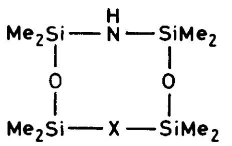


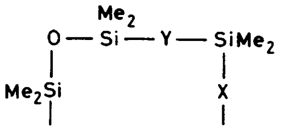
(11) X = NH

(12) X = O



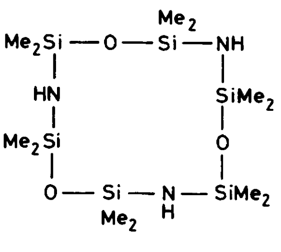
(13) X = NH

(14) X = O



(15) X = NH, Y = O

(16) X = O, Y = NH



(17)

Results and Discussion

^{15}N and ^{17}O Chemical Shifts.—It appears from Table 1 that $\delta(^{15}N)$ and $\delta(^{17}O)$ are less sensitive to the nature of the substituents at the silicon atom than $\delta(^{29}Si)$. Nevertheless, the influence over the two bonds (β effect) is important. Data obtained for the acyclic compounds (**1**)—(**5**) indicate that ^{15}N and ^{17}O shielding decreases with increase in electronegativity of the substituents at adjacent silicon atoms. For compound (**5**) this allows us to observe the ^{17}O signal of the $OSiMe_3$ end-group separately.

In cyclosilazoxane rings of equal size, substitution of one nitrogen atom by oxygen decreases the shielding of the adjacent ^{15}N by an average value of 2 p.p.m. A similar tendency is characteristic of ^{17}O n.m.r. spectra.

The influence of ring size on $\delta(^{15}N)$ is opposite to that of $\delta(^{29}Si)$. In the cyclosilazoxanes studied $\delta(^{29}Si)$ moves to higher field with increasing ring size, which is in compliance with previous investigations.[1–3] It has been suggested that this is the result of an increase in the d_π–p_π interaction along the Si–X (X = O or NH) bond. The tendency of $\delta(^{15}N)$ to move downfield with increase in ring size may be understood in similar terms. Thus, the opposite shielding sequence in the nitrogen and silicon resonances reflects an increase in Si–N bond ionicity (decrease in d_π–p_π interaction) in smaller rings.

Unexpectedly, $\delta(^{17}O)$ is practically independent of ring size in 'pure' cyclosiloxanes. This indicates that the factors governing $\delta(^{17}O)$ act in opposite directions and are balanced.

Table 1. N.m.r. parameters and NH stretching frequencies of cyclosilazoxanes and acyclic analogues[a]

Compound	$\delta(^{15}N)$	$\delta(^{17}O)$	$\delta(^{29}Si)$	$^1J(^{15}N-^{29}Si)$	$^1J(^{13}C-^{29}Si)$	$^1J(^{15}N-^1H)$	ν_{NH}
(1)	−354.2	—	2.1	13.4	56.3	69.6	3 402
(2)	—	39.0	6.5[b]	—	59.5	—	—
(3)	−334.3	—	13.3	14.4	68.1	68.1	3 364
(4)	—	70.0	6.9	—	72.6	—	—
(5)	−335.7	71.4[c]	−11.9 (α)[d,e]	17.4	69.4[f]	—	3 376
(6)	−347.3	—	−4.6	15.4	63.0	69.4	3 403
(7)	—	72.0	−8.7	—	74.2	—	—
(8)	−345.4	60.1	−4.0 (NN)	15.8	62.3	69.5	3 402
			−4.3 (ON)	15.8	68.5		
(9)	−342.9	63.0	−3.4 (ON)	15.5	68.4	69.5	3 400
			−9.0 (OO)[g]		74.0		
(10)	−341.9	56.0	−1.2 (ON)	15.7	68.2	69.6	3 396
(11)	−341.7	—	−8.2	16.9	64.0	67.0	3 385
(12)	—	71.4	−19.4	—	75.4	—	—
(13)	−334.9	68.1	−11.3	15.9	69.8	67.1	3 383
(14)	−334.9	70.9	−10.9 (ON)	15.9	69.7	67.3	3 384
		72.3	−19.8 (OO)		75.4		
(15)	−336.7	70.5	−8.3 (NN)	17.7	64.5	66.3	3 377
			−12.6 (ON)	17.7	69.4		
			−22.6 (OO)[h]		74.9		
(16)	−335.1	69.6	−12.6 (NN)	17.3	69.3	66.7	3 380
			−13.2 (ON)	17.1	69.6		
			−23.6 (OO)[i]		74.7		
(17)	−334.8	67.3	−12.3	17.2	69.2	65.9	3 373

[a] ^1J in Hz; δ in p.p.m. relative to CH_3NO_2 (^{15}N), H_2O (^{17}O), or $SiMe_4$ (^{29}Si); ν_{NH} in cm^{-1}. [b] Ref. 9. [c] 56.1 p.p.m. ($OSiMe_3$). [d] $HN-Si^{\alpha}Me_2OSi^{\beta}Me_2OSi^{\gamma}Me_2OSi^{\delta}Me_2OSi^{\varepsilon}Me_2OSi^{\zeta}Me_3$; −22.3 (β), −22.4 (γ), −22.5 (δ), −21.6 (ε), +7.1 p.p.m. (ζ). [e] $^2J(^{29}Si-^{29}Si)$ = 2.1 (α–β), 3.1 (β–γ), 2.2 (γ–δ), 2.5 (δ–ε), 1.3 (ε–ζ) Hz. [f] 74.4 (β), 74.4 (γ), 74.3 (δ), 74.3 (ε) Hz. [g] $^2J(^{29}Si-^{29}Si)$ = 1.02 Hz. [h] $^2J(^{29}Si-^{29}Si)$ = 1.54 Hz. [i] $^2J(^{29}Si-^{29}Si)$ = 1.50 Hz.

Table 2. Si–X–Si (X = O or N) valence angles (°) in some cyclosiloxanes, cyclosilazanes, cyclosilazoxanes, and acyclic analogues

Compound	Si–X–Si	Method[a]	Ref.
$(Me_2SiO)_3$	131.6	ED	*b*
$(Me_2SiO)_4$	144.8	ED	*b*
$(Me_3Si)_2O$	148.8	X,ED	*c,d*
$(Me_2SiNH)_3$	126.8	ED	*e*
$(Me_2SiNH)_4$	132[f]	X	*g*
$(Me_3Si)_2NH$	131.3	ED	*h*
$(Ph_2SiO)_2(Ph_2SiNEt)$	126.3	X	*i*
$(PhMeSiO)_2(NH)_2$- $(PhMeSiO)_2$	130.0	X	*j*

[a] ED = electron diffraction, X = *X*-ray analysis. [b] H. Oberhammer, W. Zeil, and G. Fogaresi, *J. Mol. Struct.*, 1973, **18**, 309. [c] M. J. Barrow, E. A. V. Ebsworth, and M. M. Harding, *Acta Crystallogr., Sect. B*, 1979, **35**, 2093. [d] B. Csakovari, Z. Wanger, P. Gomory, F. C. Mijlhoff, B. Roszandai, and I. Hargittai, *J. Organomet. Chem.*, 1976, **107**, 287. [e] B. Roszondai, I. Hargittai, A. Golubinski, L. V. Vilkov, and V. S. Mastryukov, *J. Mol. Struct.*, 1975, **28**, 339. [f] Mean value. [g] G. Smith and L. E. Alexander, *Acta Crystallogr.*, 1963, **16**, 1015. [h] T. Fjeldberg, *J. Mol. Struct.*, 1984, **112**, 159. [i] W. Fink and P. J. Wheatley, *J. Chem. Soc. A*, 1967, 1517. [j] V. E. Shklover, N. G. Bokij, Yu. T. Struchkov, K. A. Andrianov, A. B. Zachernyuk, and E. A. Zhdanova, *Zh. Strukt. Khim.*, 1974, **15**, 864.

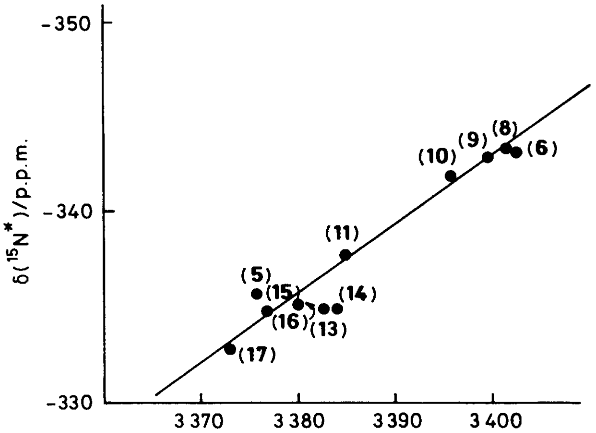


Figure 1. Plots of corrected ^{15}N chemical shifts [$\delta(^{15}N^*)$] against NH stretching frequencies. Regression analysis gave the equation $\delta(^{15}N^*) = 884.5 - 0.361\nu_{NH}$ (number of points, n = 8, correlation coefficient, r = 0.996)

The main contributor to the chemical shift is the variation in the paramagnetic term (σ_p^A) of the shielding of nucleus A.[7,8] For a second-row element this is approximated by equation (1),

$$\sigma_p^A = \frac{-\mu_0\mu_B^2\langle r^{-3}\rangle_{2p}\Sigma Q}{2\pi\Delta E} \qquad (1)$$

where μ_0 is the permeability of free space, μ_B is the Bohr magneton, and $\langle r^{-3}\rangle_{2p}$ is the radial-expansion term for the 2*p* electrons; the *Q* terms express the imbalance of charge in the valence shell of A and ΔE is the mean energy of electronic excitation.

As has been demonstrated by CNDO/2 calculations,[6] $\delta(^{15}N)$ in primary aliphatic amines is governed by the ΔE term, but in aniline derivatives by the ΣQ and $\langle r^{-3}\rangle_{2p}$ terms. Furthermore, the linear relationships of $\delta(^{15}N)$ *versus* ν_{NH} were observed with a negative slope (−1.7601) in the former case and a positive one (0.3855) in the latter.

Generally no correlation has been found between $\delta(^{15}N)$ and ν_{NH} in the cyclosilazoxanes studied. This indicates the existence of the factors which influence $\delta(^{15}N)$ but not ν_{NH}. Indeed, if the β effect is excluded by introducing the correction of ~2 p.p.m. for

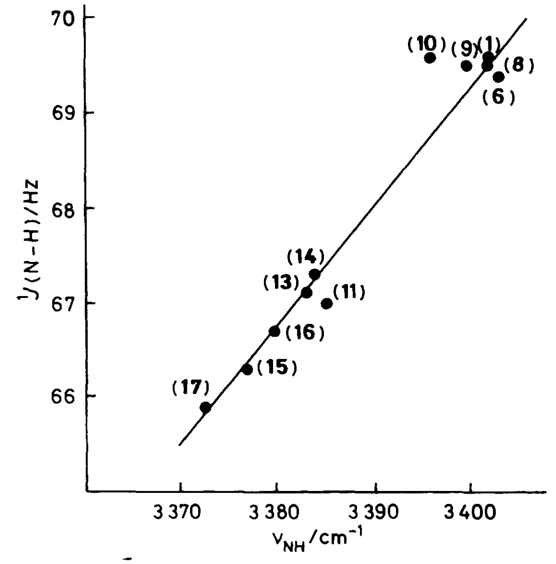


Figure 2. Plots of $^{15}N-^{1}H$ coupling constants against NH stretching frequencies. Regression analysis gave the equation $^{1}J(^{15}N-^{1}H) = 0.1278\ \nu_{NH} - 365.5$ (n = 10, r = 0.994)

the substitution of one nitrogen atom by oxygen in the β position, the resultant 'corrected' ^{15}N chemical shifts [$\delta(^{15}N^{*})$] show a good correlation with ν_{NH} (Figure 1). The slope of the line obtained (−0.3610) is *ca.* five times less steep than that found in aliphatic amines (−1.7601) and is close to that in aniline derivatives (0.3855), but with opposite sign. It seems, therefore, that $\delta(^{15}N^{*})$ in cyclosilazoxanes are also governed by the ΔE term, but the contribution of the ΣQ and $\langle r^{-3}\rangle_{2p}$ terms is significantly increased, possibly, due to the presence of $d_{\pi}-p_{\pi}$ interactions along the Si–N bonds. The lack of correlation between 'non-corrected' $\delta(^{15}N)$ and ν_{NH} may be explained by significant influence of β substitution on the ΣQ term. It may also be suggested that independence of $\delta(^{17}O)$ of ring size in cyclosiloxanes (and cyclosilazoxanes) is a consequence of equal contributions of ΔE on the one hand, and ΣQ and $\langle r^{-3}\rangle_{2p}$ terms on the other.

Coupling Constants.—Coupling constants to ^{29}Si are very sensitive to the electronegativity of the substituents at the silicon atom and usually increase with increasing electronegativity.[9,10] Similar dependences exist for $^{1}J(^{15}N-^{29}Si)$ and $^{1}J(^{13}C-^{29}Si)$ in the acyclic compounds (**1**)—(**5**) (Table 1).

In cyclosilazoxanes the $^{1}J(^{29}Si-^{13}C)$ values for the fragments N-Si-N (62.3—64.5), N-Si-O (68.2—69.8), and O-Si-O (74.0—75.4 Hz) lie in a very narrow, non-overlapping and characteristic range, which allows us to use these couplings for analytical purposes. In contrast to $^{1}J(^{13}C-^{29}Si)$, the $^{1}J(^{15}N-^{29}Si)$ values are practically independent of the substituents (N or O) at the silicon atom. This may be understood in terms of Bent's rule,[11] which suggests that major changes in *s*-orbital overlap proceed in bonds with more electropositive substituents (Si–C). The decrease of $^{1}J(^{15}N-^{29}Si)$ with diminishing ring size gives further evidence of higher Si–N bond ionicity in smaller cyclosilazoxane rings.

The effect of β substitution on $^{1}J(^{15}N-^{1}H)$ in the compounds studied seems to be negligible. The dependence of the *exo*cyclic coupling $^{1}J(^{15}N-^{1}H)$ on ring size is opposite to that of $^{1}J(^{29}Si-^{13}C)$, for example $^{1}J(^{15}N-^{1}H)$ decreases on going to larger cyclosilazoxane rings, whilst $^{1}J(^{29}Si-^{13}C)$ slightly increases. This fact is consistent with the suggested increase in ionicity of Si–X (X = O or N) bonds in smaller rings. Alternatively, the observed changes in exocyclic couplings may be explained by changes in appropriate valence angles. A greater sensitivity of $^{1}J(^{15}N-^{1}H)$ to changes in ring size as compared with $^{1}J(^{13}C-^{29}Si)$ is consistent with the observation[12] that the valence angles Si–X–Si depend on ring size to a greater extent than X–Si–X. However, it appears from the data present in Tables 1 and 2 that $^{1}J(^{15}N-^{1}H)$ decreases with an expansion of the Si–N–Si valence angle. This contradicts the situation normally observed for organic amines.[13–15]

Figure 3. An example of observation of $^{15}N-^{1}H$ coupling in a ^{1}H spectrum *via* multiple quantum n.m.r. Compound (**10**), *ca.* 20% solution in $CDCl_3$, 5-mm sample tube, sweep width 600 Hz, 200 scans. A signal marked * is due to an incompletely suppressed signal from protons bonded to ^{14}N

We have found a linear relationship between $^{1}J(^{15}N-^{1}H)$ and ν_{NH} (Figure 2). As has been demonstrated by CNDO/2 calculations,[6] such a relationship exists because both $^{1}J(^{15}N-^{1}H)$ and ν_{NH} depend primarily on the *s* character of the N–H bond. It should be noted that simultaneous decrease of $^{1}J(^{15}N-^{1}H)$ and ν_{NH} may be explained by an increase in the N–H bond length.

We have also measured some two-bond $^{29}Si-^{29}Si$ couplings (Table 1). It appears that $^{2}J(^{29}Si-^{29}Si)$ decreases with decreasing ring size, but the information is as yet insufficient. Unfortunately, the measurement of $^{2}J(^{29}Si-^{29}Si)$ in cyclosilazoxanes is difficult to perform because the values of these couplings are small (1.0—3.1 Hz). Further complications arise from broadening of the ^{29}Si signals of the silicon atoms bonded to nitrogen due to the fast quadrupolar relaxation of ^{14}N nuclei. Nevertheless, the $^{2}J(^{29}Si-^{29}Si)$ values measured for compound (**5**) allowed us to make a complete assignment of the signals in the ^{29}Si n.m.r. spectrum (Table 1).

Experimental

All compounds used were synthesized as described previously.[3,16]

The ^{15}N, ^{17}O, and ^{29}Si n.m.r. spectra were recorded on a Bruker WM-360 spectrometer at 36.5, 48.8, and 71.5 MHz, respectively. $CDCl_3$ was dried over 4Å molecular sieves and used as the solvent and internal deuterium lock material. All spectra were measured for *ca.* 20—50% solutions at 303 K in 10-mm sample tubes. The ^{15}N and ^{29}Si chemical shifts were measured using the INEPT sequence.[17]

The $^{15}N-^{1}H$ couplings were measured from the 360-MHz ^{1}H spectra *via* multiple quantum n.m.r. in 5-mm sample tubes (Figure 3). The pulse sequence used, $90^{\circ}_{x}(^{1}H)-1/(2J_{NH})-90^{\circ}_{\phi}(^{15}N)-t_1-90^{\circ}_{x}(^{15}N)$-acquire($^{1}H$), has been previously reported.[18] $^{13}C-^{29}Si$ couplings were measured from the ^{13}C n.m.r. spectra. $^{15}N-^{29}Si$ couplings were measured at natural abundance of isotopes in the ^{29}Si n.m.r. spectra for O–Si–N fragments and in the ^{15}N n.m.r. spectra for N–Si–N fragments as described elsewhere.[10,19]

I.r. spectra were recorded on a Perkin-Elmer 580 B spectrometer using the same samples as for n.m.r. spectra.

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