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Aminopropylsilanes versus silatranes: an experimental and theoretical study

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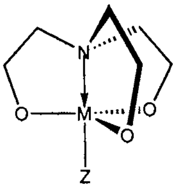
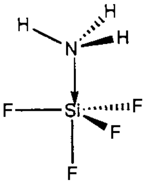
Abstract

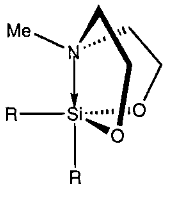
The ^{1}H-, ^{13}C-, ^{15}N- and ^{29}Si-NMR spectra of 3-aminopropyltrimethoxysilane and *N,N*-dimethylamino-propyltrimethoxysilane have been recorded. An analysis of the spectra together with GIAO calculations leads to the conclusion that these compounds exist as open-chain structures and not as ring-closed silatranes. The N → Si interaction is important only when there is at least one cycle in the structure, although two or three cycles (silatranes) are a more favorable disposition. © 2001 Elsevier Science B.V. All rights reserved.

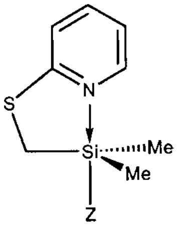
Keywords: Silanes; Silatranes; ^{29}Si-NMR; ^{15}N-NMR; GIAO calculations

1. Introduction









Atranes of type (**A**) are cyclic ethers containing a hypervalent atom M with a transannular interaction between M and the bridgehead nitrogen atom [1]. Although this structural form is now known across the periodic table [2], the most common atranes are silatranes (M = Si) and germatranes (M = Ge). Silatranes show characteristic NMR features like shifts of the ^{15}N and ^{29}Si signals (compared with open ring compounds, mainly in the case of six-membered rings [2]), as well as an interesting $^{1}J(^{15}N \rightarrow ^{29}Si)$ coupling [3].

Due to our interest in weak bonds [4–7], the problem of the N–Si bond of silatranes attracted our attention. The tricyclic structure present in (**A**) is not necessary for the stability of the cyclic compound nor are the oxygen atoms linked to M. Several complexes where a tetracoordinated silicon derivative interacts with an

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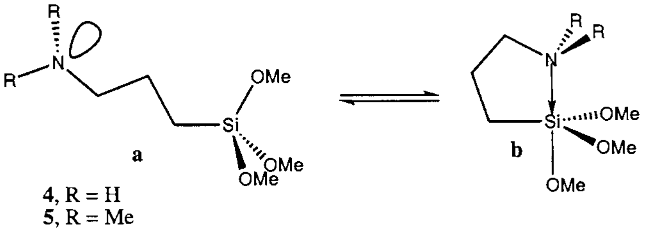
electron-rich group, in gas phase, have been described in the literature, for instance $H_3N\cdots SiF_4$ (**1**) [8]. Lukevics' silocanes (**2**) [3] and Bassindale and Taylor's pyridine derivatives (**3**) [9] are examples of molecules lacking some features of type (**A**) structure.

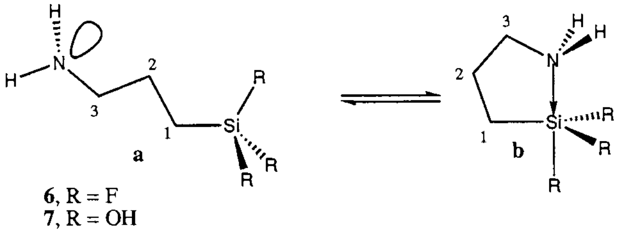
To explore the minimum requirements necessary for the stability of the N → Si bond we decided to study two compounds, 3-aminopropyltrimethoxysilane (**4**) and *N*,*N*-dimethyl-3-aminopropyltrimethoxysilane (**5**). These compounds have two possible isomeric forms, **a**, the open-chain and **b**, the ring form, or carbasilatrane, this equilibrium being related to the ring-chain tautomerism [10].



2. Results and discussion

2.1. Computational results (energies and geometries)

To begin with, we have carried out a series of calculations, at the B3LYP/6-31G* level (Section 4) of two models of compound **4**: 3-aminopropyltrifluorosilane (**6**) and 3-amino-propyltrihydroxysilane (**7**).



The first one was selected by analogy with the $H_3N\cdots SiF_4$ complex (**1**) [8] and the second as a first approximation to the real molecule **4** (note that the OMe groups are more bulky than the OH ones). The results of the calculations are reported in Table 1.

The calculated Si···N distances, between 2.2 and 2.3 Å, the experimental values (X-ray crystallography) of Refs. [2,9] are, respectively 2.2–2.7 and 1.9–2.0 Å (N sp^2, compounds type **3**). A search in the Cambridge Structural Database (October 1999 release [11]) shows a bimodal distribution centered about 1.94 Å (N–Si bonds) and 2.8 Å (N···Si interactions).

The relative energies are largely dependent on the substituents on the silicon, a fact consistent with other studies on silatranes [2,9], but also on the quality of the basis set. Nevertheless, it can be safely assumed that the trifluoro derivative **6** will exist in the **b** form and the trimethoxy derivative **4** in the **a** form.

These calculations correspond to free energies in the gas phase at 0 K. In the case of **4**, the dipole moments are almost identical, so, in a first approximation, no significant influence of the solvent on the **a**–**b** ratio is expected. The effect of the temperature should favor the open-chain isomers. This is a simple consequence of the fact that in **b** the internal rotation is significantly restrained. Qualitatively, the **b** form is more 'ordered' and, all things being equal, has less entropy than the **a** form.

Considering the entropy difference between cyclopentane and *n*-pentane, the gas-phase values [12] at 25°C and 1 atm are 347.82 and 302.25 J mol^{-1} K^{-1}, respectively, that is 45.6 J mol^{-1} K^{-1}. At 300 K, the TDS term amounts to 13.8 kJ mol^{-1}, that is, the open isomer will be favored by this amount over the silatrane.

2.2. Computational results (absolute shieldings)

For the following discussion, we need to know the chemical shifts of forms **a** and **b** because one of the most distinctive features of silatranes is the shift produced on ^{15}N and ^{29}Si signals by the N···Si interaction. For this we have calculated, within the GIAO framework (see Section 4), the absolute shieldings of a series

Table 1
B3LYP/6-31G* calculations [a]

Molecule	Open-chain **a**		Ring (N···Si) **b**			
	E_T	μ	E_T	E_{rel}	μ	Si–N distance
6	−763.104486	3.41	−763.114628	26.6	5.64	2.286
7	−690.988165	2.28	−690.995627	19.6 [b]	2.67	2.184
4	−808.896642	2.17	−808.896341	−0.8	2.11	2.242

[a] Absolute values in hartrees, relative values in kJ mol^{-1}, dipole moments in D and distances in Å.

[b] A B3LYP/6-311++G** calculation yields $E_{rel} = 5.3$ kJ mol^{-1}.

Table 2
Absolute shieldings, calculated and experimental chemical shifts [a]

Compound	Absolute shieldings (ppm)			Calculated chemical shifts (ppm)			Experimental chemical shifts		
	^{13}C	^{15}N	^{29}Si	^{13}C	^{15}N	^{29}Si	^{13}C [b]	^{15}N [c]	^{29}Si [d]
$MeNH_2$	151.78	238.13		26.4	−377.1		28.3	−377.20	
$EtNH_2$	141.35 [e]	217.55		36.9	−356.5		36.9	−355.40	
$PrNH_2$	133.10 [e]	219.90		45.1	−358.8		44.6	−359.60	
$BuNH_2$	134.58 [e]	220.16		43.6	−359.1		42.3	−359.40	
SiH_4			448.28			−108.5			−106.8
$Si(OH)_4$			407.85			−68.1			−73.3
$Si(Ome)_4$			422.37			−82.6			−79.2
7a	168.68 [f]	219.69	371.20	9.6	−358.6	−31.4			
	153.04 [g]			25.2					
	131.23 [h]			47.0					
7b	168.17 [f]	219.69	371.20	10.1	−336.7	−68.7			
	154.19 [g]			24.0					
	140.52 [h]			37.7					
4a							6.5	−359.3	−42.2
							28.0		
							45.3		

[a] Absolute shieldings (ppm): GIAO//B3LYP/6-311++G** calculations. Experimental chemical shifts (ppm) from TMS (^{13}C, ^{29}Si) and nitromethane (^{15}N). Calculated chemical shifts are obtained from absolute shieldings using the values 178.23 TMS ^{13}C, −138.95 nitromethane ^{15}N and 339.80 TMS ^{29}Si.

[b] Data from Ref. [15].

[c] Data from Ref. [16].

[d] Data from Refs [14,17].

[e] C–N.

[f] C1.

[g] C2.

[h] C3.

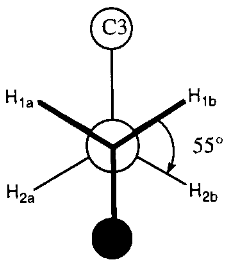
of model compounds (Table 2). We have used for these calculations a higher theoretical level (GIAO/B3LYP/6-311++G**). The compounds used as references, TMS and nitromethane, usually have chemical shifts far away from those of the studied compounds and, moreover, some of them, like nitromethane, are difficult to calculate [13,14]. For this reason we have used for the references, not the actual calculated values but values that yield reasonable chemical shifts for the model compounds of Table 1 (^{13}C 178.23, ^{15}N −138.95 and ^{29}Si 339.80 ppm). With Refs [14–17] we have estimated the 'Calculated chemical shifts' of Table 2, which compare reasonably well with the 'Experimental chemical shifts'. The values predicted for **7a** and **7b** are also reported in Table 2.

2.3. NMR experiments

The ^1H-NMR spectrum of compound **4** recorded in $CDCl_3$ is not first-order. It shows three very different multiplets for each CH_2. However, once analyzed as an AA′MM′XX′ spin system, it provided a normal set of coupling constants, except that J_{AX} and $J_{AX'}$ of the $Si–CH_2–CH_2$ fragment are definitely different unlike those of the $N–CH_2–CH_2$ one. We also recorded the spectrum of **4** at other temperatures as well as in C_6D_6 (Fig. 1), but only minor changes in the chemical shifts were observed. The spectrum of **5** in $CDCl_3$ was similarly studied because it is known that the structures obtained with aminopropylsilanes are not always the same as with dimethylaminopropylsilanes [18]. All the results are reported in Table 3.

From the ^3J vicinal coupling constants and the Karplus relation it is possible to determine the preferred conformation of these molecules (since the values are similar we will limit ourselves to **4** in $CDCl_3$). We have advocated the use of the ratio between two vicinal coupling constants to avoid the effect of the electronegativity of the α-substituents [19].

Between positions 1 and 2 the ratio is 2.1 and between positions 2 and 3 the ratio is 1. To these ratios correspond tabulated values of dihedral angles of 55 and 60°, that is, an almost perfect trans conformation. Therefore, according to this analysis, the compounds have predominantly the extended 'all-*trans*' **a** structure (the silatrane **b** should have dihedral angles close to 0°).



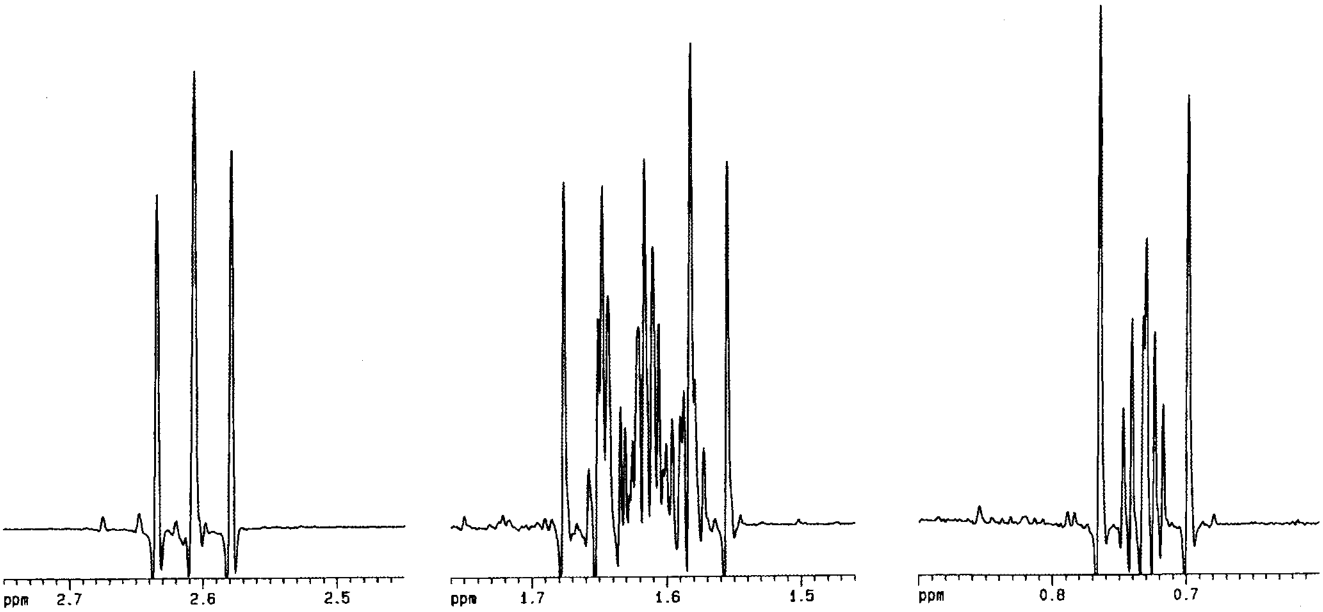
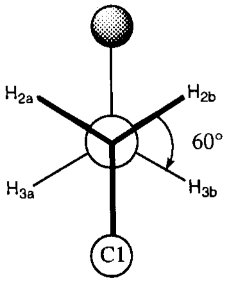


Fig. 1. ^{1}H-NMR spectrum of 3-aminopropyltrimethoxysilane **4** in C_6D_6 (methylene signals only).



The ^{13}C, ^{15}N and ^{29}Si chemical shifts of compounds **4** and **5** are reported in Table 4. If one compares the experimental values for compound **4** (compound **5** is similar taking into account the effect of the methyl groups on the nitrogen on C2 and C3) to the calculated values for **7a** and **7b** (Table 2), the chemical shifts of all nuclei indicate that the compounds exist in the **a** conformation, **4a** and **5a**.

The most characteristic signals are those of C3, NH_2 and $Si(OR)_3$. For the first two, there is an almost perfect coincidence (47.0/45.3 and −358.6/−359.3). For the ^{29}Si chemical shift, the difference (−42.2 experimental, −31.4 calculated) is due to the fact that the experimental value corresponds to $Si(OMe)_3$ while the calculated one corresponds to $Si(OH)_3$. If one compares, for instance, the ^{29}Si absolute shieldings of $Si(OH)_4$ 407.85 and $Si(OMe)_4$ 422.37 (Table 2), there is a difference of 3.6 ppm for each pair OH/OMe. Considering that between **4a** and **7a** there are three OH–OMe pairs a difference of $3 \times 3.6 = 10.8$ ppm is normal.

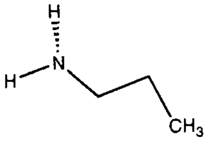


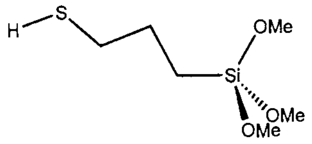
Table 3
^{1}H-NMR results: chemical shifts (ppm) and ^{1}H–^{1}H coupling constants (Hz)

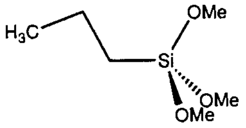
Compound	**4** ($CDCl_3$)	**4** (C_6D_6)	**5** ($CDCl_3$)
NH_2 (or NMe_2)	1.070 (br)	0.886 (br)	2.119
CH_2 (1)	0.540	0.733	0.545
CH_2 (2)	1.436	1.616	1.479
CH_2 (3)	2.568	2.607	2.159
$(OMe)_3$	3.376	3.550	3.474
^{2}J(1a,1b)	−14.8	−15.0	−15.0
^{2}J(2a,2b)	−13.4	−13.3	−13.5
^{2}J(3a,3b)	−9.3	−10.5	−10.5
^{3}J(1a,2a) = ^{3}J(1b,2b)	11.3	11.1	11.4
^{3}J(1a,2b) = ^{3}J(1b,2a)	5.4	5.5	5.4
^{3}J(2a,3a) = ^{3}J(2b,3b)	7.1	6.9	7.7
^{3}J(2a,3b) = ^{3}J(2b,3a)	7.1	6.9	7.3

Table 4
^{13}C-, ^{15}N- and ^{29}Si-NMR results: chemical shifts (ppm) in $CDCl_3$

Compound	**4**	**5**	**9**	**10**
^{13}C (OMe)	50.77	49.79	50.87	50.70
^{13}C (C1)	6.53	6.30	8.56	11.87
^{13}C (C2)	28.03	20.61	27.80*	16.52
^{13}C (C3)	45.27	62.17	27.89*	17.96
^{15}N	−359.30 (NH_2)	−357.35 (NMe_2) [a]		
^{29}Si	−42.20 [b]	−42.41	−42.49 [c]	−42.40 [d]

[a] N-Methyl groups (^{13}C): 44.94 ppm.
[b] Literature result [20]: −41.7 ppm.
[c] Literature result [20]: −42.5 ppm.
[d] Literature result [20]: −41.8 ppm.





To explore what are the structural elements that confer the ^{1}H-NMR spectrum of compound **4** the unusual aspect shown in Fig. 1, we recorded (at 500 MHz) the spectra of three compounds in $CDCl_3$. That of propylamine **8** has a first-order appearance. Very similar spectra to those of Fig. 1 were obtained with 3-mercaptopropyltrimethoxysilane **9** and even with propyltrimethoxysilane **10**. The ^{13}C and ^{29}Si chemical shifts of **8** and **9** are reported in Table 4.

3. Conclusions

The fact that compounds **4** and **5** are open-chain structures can account for the lack of $^1J(^{15}N,^{29}Si)$ coupling in their spectra. However, the presence of a small amount of **5b** in equilibrium with **5a** cannot be excluded. For example, the displacement of the ^{15}N chemical shift from -359.30 ppm in **4a** to -357.35 ppm ($+1.95$ ppm) in **5** [compare with butylamine (-359.4 ppm) and *N*,*N*-dimethylbutylamine (-352.8 ppm, $\Delta\delta = +6.6$ ppm)] may be due to the presence of a small amount of **5b** (**7a**–**7b**, $\Delta\delta = +49.1$). Finally, the explanation for the curious aspect of the ^{1}H-NMR spectra of compounds **4**, **5**, **9** and **10** could be the presence of the trimethoxysilyl group and its effects on the ^{1}H chemical shifts and ^{1}H–^{1}H coupling constants.

4. Experimental

4.1. Origin of the compounds

3-Aminopropyltrimethoxysilane (**4**) is a very important and much studied compound, available from many sources, for instance, Aldrich. *N*,*N*-Dimethyl-3-aminopropyltrimethoxysilane (**5**) is much less common [18,21] but can be purchased from Fluorochem (Derbyshire, UK), 95% [the product has been purified by fractional distillation (b.p.$_{30}$ = 106°C)]. Both are moisture-sensitive.

4.2. Computational methods

All the molecules have been fully optimized at the B3LYP/6-31G* level [22,23] with the GAUSSIAN-98 program [24]. The theoretical absolute NMR shieldings has been computed using the GIAO method [25] at a higher computational level, B3LYP/6-311++G** [26].

4.3. NMR experiments

Nuclear magnetic resonance spectra were obtained in a Bruker Avance 500 provided with a 5-mm triple probe (^{1}H/^{13}C/X). ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ solution. ^{15}N- and ^{29}Si-NMR spectra were obtained using an 80% solution in DMSO-d_6. In the last cases, an inverse gated decoupling sequence was used with a delay between pulses of 5 s. Chemical shifts are given from TMS in the case of proton, carbon and silicon and from formamide in the case of nitrogen. The resolution of ^{1}H-NMR spectra were improved after a Gaussian multiplication ($l_b = -0.8$, $g_b = 0.8$) of the FID previously to the Fourier transform. The sensitivity of the other nucleus was increased using an exponential multiplication ($l_b = 2$) before Fourier transform. Homodecoupling experiments were achieved using an effective field $\gamma B_1/2\pi = 100$ Hz.

^{1}H spectrum of **4** in C_6D_6 has been recorded on a Bruker DRX-250 spectrometer with a digital resolution of 0.06 Hz/pt and analyzed with the help of *g*NMR-3.6 from Cherwell Scientific Publishing Ltd. and NMR-SIM-2.6 from Bruker. We observed that, because of unresolved long-range coupling constants, the N–CH_2 signal has to be irradiated to allow the observation of all the transitions in the Si–CH_2 signal.

Acknowledgements

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