Model of the S_N2 Nucleophilic Substitution at the Si Atom: X-Ray Structural Study of N-(Halogenodimethylsilylmethyl) Lactams

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X-ray studies show that Si–O and Si–X (X = I, Br, Cl, F) distances at the pentaco-ordinated Si atom in N-(halogenodimethylsilylmethyl)lactams vary over a wide range [1.749(2)—2.461(8) and 3.734(1)—1.630(7) Å, respectively] in the series X = I → Br → Cl → F; hence these compounds can be regarded as models of intermediate stages of S_N2 substitution at the tetrahedral Si atom.

Bürgi[1] was the first to map the reaction pathway of the S_N2 nucleophilic substitution on the basis of X-ray data for complexes with the intermediate (tetrahedral vs. trigonal-bipyramidal) co-ordination. Later this 'structural correlation' approach was applied to organosilicon compounds, viz. derivatives of the pentaco-ordinated Si atom.[2]

Here we report some novel features of the Si atom

pentaco-ordination in the derivatives of N-(halogeno-dimethylsilylmethyl)lactams, recently prepared by us[3] [Figure 1, compounds (1), (2), (4)—(8); (3) was prepared and structurally characterised earlier by Onan et al.[4]]. The interesting feature of these molecules is the involvement of the Si atom in the five-membered heterocycle closed by the hypervalent Si–O bond.

Table 1.

Compound	$\Delta_{Si-O}/\text{Å}$ (%)	$\Delta_{Si-X}/\text{Å}$ (%)	$h_{Si}/\text{Å}$	n_{Si-O}	n_{Si-X}
(1)	0.113 (4)	1.274 (52)	0.348	0.85	0.15
(2)	0.164 (7)	0.912 (41)	0.218	0.77	0.23
(3)	0.282 (14)	0.329 (16)	0.029	0.53	0.47
(4)	0.318 (16)	0.288 (14)	−0.058	0.48	0.52
(5)	0.314 (16)	0.292 (14)	−0.055	0.49	0.51
(6)	0.354 (18)	0.290 (14)	−0.065	0.47	0.53
(7)	0.789 (44)	0.129 (6)	−0.251	0.22	0.78
(8)	0.759 (42)	0.091 (7)	−0.286	0.18	0.82

A sharp change in the electroconductivity of CH_2Cl_2 solutions of these compounds (decrease by a factor of 100 in the series X = I → Br → Cl → F) has lead to the assumption of the change in the nature of the Si–X interaction from essentially ionic in (1) to covalent in (8), with an accompanying weakening of the Si–O interaction. The i.r. spectra show that on going from iodide to fluoride, the weakening of Si–O interaction is accompanied by weakening and strengthening of the C⋯N and C⋯O bonds, respectively. We have also found that the N-(halogenodimethylsilylmethyl)lactams exhibit a remarkably high tendency to exchange halogen substituents at the Si atom[5] and a high silylating ability towards carbonyl compounds resulting in formation of O-silylsubstituted enols.[6]

We carried out X-ray crystallographic analyses of (1), (2), and (4)—(8),† compounds with different halogen substituents

† *Crystal data* for (1): $C_8H_{16}INOSi$, $M = 296.9$, orthorhombic, space group $Pna2_1$, $a = 12.633(5)$, $b = 8.189(3)$, $c = 10.874(5)$ Å, $U = 1124.9(9)$ Å³, $Z = 4$, $D_c = 1.76$ g cm⁻³; $R = 0.018$ and $R_w = 0.027$ for 1665 unique reflections with $I \geq 2\sigma(I)$.

For (2): $C_8H_{16}BrNOSi \cdot \frac{1}{2}C_6H_6$, $M = 288.9$, monoclinic, space group $C2$, $a = 18.466(9)$, $b = 7.247(3)$, $c = 10.202(5)$ Å, $\beta = 91.05(4)°$, $U = 1365.0(1)$ Å³, $Z = 4$, $D_c = 1.414$ g cm⁻³; $R = 0.079$ and $R_w = 0.042$ for 1772 unique reflections with $I \geq 2\sigma(I)$.

For (4): $C_8H_{16}ClNOSi$, $M = 205.5$, orthorhombic, space group $P2_12_12_1$, $a = 9.396(3)$, $b = 9.500(3)$, $c = 11.853(5)$ Å, $U = 1057.9(7)$ Å³, $Z = 4$, $D_c = 1.292$ g cm⁻³; $R = 0.027$ and $R_w = 0.025$ for 1608 unique reflections with $I \geq 2\sigma(I)$.

For (5): $C_9H_{18}ClNOSi$, $M = 219.5$, triclinic, space group $P\bar{1}$, $a = 6.194(1)$, $b = 8.770(2)$, $c = 11.329(3)$ Å, $\alpha = 69.23(2)$, $\beta = 87.59(2)$, $\gamma = 87.64(2)°$, $U = 574.7(2)$ Å³, $Z = 2$, $D_c = 1.270$ g cm⁻³; $R = 0.052$ and $R_w = 0.046$ for 2909 unique reflections with $I \geq 2\sigma(I)$.

For (6): $C_{13}H_{18}ClNO_2Si$, $M = 283.5$, triclinic, space group $P\bar{1}$, $a = 7.586(3)$, $b = 8.701(3)$, $c = 22.460(9)$ Å, $\alpha = 90.48(3)$, $\beta = 90.48(3)$, $\gamma = 95.43(3)°$, $U = 1475.7(9)$ Å³, $Z = 4$, $D_c = 1.283$ g cm⁻³, two independent molecules; $R = 0.060$ and $R_w = 0.065$ for 4778 unique reflections with $I \geq 2\sigma(I)$.

For (7): $C_9H_{16}ClNO_2Si$, $M = 233.5$, monoclinic, space group $P2_1/n$, $a = 11.432(6)$, $b = 6.443(3)$, $c = 18.156(8)$ Å, $\beta = 107.66(3)°$, $U = 1274.3(5)$ Å³, $Z = 4$, $D_c = 1.229$ g cm⁻³; $R = 0.069$ and $R_w = 0.053$ for 1884 unique reflections with $I \geq 2\sigma(I)$.

For (8): $C_7H_{14}FNOSi$, $M = 175.0$, triclinic, space group $P\bar{1}$, $a = 9.48(1)$, $b = 12.15(6)$, $c = 16.48(3)$ Å, $\alpha = 100.2(1)$, $\beta = 95.3(1)$, $\gamma = 90.3(1)°$, $U = 1860(5)$ Å³, $Z = 8$, $D_c = 1.25$ g cm⁻³, four independent molecules; $R = 0.077$ and $R_w = 0.066$ for 2257 unique reflections with $I \geq 2\sigma(I)$.

The analyses of (1), (2), and (4)—(8) were carried out with a Syntex $P2_1$ automated diffractometer at 153 K (Mo-K_α radiation, θ—2θ scan, θ_{max} 30.5°). The structures were solved by the direct method and refined by block-diagonal least-squares in anisotropic (isotropic for H atoms located in the difference Fourier maps) approximation. For (1) and (2) absorption corrections according to DIFABS technique[7] were applied. All calculations were performed with an Eclipse S/200 computer using INEXTL programmes.[8]

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
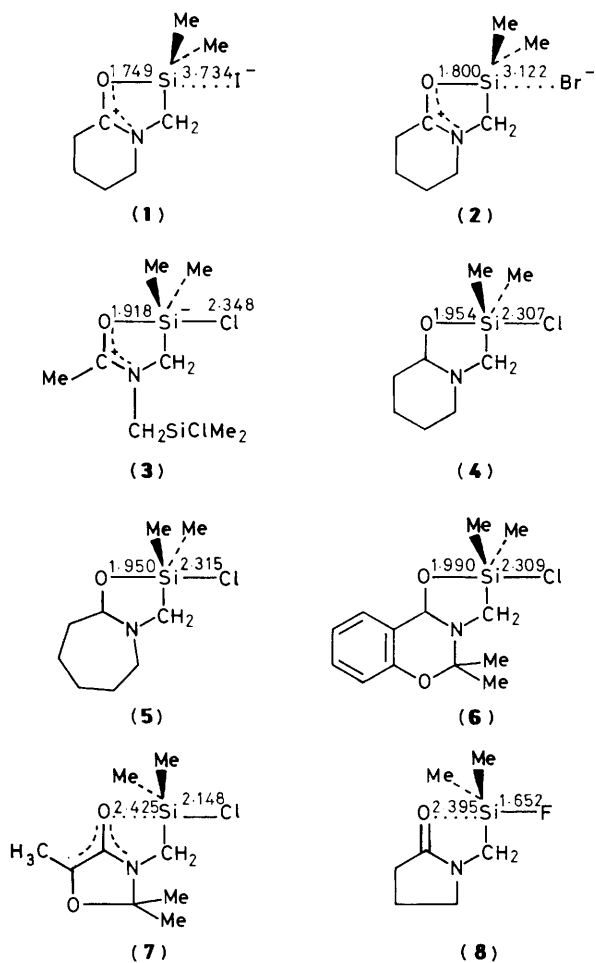

Figure 1. Structures of compounds (1)—(8) showing axial Si–O and Si–X bond distances (Å). See Table 1 for deviations (Δ) from the corresponding standard bond lengths for a tetrahedral Si atom, displacements (h_{Si}) of the Si atom from the C_3 equatorial plane towards the axial O atom, the Si–O and Si–X bond orders n_{Si-O} and n_{Si-X}.

at the Si atom and lactam cycles differing in size and composition.

This series of compounds can be regarded as a model of the whole route of the S_N2 reaction at the Si atom. Indeed, the axial Si–O distances vary from 1.749(2) Å in the iodide (1), comparable to the covalent bond length (1.68 Å),[9] to 2.395(8) Å in the fluoride (8), while the Si–X distances vary from 3.734(1) Å in (1), close to the Van-der-Waals contact, to 1.652(7) Å in (8), corresponding to the length of the

almost-covalent bond (1.55 Å).[10] Accordingly, a regular change of the Si atom position relative to the plane of the three equatorial C atoms is observed in the series (1)—(8): the displacement of the Si atom from this plane towards the O atom ranges between 0.348(1) Å in (1) and −0.286(3) Å in (8) (note the change of the sign) (see Figure 1 and Table 1).

The Pauling–Bürgi[1,11] Si–O and Si–X bond orders vary from 0.85 and 0.15 in (1) to 0.18 and 0.82 in (8), being almost equal (~0.5) in the 'intermediate' chlorides (3)—(6) (Figure 1). The Si atom co-ordination changes in the series (1)—(8) from [4 + 1] (i.e. somewhat distorted tetrahedral with a secondary[12] Si · · · X bond) in (1) and (2), through trigonal bipyramidal [3 + 2] in (3)—(6), and back to the distorted tetrahedral, but inverted, [1 + 4] co-ordination in (7) and (8).

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