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Molecular and crystal structure of *N*-(fluorodimethylsilylmethyl)pyrrolidone-2

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Abstract

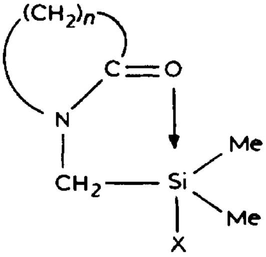
An X-ray diffraction study of *N*-(fluorodimethylsilylmethyl)pyrrolidone-2 was carried out ($R = 0.077$ for 2256 reflections with $I \geqslant 2\sigma(I)$. The Si atom has distorted trigonal-bipyramidal [4 + 1] coordination with the F and O atoms in axial positions. The Si–F and Si ← O distances in four independent molecules are 1.630–1.665(7) and 2.316–2.461(8) Å, respectively.

Introduction

The five-coordinated Si atom in *N*-(halogenodimethylsilylmethyl)lactams has trigonal-bipyramidal coordination with the X and O atoms in axial positions, the strength of the Si ← O interaction being strongly dependent on the character of the X substituent [1].

Thus there is strong secondary Si ← O interaction in the Cl derivative (I) of valerolactam, which causes weakening of the Si–Cl bond [2], whereas in the bromo and iodo derivatives II and III of valerolactam [3,4] the Si ← O bond is almost covalent and only a weak residual X → Si coordination is observed.

The IR spectra indicate that the intramolecular Si ← O interaction is not only present in the chloro, bromo and iodo derivatives I–III but also in molecules with $X = OCOCF_3$, OSO_2CH_3, OSO_2Ph, F, although the strength of the secondary interaction is different in this series, a feature which is reflected in the shift of the ν(C=O) band. Thus the substitution of F for Cl in the butyrolactam derivatives ($n = 3$) shifts the ν(CO) band from 1630 to 1660 cm^{-1}, which indicates that some weakening of the Si ← O coordination bond has occurred. On the other hand, an



(I : $n = 4$, X = Cl ;
II : $n = 4$, X = Br ;
III : $n = 4$, X = I)

increase in the electron-accepting inductive effect of the X substituent should cause an increase in the positive charge on the Si atom and consequently the donor–acceptor Si ← O bond should be stronger in the fluoro than in the chloro derivative.

An X-ray study of the homologue of the compounds I–III with X = F and $n = 3$, i.e. the *N*-(fluorodimethylsilylmethyl)pyrrolidone-2 (IV) is thus of special interest, and should allow comparison of the Si ← O interactions in I–IV, and should also help to clarify the more general problem concerning the pathway of the $S_{\mathrm{N}}2$ nucleophilic substitution at the tetrahedral Si atom. When the substituent X is replaced with another the X...Si and Si...O distances are changed such that the simultaneous approach to and removal from the Si atom of the substituents resembles the behaviour of reagents during an $S_{\mathrm{N}}2$ reaction.

Results and discussion

Crystals of IV contain asymmetric units comprising the four molecules A–D. The Si atom in all molecules has trigonal-bipyramydal coordination with the O and F atoms in axial, and the three C atoms in equatorial positions. The length of the axial Si–F bond in the four independent molecules varies from 1.630(7) to 1.665(7) Å being only 0.1 Å longer than the Si–F distances typical of the tetrahedral Si atom (e.g. 1.55 Å in $F_3SiOSiF_3$ [15]). The Si ← O distance varies from 2.316 to 2.461(8) Å and are thus much longer than the Si ← O distance of 1.954(2) Å in the chloro derivative I. A rather large variation of the Si ← O distances in IV can be attributed to the relative weakness of the Si ← O interaction under the influence of the crystal field. Indeed the average Si ← O bond order (n(Si–O)) in IV calculated by the method of Pauling [6] (with a value of 1.68 Å as a standard Si–O bond length for the tetrahedral Si atom [7]) was found to be 0.18. The average order (n(Si–F)) of the Si–F bonds (calculated using the standard Si–F bond length of 1.55 Å) was found to be 0.82.

The Si atom in IV is displaced from the equatorial plane towards the F atom by 0.238–0.305(3) Å, which is considerably greater than the displacement of silicon (ΔSi) of 0.058(2) Å in I and approaches the absolute value of 0.218(2) Å in II and 0.348(1) in III, though in II and III the Si atom is displaced in the opposite direction, i.e. towards the O atom.

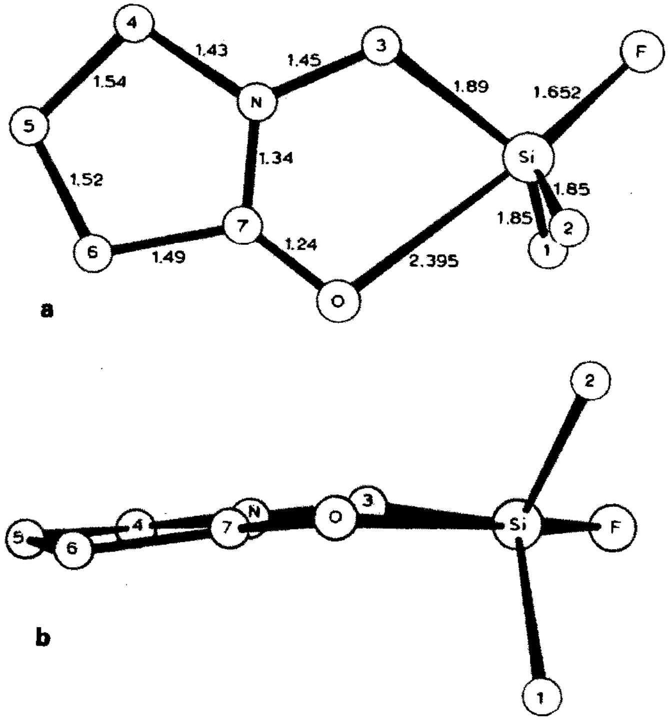


Fig. 1. Structure of molecule IV: (a) projection onto the mean plane of the molecule (excluding the Si, F, C(1) and C(2) atoms), the mean values of the bond lengths in the four independent molecules are given; (b) projection onto the plane normal to the mean plane of the molecule and passing through its long axis.

The angle between the axial substituents OSiX in IV, of 171.3–174.0(3)°, is closer to the value in I (171.66°) than to those in II (162.6(3)°) and in III (161.90 (7)°). The difference between the OSiX bond angles in I and those in IV, on one

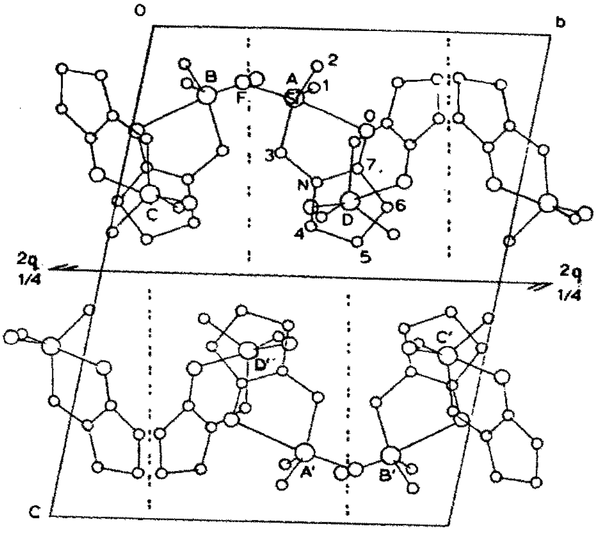


Fig. 2. Projection of the structure of IV onto the *bc* plane. The supersymmetry is marked by double dotted lines; a double-headed arrow represents the supersymmetry axis.

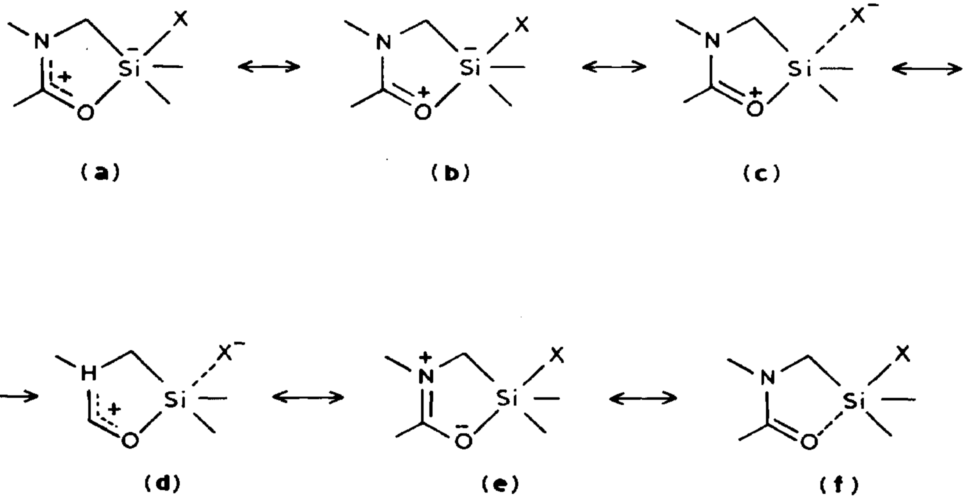
hand, and the corresponding angles in II and III, on the other, is evidently a result of greater Si...X separations and therefore weaker Si...X interactions in II and III, which give rise to a greater influence by the non-bonded Br...C and I...C interactions on the position of the bulky Br (in II) and I (in III) atoms. In the case of the more rigid "chelate" cycle $\overline{\text{C–N–C–O–Si}}$ these interactions result in a more pronounced non-linearity of the axial bonds.

The coordination environment of the Si atom in IV is best described as [4 + 1] (the weakest interaction with the O atom) just as in molecules II and III (with the weakest interactions with Br and I atoms) but is in contrast to molecule I which has [3 + 2] coordination.

In IV the C–O bonds (1.21–1.25(1) Å) are somewhat longer and the C–N bonds (1.32–1.37(1) Å) are markedly longer than the corresponding standard double bond lengths (1.215(5) and 1.255 Å [8]).

The bond orders, $n(\text{CO}) = 1.62$ and $n(\text{CN}) = 1.37$, for the fragment $\text{N}{=}\overset{+}{\text{C}}{=}\text{O}$, calculated by use of a published method [9] indicate a pronounced delocalization in this system which is in good agreement with the greater $\text{C}{=}\text{O}$ bond order and the weakness of the Si ← O interaction. The Si atom in molecule IV is displaced from the mean plane of the four atoms of the "chelate" cycle by 0.010(3)–0.314(3) Å. Such significant variation is evidently caused by weakness in the Si ← O interaction which results in a flexible conformation of the cycle and its variability under the influence of the different crystal surroundings of the independent molecules in IV. The differences in conformation of the more rigid pyrrolidone cycles in molecules IV are naturally smaller: the C(5) atom is displaced from the plane of the four other atoms of the cycle by 0.10(1)–0.28(1) Å. Both "chelate" and pyrrolidone cycles (the dihedral angle between their mean planes 170.1–178.3°) have an envelope conformation, the C(5) and Si atoms located in the envelope flaps are displaced from the mean planes of both cycles in opposite directions.

The bond length distribution in IV allows the structure to be represented as the canonic forms (a)–(f) with a predominant contribution by structure f:



(a) (b) (c)

(d) (e) (f)

Table 1

Atomic coordinates ($\times 10^4$ for F and Si, $\times 10^3$ for N, O, C, $\times 10^2$ for H) and equivalent isotropic (isotropic for H atoms) temperature factors B (Å^2)

Atom	Molecule A				Molecule B			
	x	*y*	*z*	***B***	*x*	*y*	*z*	***B***
Si	528(3)	3945(3)	1416(2)	2.8(1)	5458(3)	1752(3)	1393(2)	2.7(1)
F	520(6)	2575(5)	1085(4)	4.4(2)	5476(6)	2919(5)	1035(4)	4.3(2)
N	557(9)	4940(8)	3083(6)	3.3(3)	5393(8)	1706(7)	3101(6)	2.9(3)
O	500(7)	5928(6)	2049(5)	3.7(3)	5440(7)	171(6)	2143(5)	3.8(3)
C(1)	231(1)	436(1)	119(1)	3.8(4)	726(1)	118(1)	115(1)	3.8(4)
C(2)	−102(1)	433(1)	76(1)	3.5(4)	395(1)	102(1)	76(1)	4.3(4)
C(3)	39(1)	389(1)	254(1)	4.4(4)	527(1)	244(1)	250(1)	3.2(4)
C(4)	74(1)	503(1)	400(1)	4.8(5)	551(1)	209(1)	399(1)	3.4(4)
C(5)	86(1)	627(1)	428(1)	5.3(5)	557(1)	100(1)	434(1)	5.0(5)
C(6)	91(1)	683(1)	356(1)	4.6(5)	571(1)	6(1)	360(1)	3.7(4)
C(7)	66(1)	588(1)	280(1)	3.0(4)	548(1)	61(1)	286(1)	3.0(4)
H(1.1)	25(1)	52(1)	13(1)	7(3)	−25(1)	10(1)	21(1)	8(3)
H(1.2)	27(1)	42(1)	16(1)	10(4)	−20(1)	16(1)	17(0)	0(2)
H(1.3)	22(1)	42(1)	6(1)	15?(4)	27(1)	83(1)	95(1)	5(3)
H(2.1)	−9(1)	41(1)	2(1)	8(4)	63(1)	86(1)	87(1)	5(3)
H(2.2)	−18(1)	41(1)	11(1)	12(4)	61(1)	88(1)	98(1)	2(2)
H(2.3)	−9(1)	52(1)	8(1)	9(4)	60(1)	96(1)	91(1)	3(2)
H(3.1)	13(1)	32(1)	25(1)	7(3)	39(1)	68(1)	73(1)	4(2)
H(3.2)	−3(1)	38(1)	25(1)	3(2)	57(1)	73(1)	75(1)	3(2)
H(4.1)	18(1)	47(1)	41(0)	0(1)	33(1)	75(1)	57(1)	6(3)
H(5.1)	17(1)	64(1)	48(1)	0(2)	33(1)	90(1)	51(1)	8(4)
H(5.2)	−1(1)	67(1)	45(1)	5(3)	40(1)	26(1)	52(2)	4(2)
H(6.1)	21(1)	71(1)	36(1)	2(2)	−32(1)	87(1)	35(1)	3(2)
H(6.2)	11(2)	78(1)	36(1)	15(5)	50(1)	5(1)	64(0)	1(2)

Atom	Molecule C				Molecule D			
	x	*y*	*z*	***B***	*x*	*y*	*z*	***B***
Si	844(3)	865(3)	3432(2)	3.2(1)	6095(3)	5869(3)	3457(2)	3.5(1)
F	2058(6)	1884(5)	3590(5)	5.0(3)	7293(6)	4909(6)	3609(5)	5.4(3)
N	222(9)	9495(7)	1870(6)	3.5(3)	5314(8)	6414(7)	1876(5)	2.7(3)
O	−786(7)	9398(6)	3049(5)	3.4(3)	4413(7)	7136(6)	3062(5)	3.5(3)
C(1)	164(1)	1008(1)	420(10)	6.6(6)	690(1)	713(1)	1410(1)	4.4(4)
C(2)	−77(1)	1165(1)	369(1)	3.6(4)	450(1)	524(1)	1379(1)	4.1(4)
C(3)	110(1)	1046(1)	232(1)	3.1(4)	616(1)	567(1)	1229(1)	4.7(5)
C(4)	8(1)	902(1)	103(1)	4.4(4)	517(1)	645(1)	1104(1)	5.1(5)
C(5)	−91(1)	797(1)	93(1)	5.0(5)	411(1)	740(1)	1093(1)	5.7(5)
C(6)	−162(1)	817(1)	174(1)	4.3(4)	350(1)	766(1)	1177(1)	3.9(4)
C(7)	−74(1)	905(1)	230(1)	2.8(4)	442(1)	709(1)	1231(1)	2.9(4)
H(1.1)	24(1)	96(1)	41(1)	9(3)	−25(1)	70(1)	47(1)	5(3)
H(1.2)	15(1)	0(1)	44(1)	2(2)	56(1)	74(1)	40(1)	8(4)
H(1.3)	9(1)	97(1)	42(0)	0(2)	73(1)	77(1)	37(1)	19(5)
H(2.1)	−6(1)	24(1)	38(1)	3(2)	36(1)	51(1)	33(1)	5(3)
H(2.2)	−13(1)	19(1)	32(1)	6(3)	50(1)	47(1)	44(1)	4(2)
H(2.3)	−17(2)	14(1)	38(1)	20(7)	44(1)	57(1)	44(1)	8(3)
H(3.1)	23(1)	3(1)	24(1)	4(2)	66(1)	57(1)	18(1)	13(5)
H(3.2)	14(1)	14(1)	24(1)	3(2)	40(1)	52(0)	80(0)	−1(1)
H(4.1)	8(1)	90(1)	10(1)	13(5)	−38(1)	68(1)	12(1)	9(3)
H(4.2)	−5(1)	97(1)	7(1)	4(2)	46(1)	59(1)	8(1)	3(2)
H(5.1)	4(2)	73(1)	10(1)	16(6)	53(1)	60(1)	12(1)	4(2)
H(5.2)	−15(1)	81(1)	4(1)	3(2)	33(1)	73(1)	3(1)	6(3)
H(6.1)	−13(2)	75(1)	23(1)	16(6)	35(1)	86(1)	24(1)	6(3)
H(6.2)	−31(1)	81(1)	12(1)	8(4)	25(1)	69(1)	12(1)	9(4)

The molecules in crystal IV (Fig. 1) are separated by the normal Van der Waals distances (see Fig. 2) and form the infinite layers parallel to the *ab* plane of the crystal. The crystallographically independent molecules **A**–**D** are related by non-crystallographic supersymmetry operations [10]. Thus within the layers the molecules **B** are related to the molecules **A**, and the molecules **D** are related to the molecules **C** by the glideplane which is normal to the *b* axis at $y = 1/4$ with the translation component (δ) of ($a/200$). Supersymmetry relations are also found between the molecules in the different layers. The molecule **A** is related to the molecule **B′** (which is derived from the reference molecule **B** by the inversion center (0, 1/2, 1/2)) and molecule **C** is related to molecule **D′** by the $2q$ supersymmetry operation (a 180° rotation accompanied by the translation along the rotation axis). The $2q$ supersymmetry axis is parallel to the y axis, passes through the point (1/4, 0, 1/2), and the translation along the axis is equal to $b/4$).

There are no supersymmetry relations between molecules **A** and **B**, or between molecules **C** and **D**. Thus, the pairs **A** and **C**, **A** and **D**, **B** and **C**, and **B** and **D** molecules are not related by supersymmetry operations.

The search for the supersymmetry relations was carried out with the aid of the SUSY programme [11]. Deviations in the supersymmetry transformations do not exceed 0.10 Å.

Thus the present study confirms the suggestion that weakening of the Si ← O interaction takes place in the *N*-(halogenodimethylsilylmethyl) lactam molecules on replacement of Cl by F atom. The precise molecular geometry has been determined of one of the extreme forms on the $S_{N}2$ reaction pathway at the tetrahedral Si atom. In this molecular from, in which the Si atom tetrahedron is inverted relative to that in the bromo and iodo derivatives, the longest of the Si ← O distances found previously and, the almost covalent Si–X(F) bond are observed.

Experimental

N-(Fluorodimethylsilylmethyl)pyrrolidone-2 (IV) was prepared by an exchange reaction between the sulphonate and potassium fluoride [12]. At room temperature

Table 2

Bond lengths d (Å) in the molecules **A**–**D** in the structure IV

Bond	d			
	A	**B**	**C**	**D**
Si–F	1.658(7)	1.630(7)	1.656(7)	1.665(7)
Si–O	2.451(8)	2.461(8)	2.316(8)	2.350(8)
Si–C(1)	1.85(1)	1.90(1)	1.83(2)	1.83(1)
Si–C(2)	1.86(1)	1.82(1)	1.85(1)	1.86(1)
Si–C(3)	1.89(1)	1.88(1)	1.85(1)	1.90(1)
O–C(7)	1.25(1)	1.21(1)	1.25(1)	1.23(1)
N–C(3)	1.42(2)	1.45(1)	1.48(1)	1.43(1)
N–C(4)	1.48(2)	1.45(1)	1.40(2)	1.38(2)
N–C(7)	1.32(1)	1.33(1)	1.37(1)	1.36(1)
C(4)–C(5)	1.50(2)	1.54(2)	1.55(2)	1.56(2)
C(5)–C(6)	1.48(2)	1.54(2)	1.53(2)	1.53(2)
C(6)–C(7)	1.55(2)	1.48(2)	1.48(2)	1.46(2)

Table 3

Bond angles ω (°) in the molecules A–D in the structure IV

Angle	ω			
	A	B	C	D
FSiO	174.0(3)	171.3(3)	173.1(4)	172.7(4)
FSiC(1)	101.6(5)	101.5(5)	97.1(5)	102.1(5)
FSiC(2)	99.9(5)	100.9(5)	101.7(5)	100.4(5)
FSiC(3)	96.6(5)	95.1(4)	93.6(4)	95.7(5)
OSiC(1)	91.5(4)	81.9(4)	86.5(5)	82.7(4)
OSiC(2)	83.1(4)	84.6(4)	81.7(4)	81.8(4)
OSiC(3)	77.4(4)	76.3(4)	79.6(4)	77.1(4)
C(1)SiC(2)	117.6(5)	115.5(6)	117.0(6)	118.7(6)
C(1)SiC(3)	114.0(6)	117.1(5)	121.4(6)	118.7(6)
C(2)SiC(3)	120.7(5)	119.9(5)	116.7(5)	114.7(6)
SiOC(7)	101.8(7)	104.1(7)	107.4(4)	107.4(7)
C(3)NC(4)	121.8(9)	124.0(9)	130.1(9)	127.8(9)
C(3)NC(7)	121.8(9)	120.5(9)	117.6(9)	118.7(9)
C(4)NC(7)	116.3(9)	115.4(9)	111.8(9)	113.0(9)
SiC(3)N	114.6(8)	115.7(8)	115.2(7)	115.8(8)
NC(4)C(5)	101.9(9)	103.4(9)	107.2(9)	106 (1)
C(4)C(5)C(6)	109 (1)	105.8(9)	102 (1)	103 (1)
C(5)C(6)C(7)	104.7(9)	104.5(9)	105.4(9)	104.7(9)
OC(7)N	122.7(9)	123 (1)	120.1(9)	120.5(9)
OC(7)C(6)	130 (1)	127 (1)	130 (1)	128 (1)
NC(7)C(6)	107.2(9)	110.1(9)	110.4(9)	111.2(9)

IV is a colourless liquid. The single crystal of IV was grown, in a capillary by slow cooling to crystallization temperature (about −35 °C), directly in the "Syntex $P2_1$" diffractometer equipped with a low-temperature device. The crystal thus obtained was slowly cooled to −120 °C, so that X-ray diffraction measurements could be carried out.

Crystals IV are triclinic; at −120 °C: a 9.48(1), b 12.15(6), c 16.48(3) Å, α 100.2(1), β 95.3(1), γ 90.3(1)°, V 1860(5) Å^3, d_{calc} 1.25 g cm^{-3}, $Z = 8$ ($C_{17}H_{14}FNOSi$), the space group $P\bar{1}$; 4330 reflections were measured (Mo-K_α, $\theta/2\theta$ scan, θ_{max} 30°). The structure was solved by the direct method using MULTAN [13] programme and refined anisotropically for non-hydrogen atoms by block diagonal least squares. The H atoms of the methyl groups were located in the difference Fourier synthesis (the positions of other H atoms were calculated) and refined isotropically. The final discrepancy factors are $R = 0.077$, $R_w = 0.066$ for a total of 2257 independent reflections with $I \geqslant 2\sigma(I)$. All calculations were carried out using INEXTL programmes [14] with an "Eclipse S/200" computer.

In Tables 1–3 are given the relevant atomic coordinates, temperature factors, bond angles and bond lengths.

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