Journal of Organometallic Chemistry, 461 (1993) 27–30

JOM 23746

Crystal structure of hypervalent silicon compounds. (N → Si)(2-benzothiazolylthiomethyl)trifluorosilane and (N → Si)(2-benzoxazolylthiomethyl)trifluorosilane

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(Received February 28, 1993)

Abstract

The crystal structures of two hypervalent silicon compounds (N → Si) (2-benzothiazolylthiomethyl)trifluorosilane and (N → Si) (2-benzoxazolylthiomethyl)trifluorosilane have been determined. Both molecules have similar geometrical parameters. The Si atom acquires a distorted trigonal bipyramidal penta-coordination due to five-membered ring closure by a donor-acceptor N → Si bond of lengths of 1.988(3) and 1.967(4) Å, respectively. In the second crystal structure, molecules form a stacked packing with the distance between the planar parts of the neighbouring molecules in the stacks equal to 3.45 Å.

1. Introduction

Compounds with silicon atoms having coordination numbers greater than 4 (hypervalent compounds) may hardly be considered exotic at present. This notwithstanding, the known relevant crystal structures are not very numerous, especially among certain classes of hypervalent compounds, *e.g.* with the same type of Si atom coordination. Taking into account the low accuracy of many early X-ray structural studies in this area, the scope of structures allowing such important geometrical parameters as the bond lengths of hypervalent Si atoms to be discussed, remains rather limited. In the present paper, we report on the crystal structures of two similar hypervalent silicon compounds with the same Si atom environment, *viz.* (N → Si) (2-benzothiazolylthiomethyl) trifluorosilane (**I**) and (N → Si) (2-benzoxazolylthiomethyl)trifluorosilane (**II**).

2. Experimental details

Compounds **I** and **II** were prepared by interaction of (2-benzothiazolylthiomethyl)- and (2-benzoxazolylthiomethyl)trimethoxysilanes with $BF_3 \cdot Et_2O$ and purified by crystallization from benzene.

Crystals of **I** (m.p. 170°C) are triclinic, at 293 K a = 7.266(2); b = 7.495(2), c = 10.273(2) Å, α = 68.91(2), β = 88.23(2), γ = 82.67(2)°, V = 517.6(3) Å^3, D_x = 1.702 g cm^{-3}, Z = 2($C_8H_6NF_3SiS_2$), space group $P\bar{1}$.

Crystals of **II** (m.p. 173°C) are monoclinic, at 293 K a = 7.080(2), b = 6.891(2), c = 10.379(3) Å, β = 106.92(2)°, V = 484.5(5) Å^3, D_x = 1.709 g cm^{-3}, Z = 2($C_8H_6NOF_3SiS$), space group $P2_1$. Unit cell parameters and intensities of 2148 (**I**) and 1036 (**II**) reflections were measured with a Siemens P3/PC diffractometer (λ(Mo Kα), graphite monochromator, θ–2θ scan, $2\theta_{max}$ = 60° (**I**) and 52° (**II**)). Both structures were solved by direct methods. Structure **I** was refined by the full-matrix least-squares procedure in the anisotropic approximation for non-hydrogen atoms and isotropic for H atoms localized in the difference Fourier map. The final discrepancy factor $R = 0.067$ ($R_w = 0.062$) on 1930 reflections with $I > 2\sigma(I)$.

For structure **II**, systematic reflection absences are satisfied by the space groups $P2_1$ and $P2_1/m$. However, in the latter space group, where the molecule of **II** occupies a special position across the mirror symme-

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TABLE 1. Coordinates ($\times 10^4$, $\times 10^3$ for H) and equivalent isotropic thermal parameters ($\times 10^3$) of the atoms in **I**

Atoms	x	y	z	U (Å^2)
S(1)	1805(2)	−21(2)	3672(1)	60(1)
S(2)	2012(2)	1967(1)	540(1)	57(1)
Si(1)	2488(2)	−4131(2)	3464(1)	55(1)
F(1)	2532(5)	−6103(4)	4836(3)	93(1)
F(2)	907(4)	−4676(3)	2686(3)	71(1)
F(3)	4515(4)	−4683(3)	2983(3)	72(1)
N(1)	2410(4)	−1701(4)	1813(3)	40(1)
C(1)	2070(9)	−2592(7)	4550(5)	70(2)
C(2)	2092(5)	−61(5)	2014(4)	43(1)
C(3)	2485(5)	519(5)	−462(4)	46(1)
C(4)	2680(6)	1083(7)	−1908(4)	59(2)
C(5)	3047(6)	−342(8)	−2446(5)	67(2)
C(6)	3203(6)	−2265(8)	−1608(5)	66(2)
C(7)	3013(6)	−2828(7)	−186(4)	55(2)
C(8)	2642(5)	−1408(5)	395(4)	40(1)
H(1.1)	305(9)	−313(9)	551(7)	120(20)
H(2.2)	111(9)	−283(9)	508(7)	110(20)
H(4)	266(6)	239(7)	−243(5)	80(10)
H(5)	317(6)	7(6)	−341(5)	70(10)
H(6)	342(6)	−322(7)	−197(5)	70(10)
H(7)	304(5)	−401(6)	37(4)	40(10)

TABLE 2. Coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) of the atoms in **II**

Atom	x	y	z	U (Å^2)
S(1)	5168(3)	2500 [a]	1360(2)	56(1)
Si(1)	735(3)	2451(5)	1441(2)	41(1)
F(1)	−1093(5)	2440(9)	66(4)	62(1)
F(2)	13(6)	4381(6)	2000(5)	44(1)
F(3)	63(8)	555(6)	2069(6)	75(1)
O(1)	6251(6)	2450(9)	4046(5)	53(1)
N(1)	3028(6)	2452(9)	3059(5)	37(1)
C(1)	2583(7)	2481(9)	445(6)	52(1)
C(2)	4753(7)	2403(9)	2919(6)	43(1)
C(3) [b]	5363(5)	2399(7)	5040(3)	47(1)
C(4)	6114(5)	2335(7)	6440(3)	57(1)
C(5)	4829(5)	2315(7)	7235(3)	58(1)
C(6)	2794(5)	2360(7)	6631(3)	63(1)
C(7)	2042(5)	2425(7)	5231(3)	55(1)
C(8)	3327(5)	2444(7)	4435(3)	40(1)

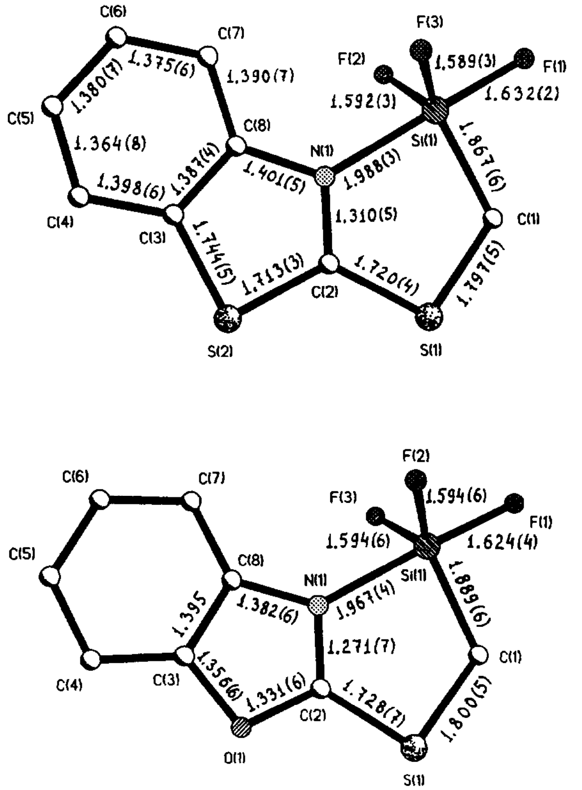
[a] Given to fix the coordinate origin. [b] Sites of the C(3)$\cdots$C(8) atoms were refined as corners of a regular hexagon with sides of 1.395 Å.

try plane, some geometrical parameters in the course of refinement deviated strongly from the standard values. Thus the difference of O(1)–C(2) and O(1)–C(3) bond lengths reached 0.07 Å and the benzene ring bond angles varied in the range 115–125°. The refinement in the space group $P2_1$ gave better results. In order to decrease the number of refined parameters, the benzene ring atoms were refined in the rigid model of a regular hexagon with sides of 1.395 Å. Furthermore, the Si(2)–F(2) and Si(1)–F(3) bond lengths were refined as a single parameter. Structure **II** was refined by the anisotropic least-squares procedure for non-hydrogen atoms. H atoms were placed in calculated positions and were not refined but their contribution was included in the F_{calc} values with fixed $U = 0.08$ Å^2. Finally, $R = 0.065$ ($R_w = 0.065$) on 859 reflections with $I > 2\sigma(I)$.

All calculations were carried out with an IBM PC/AT computer using the SHELXTL programs [1]. Atomic coordinates in structures **I** and **II** are listed in Tables 1 and 2.

3. Discussion

A general view of molecules **I** and **II** with bond lengths is shown in Fig. 1 and the main bond angles are given in Table 3. A Similarity in the chemical composition of molecules **I** and **II** leads to the closeness in their respective structural parameters. The coordination polyhedron of the pentacoordinated Si atom, *viz.* a distorted trigonal bipyramid, is essentially the same in both structures. The replacement of S by an O atom in the 5-membered ring on going from **I** to **II** almost does



(I)

(II)

Fig. 1. A general view of molecules **I** and **II** with the bond lengths in Å. Hydrogen atoms are not shown. The benzene ring bond lengths of **II** are fixed at 1.395 Å.

not change the donor–acceptor N → Si bond length (1.988(3) and 1.967(4) Å, respectively) and the increase in the axial Si–F(1) bond length relative to the equatorial bond lengths. These geometrical parameters are close to those observed in other hypervalent silicon compounds, where the Si atom is bonded to three atoms and the donor–acceptor N(sp^2) → Si bond closes a 5-membered ring, even if the latter is not involved in a polycyclic system [2,3]. At the same time, in the 4-membered Si_2N_2 cycle [4], the $N_{ax} \rightarrow Si$ distance is considerably shorter (1.857(4) Å) and the corresponding bond order is comparable to that of the Si–F_{ax} bond (1.668(3) Å and the Si atom is in the plane of its equatorial substituents).

Some shortening of the endocyclic S–C(2) and S–C(3) bonds in **I** and the respective bonds in **II** in comparison with standard values of 1.751(17) Å (S–C (sp^2), 1.773(9) Å (S–C_{ar}), ~ 1.36 Å (O=C(sp^2)) in 5-membered rings and 1.37–1.38 Å (O–C_{ar}) [5] may be due to electron delocalization in benzothiazole and benzoxazole derivatives. Geometric analysis of some 20 accurate structures ($R < 0.04$, $\delta(C–C) < 0.005$ Å) with the –S– C(sp^2)–S– units retrieved from the Cambridge Structural Database (Release 1992) has shown delocalization to be favoured by the symmetry of the chemical surroundings of such moieties or the topological symmetry of their relative arrangement in a molecule [6–8]. The geometry of the mercaptothiazolyl fragment in this group of structures is unexceptional [9]. However, in some less accurate structures with benzothiazole fragments, the shortening of S–C(sp^2) bonds in comparison with the standard bond length seems to be as significant as in molecule **I**: 1.717 and 1.729(4) Å [10], 1.712(5) and 1.696(4) Å [11]. In molecule **II**, the bond shortening is only (5–6)σ and this fact, along with the normal C(2)–N(1) bond length (in molecule **I** it exceeds the standard value by 0.03 Å), testifies to a low probability of delocalization. The latter assumption agrees with a lesser mobility of electrons of the O atom in comparison with the S atom.

TABLE 3. Relevant bond angles (°) in structures I and II

	I	II
C(1)S(1)C(2)	96.0(2)	94.0(3)
C(2)S(2)C(3)	89.6(2)	–
C(2)O(1)C(3)	–	103.9(4)
F(1)Si(1)F(2)	93.9(2)	93.8(3)
F(1)Si(1)F(3)	94.4(1)	95.7(3)
F(2)Si(1)F(3)	112.7(2)	111.7(3)
F(1)Si(1)N(1)	178.9(2)	177.5(3)
F(2)Si(1)N(1)	86.4(1)	87.8(2)
F(3)Si(1)N(1)	86.5(1)	85.5(3)
F(1)Si(1)C(1)	91.9(2)	91.2(2)
F(2)Si(1)C(1)	124.8(2)	122.5(3)
F(3)Si(1)C(1)	121.6(2)	124.7(3)
N(1)Si(1)C(1)	87.1(2)	86.3(2)
Si(1)N(1)C(2)	118.3(2)	119.0(4)
C(2)N(1)C(8)	111.3(3)	104.7(4)
S(1)C(1)Si(1)	117.9(3)	118.1(3)
S(1)C(2)N(1)	120.6(2)	122.4(4)
S(2)C(2)N(1)	115.6(3)	–
O(1)C(2)N(1)	–	116.5(6)

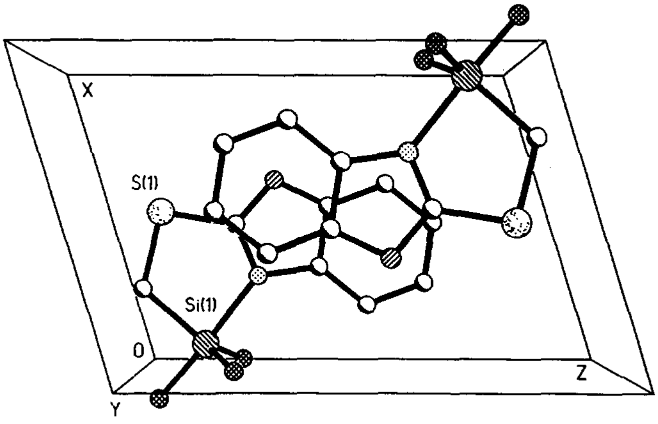


Fig. 2. The perspective projection along the *b* axis of two molecules of **II**, related by the crystallographic 2_1 axis.

The molecular packing in structure **II** is of a stack-layer type, which is favoured by a planar form of the main part of the molecule. Adjacent molecules in the stack, which is parallel to the *y* axis, are related by the crystallographic 2_1 axis and are situated, in fact, in the $y = 1/4, 3/4, \ldots$ planes with rather short intermolecular contacts of $b/2 = 3.45$ Å between the ring planes. A similar packing in structure **I** is evidently unfavourable because of the greater size of an S atom. One cannot rule out that the relative arrangement of neighbouring molecules **II** (Fig. 2) provides some additional interaction of their π-systems, which favours the observed packing. Somewhat great non-planarity of the molecular cycles in structure **II** is probably due to this interaction; the maximum deviations of thiazole and chelate ring atoms out of their mean planes are equal to 0.006 and 0.009 Å in **I** and 0.021 and 0.024 Å in **II**.

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