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Pentacoordinate Organosilicon Compounds—Molecular Structure and Stereodynamic Behavior of (Trifluorosilylmethyl)succinimide and (Trifluorosilylmethyl)glutarimide

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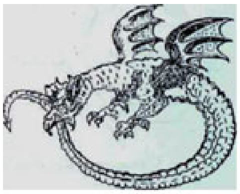
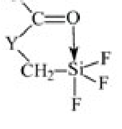
ABSTRACT: *The synthesis of pentacoordinate organosilicon compounds, N-(trifluorosilylmethyl)succinimide (**1**) and N-(trifluorosilylmethyl)glutarimide (**2**) is described. The X-ray crystal analysis of compound **1** shows a slightly distorted trigonal-bipyramidal coordination at silicon. Dynamic ^{19}F, ^{13}C, and ^{29}Si NMR studies confirm the existence of an $O \rightarrow Si$ intramolecular hypervalent bond in solution.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:567–571, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20278

INTRODUCTION

At the end of 1970s, a new class of the stable pentacoordinate organosilicon compounds having O → Si intramolecular bond (structure **A**) was discovered in the laboratory of the first author. The compounds were called dragonoids because their structure is like a famous alchemists' symbol, namely, dragon devouring his tail [1].

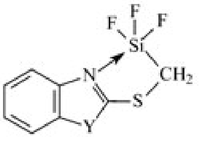
Hypervalent organosilicon complexes with N → Si coordinate bond (structures **B** and **C**) [2–7] can also be classified as dragonoids. The synthesis, structure, and reactivity of the compounds having $OCSiF_3$ coordinate framework have been extensively studied [8–12] and reviewed [1,13,14].





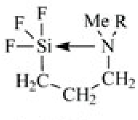
Y = O, S, NR', CH_2; R' = H, Alk;
R = Alk, Ar

A



Y = O, S

B



R = H, Me

C

Recently a first representative of dragonoids, *N*-(trifluorosilylmethyl) derivative of phthalimide (**3**) having two donating carbonyl groups was pre-

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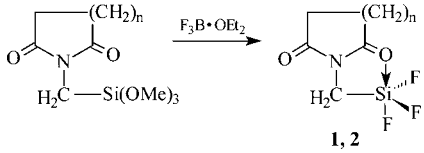
pared [15,16]. X-ray electron diffraction analysis supported the existence of the intramolecular O → Si hypervalent bond between the silicon atom and only one of the two carbonyl oxygens. The Si–O distance of 2.654 Å is much shorter than the sum of the van der Waals radii of 3.62 Å which indicates a weak donor–acceptor interaction in **3**.

Here we report the synthesis and study on the structure of new related compounds in order to elucidate the donor effect of the carbonyl group of the imides on their ability to form O → Si bond.

RESULTS AND DISCUSSION

New pentacoordinate organosilicon compounds *N*-(trifluorosilylmethyl)succinimide (**1**) and *N*-(trifluorosilylmethyl)glutarimide (**2**) were obtained by the reaction of the corresponding trimethoxy derivatives with boron trifluoride etherate.



1, 2

n = 1(**1**), 2 (**2**).

The X-ray crystal structure of *N*-(trifluorosilylmethyl)succinimide **1** is shown in Fig. 1. Selected interatomic distances and angles as well as dihedral angles are listed in Table 1. Bond lengths in **1** are in the typical ranges of other dragonoids [1].

The data confirm pentacoordination of the silicon atom in **1** arising from its donor–acceptor interaction with one of the carbonyl oxygen (O_1). The compound is characterized by a slightly distorted trigonal-bipyramidal (TBP) geometry at silicon. The axial positions are occupied by the fluorine (F_1) and the oxygen (O_1) atoms. Two fluorine (F_2) and (F_3) and (C_1) atoms form the equatorial plane of the trigonal bipyramid. The silicon atom is placed 0.19 Å outside of this plane in the direction of the fluorine substituent. This deviation results in the increase of the axial angles F_1SiF_2, F_1SiF_3, and F_1SiC_1 and decreases the angles O_1SiF_2, O_1SiF_3, and O_1SiC_1 relative to the angle value of 90°. The arrangement of (F_1), Si, and (O_1) is nearly linear.

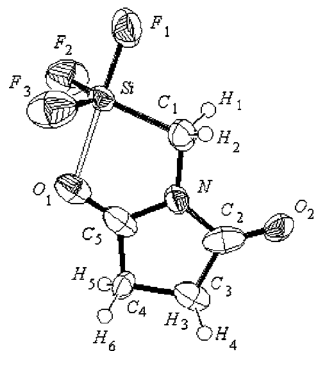


FIGURE 1 Molecular structure and atom-numbering scheme for *N*-(trifluorosilylmethyl)succinimide (**1**).

The interatomic distance between the oxygen atom and the pentacoordinate silicon atom in **1** is 2.096 Å and in the usual range values of 1.94–2.08 Å in other dragonoids and TBP organosilicon compounds [1]. The $Si—F_{ax}$ is slightly longer than the $Si—F_{eq}$ bonds (Table 1) and is similar to the length in ordinary tetracoordinate fluorosilanes (1.55–1.60 Å).

The donor–acceptor bonding between the O_1 and Si atoms results in the marked discrimination of two N—C=O imide units. In comparison to free carbonyl group, $C_2—O_2$, the $C_5—O_1$ bond involved in five-membered coordinated cycle is slightly elongated (0.04 Å) whereas the endocyclic $C_5—N$ bond is shorter than the $C_2—N$ bond (0.077 Å). These data suggest higher p,π-conjugation between the nitrogen atom and coordinated $C_5—O_1$ unit.

The O → Si bond distance in molecule **1** is significantly shorter than in molecule **3** (2.096 and 2.654 Å, respectively) that indicates stronger donor–acceptor interaction in **1** relating to **3**. It arises from higher nucleophilicity of the carbonyl group in **1** by comparing with that in benzoannulated imide **3**. The endocyclic C—C bond lengths lies within the typical limits of N-substituted succinimide [17–20].

The structure and the stereodynamic processes in compounds **1** and **2** involving all the ligands attached to the pentacoordinate silicon atom have been studied by ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectroscopic methods. According to the NMR data for **1** (Table 2), a trigonal-bipyramidal geometry at silicon found in the solid state is also present in solution.

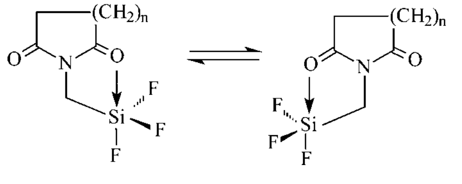
At room temperature, the ^1H spectrum of **2** exhibits a quintet and a triplet for endocyclic H-4 and H-3,5 protons, respectively. The latter signal has twice the intensity of the former. The ^1H resonance in **2** for NCH_2Si group is observed as a sharp unsolved multiplet at 2.85 ppm and does not display the coupling with fluorine atoms. Loss of fluorine coupling is probably due to HF (hydrofluoric acid) traces in the sample owing to hydrolysis of the compound.

However, ^{13}C NMR spectra of **1** and **2** exhibit a broad signal ($^2J_{C-F} = 24.6$ Hz) and a quartet ($^2J_{C-F} = 25.4$ Hz) for NCH_2Si group, respectively.

TABLE 1 Bond Lengths (Å) and Angles (°) for *N*-(trifluorosilylmethyl)succinimide (**1**)

Bond	*d (Å)*	*ω*	*Angle (°)*	*Bond*	*d (Å)*	*ω*	*Angle (°)*
Si—F_3	1.570	F_1SiO_1	177.6	C_2—C_3	1.499	F_2SiO_1	83.1
Si—F_2	1.573	F_3SiF_2	111.5	C_3—C_4	1.515	C_1SiO_1	82.6
Si—F_1	1.607	F_3SiC_1	120.6	N—C_5	1.323	NC_5C_4	110.8
Si—C_1	1.862	F_2SiC_1	123.9	N—C_2	1.400	NC_5O_1	120.1
Si—O_1	2.096	F_1SiF_3	97.6	N—C_1	1.447	$O_1C_5C_4$	129.2
O_2—C_2	1.202	F_2SiF_1	96.7			$O_2C_2C_3$	129.9
C_4—C_5	1.503	F_1SiC_1	95.5			O_2C_2N	123.1
O_1—C_5	1.242	F_3SiO_1	84.6			C_3C_2N	106.9
		SiC_1N	110.5			$C_2C_3C_4$	106.0
		C_5NC_2	113.0			C_2NC_1	129.3
		C_5NC_1	117.3			$C_5C_4C_3$	103.2
		SiO_1C_5	109.3				

The ^{13}C resonance of two carbonyl carbon atoms is displayed in the ^{13}C NMR spectra of **1** and **2** as a sharp singlet at 177.6 and 174.6 ppm, respectively. The equivalency for these atoms arises from a dynamic coordination–decoordination process—the carbonyl group replacing each other fast on the NMR timescale.



The similarity of these ^{13}C chemical shifts of compounds **1** and **2** to that for $^{13}C{=}O$ of *N*-methylsuccinimide (177.5 ppm, [21]) reveals that carbonyl carbon atoms are unaffected by the pentacoordination.

As typical for hypervalent silicon compounds, the ^{29}Si resonance signals of compounds **1** and **2** are shifted upfield and coupling constants between the silicon and fluorine atoms are lower compared with tetravalent chloromethyltrifluorosilanes ($\delta_{Si} = -71.3$ ppm, $^1J_{Si-F} = 267$ Hz) [22]. In this case, the shift difference $\Delta\delta$ for **2** (-23 ppm) is higher than in **1** (-4 ppm), indicating a rather strong $O \rightarrow Si$ interaction in the former compound as compared with the latter one. As temperature decreases to 0°C, ^{29}Si chemical shift of compounds **1** and **2** is shifted to higher field (0.4 and 1.3 ppm, respectively) which is consistent with strengthening coordinative $O \rightarrow Si$ bonding without marked weakening of the Si—F_{ax} bond.

At room temperature, ^{19}F NMR chemical shifts for compounds **1** and **2** (-133.5 and -134.19 ppm, respectively) are low fielded (10 ppm) relative to $ClCH_2SiF_3$ ($\delta_F = -143.99$ ppm). However, decreasing solution temperature to -90°C does not lead to the distinct appearance ^{13}C and ^{19}F signals from fluorine atoms occupying axial and equatorial positions, respectively. This supports rapid fluxional exchange (on the NMR timescale) of fluorine atoms even at this temperature. Unfortunately, low solubility of **1** in solvent mixture (CD_2Cl_2:$CHCl_3$:$CDCl_3$:CCl_4) makes further low-temperature ^{19}F and ^{13}C NMR study impossible.

For compound **2**, decreasing the temperature leads to a shift of ^{19}F resonance signal to low field and its broadening. At -100°C, ^{19}F NMR spectrum displays a triplet at –121.77 ppm ($^2J_{F-F} = 43.0$ Hz; $^1J_{F-Si} = 232.0$ Hz) for axial fluorine and a doublet at -138.20 ppm ($^1J_{F-Si} = 216.0$ Hz) for two equatorial fluorine atoms. Based on the coalescence temperature, the free energy of activation $\Delta G^{\neq}_{-60^\circ C}$ for the permutation process of fluorine atoms was estimated to be 8.5 kcal mol^{-1}.

In the ^{13}C NMR spectra of compound **2** and as the temperature decreases to -80°C, resonance signals for C(3,5) and carbonyl carbon atoms broaden and suggest the occurrence of a dynamic process, which is probably averaging the chemical shifts of two carbonyl carbon. At -100°C, ^{13}C spectrum displays two separate resonance signals at 181.48 and 170.61 ppm, which are assigned to the coordinate and free carbonyl carbon, respectively. The distinct resonances are also observed at 31.68 and 28.26 ppm for endocyclic C3 and C5 atoms, while a quartet for NCH_2Si group is turned to a broad doublet by different coupling with F_{ax} and F_{eq} atoms. Free energy of activation $\Delta G^{\neq}_{-75^\circ C}$ for the coordination–decoordination process of the carbonyl groups calculated from coalescence temperature has the value of 8.4 kcal mol^{-1}. Minor difference in $\Delta G^{\neq}_c$ values for both ligand exchange processes is

TABLE 2 ^1H, ^{13}C, ^{19}F, and ^{29}Si Chemical Shifts and Coupling Constants of Compounds **1** and **2**

	δ ^1H (ppm)			δ ^{13}C (ppm) (J, Hz)					
Compound	CH_2-3(5)	CH_2-4	NCH_2	C-3(5)	C-4	NCH_2	C═O	δ ^{19}F (ppm); J (Hz)	δ ^{29}Si (ppm)
1						20.97 q		−133.5 (26°C); $J_{F–Si} = 248.8$	−75.7 (26°C)
	2.86 s	2.86 s	2.94	27.78	27.78	(24.57)	177.59	−132.2 (−35°C); $J_{F–Si} = 241.5$	−75.3 (50°C)
2	2.83 tr	2.08 k	2.87	30.20	16.42	23.15 q	174.59	−134.19 (26°C); $J_{F–Si} = 224.5$	−94.2 (26°C)
				28.26 (−100°C)		(25.4)	170.61 (−100°C)	−138.2 (−100°C) d, F_{eq}	−92.9 (50°C)
				31.68 (−100°C)				$J_{F–F} = 43.0$ $J_{F–Si} = 216.0$	
							181.48 (−100°C)	−121.8 (−100°C) tr, F_{ax} $J_{F–Si} = 232.0$	

within the experimental errors. It may be concluded that in compounds **1** and **2**, exchange rate between F_{ax} and F_{eq} is determined by process rate involving two carbonyl groups, namely breaking Si ← O=C coordinate bond, rotation around Si—C bond and the formation of intramolecular Si←O—C* bond with other carbonyl group.

The solid-state IR spectrum of compound **1** shows two stretching vibrations for SiF_{eq} at 932 cm^{-1} (ν^{as}) and at 870 cm^{-1} (ν^{s}) and a stretching vibration for SiF_{ax} at 778 cm^{-1} that is common to a wide variety of trigonal-bipyramidal silicon compounds [1,23]. As in the case of other dragonoids [1], in going from crystal to C_6H_6 solution of **1**, these bands are shifted to higher wave numbers (965, 889, and 820 cm^{-1}, respectively). The most notable shift (42 cm^{-1}) is observed for a band assigned to Si–F_{ax} bond. The frequencies observed in IR spectrum of solid compound **2** for Si—F bond (ν^{as} SiF_{eq} at 941 cm^{-1}, ν^{s} SiF_{eq} at 869 cm^{-1}, and νSiF_{ax} at 783 cm^{-1}) are nearly the same as those for compound **1**. This is sufficient evidence that both compounds have similar O → Si intramolecular hypervalent bonding.

EXPERIMENTAL

IR spectra of compounds **1** and **2** were obtained with a Specord 75 IR spectrophotometer as KBr and in C_6H_6 solution. NMR spectra were recorded on a Bruker DPX 400 spectrometer operated at 400 MHz for ^1H, 100.61 MHz for ^{13}C, 376.50 for ^{19}F, and 79.50 MHz for ^{29}Si. ^1H and ^{13}C chemical shifts were referenced to residual solvent resonances, ^{19}F chemical shifts to external CCl_3F, and ^{29}Si chemical shifts to external Me_4Si. The low-temperature NMR spectra were recorded in CD_2Cl_2:$CDCl_3$:CCl_4 (60:27:13).

X-ray diffraction analysis was recorded on a “SYNTEX P2_1” monochromated diffractometer. *N*-(Trimethoxysilylmethyl)succinimide and *N*-(trifluorosilylmethyl)succinimide were obtained by a described method [24,25].

N-(Trimethoxysilylmethyl)glutarimide. A solution of CH_3ONa (prepared from sodium (0.46 g, 0.02 mol) and 3 mL of methanol) was added to a solution of glutarimide (2.26 g, 0.02 mol) in methanol (5 mL). After evaporation of methanol on a rotary evaporator, DMF (10 mL) and (chloromethyl)trimethoxysilane (3.41 g, 0.02 mol) were added to the reaction mixture. After stirring the mixture for 1 h at 80–90°C, filtration and distillation of the eluate obtained in vacuum gave trimethoxy derivative (3.51 g, 71%), bp 154°C at 6 mmHg. Anal. Calcd for $C_9H_{17}NO_5Si$: C, 43.81; H, 7.01; N, 5.54; Si, 11.21. Found: C, 43.7; H, 6.93; N, 5.66; Si, 11.36.

N-(Trifluorosilylmethyl)glutarimide (**2**). $F_3B{\cdot}Et_2O$ (4.25 g, 0.03 mol) was added in drops to a solution of trimethoxy derivative (2.47 g, 0.01 mol). After stirring the mixture for 1 h at 34°C, the precipitate was filtered and washed with ether to afford **2** (1.73 g, 82%). Anal. Calcd for $C_6H_8NO_2SiF_3$: C, 34.27; H, 3.98; N, 6.35; F, 27.09. Found: C, 34.12; H, 3.82; N, 6.63; F, 26.98.

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