Chemistry of Heterocyclic Compounds, Vol. 42, No. 12, 2006

SYNTHESIS, MOLECULAR AND CRYSTAL STRUCTURE, AND FEATURES OF THE ELECTRONIC STRUCTURE OF BIS(O→Si)-CHELATED BIS(2,2-DIMETHYLBENZO-[2H]-4-OXO-1,3-OXAZINO-3-METHYL)DIFLUOROSILANE

A. A. Korlyukov[1], K. A. Lysenko[1], M. Yu. Antipin[1], A. G. Shipov[2],
E. P. Kramarova[2], T. P. Murasheva[2], Vad. V. Negrebetskii[2],
Yu. E. Ovchinnikov[3], S. A. Pogozhikh[3], I. P. Yakovlev[4], and Yu. I. Baukov[2]

A method has been developed for the synthesis of a bis(O→Si)-chelated bis(2,2-dimethylbenzo[2H]-4-oxo-1,3-oxazino-3-methyl)difluorosilane from 2,2-dimethyl-3-trimethylsilylbenzo[2H]-1,3-oxazin-4-one and bis(chloromethyl)dichlorosilane via the intermediate formation of the corresponding unstable bis-chelated dichloride, subsequent hydrolysis with $NaHCO_3$ *and, without separation, treatment of the hydrolysis product with boron trifluoride etherate. Analysis of the electron density distribution showed the presence of dative bonding in both O→*Si–F fragments.

Keywords: compounds of hexacoordinated silicon, hypervalency, quantum-chemical calculations, electron density distribution, X-ray structural investigation, synthesis.

Neutral bis-chelated $(LCH_2)_2MHal_2$ which contain a bidentate, monoionic, C,X-coordinated LCH_2 ligands (X = N, O) are quite well investigated compounds of hexacoordinated germanium and tin [1]. According to X-ray analysis the majority of them in the solid phase have a close to octahedral configuration with carbon atoms in *trans* and with the coordinated X and halogen atoms in *cis* positions relative to one another. At the same time their silicon analogs are virtually unstudied [2] and only a few examples of this type of compound with N→Si coordinated bis(8-dimethylamino-1-naphthyl)dichloro- and -difluorosilanes [3] and also (8-dimethylamino-1-naphthyl)(2-dimethylaminomethylphenyl)difluorosilanes [4] have been reported. In the case of the latter an X-ray investigation of the coordination about the Si atom has reported a doubly capped tetrahedron.

We set out to attempt the preparation of neutral hexacoordinated dichlorosilanes $(LCH_2)_2SiCl_2$ by treating trimethylsilyl (TMS) derivatives of five-, six-, and seven-membered lactams with bis(chloromethyl)dichlorosilane $(ClCH_2)_2SiCl_2$ in the ratio 2 : 1 and obtained unstable, readily hydrolyzed materials. Treatment of the latter with Me_3SiOTf or $HgCl_2$ under conditions which did not exclude access of the

---

* Dedicated to Prof. Edmunds Lukevics on the occasion of his 70th birthday

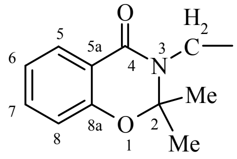
---

[1]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 119991; e-mail: alex@ineos.ac.ru. [2]Russian State Medical University, Moscow 117997, [3]Novosibirsk State Pedagogical University, Novosibirsk 630126, Russia, [4]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 119991. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1866-1879, December, 2006. Original article submitted September 19, 2006.

moisture of the air led to binuclear, disiloxane cation-anion complexes of pentacoordinate silicon $\{[(LCH_2)_2Si]_2O\}^{2+}.2X^-$ (where X^- is a nucleophilic anion, OTf^-, $H_gCl_3^-$, $½HgCl_4^{2-}$), and these contained disilyl dications stabilized by intraionic O→Si [5, 6] coordination interaction from X-ray analysis data.

In the single example of N–TMS–N–methylacetamide under similar conditions the final product could be separated without subsequent treatment with mercuric chloride or trimethylsilyltriflate as the binuclear complex $\{[(MeC(O)N)Me(CH_2)_2Si]_2O\}^{2+}\cdot[H_3O]^+\cdot3Cl^-$ [6]. By varying the experimental conditions most recently we have been able for the first time in this reaction to separate and structurally characterize the first mononuclear bis-chelate cation-anion complex of a similar type, i.e. the $[(MeC(O)N(Me)CH_2)_2Si(Cl)]^+.[ClHCl]^-$ hydrochloride which contains a pentacoordinated silyl cation stabilized by O→Si coordination [7].

In continuing this work we also reported the first representative of stable bis(C,O)-chelates of hexacoordinated silicon compounds as the $[(MeC(O)N(CHMePh)CH_2)]_2SiF_2$ difluoride [8]. In the current work we report data for the synthesis, X-ray analysis, and quantum-chemical investigation of the second member of such neutral mononuclear bis-chelates $(BonCH_2)_2SiF_2$ (**1**). The presence in the structure of the very bulky 2,2-dimethylbenzo[2H]-4-oxo-1,3-oxazino-3-methyl ($BonCH_2$) C,O-chelated ligand which includes an annelated benzene ring leads one to anticipate the preparation of quite stable compounds based on it.

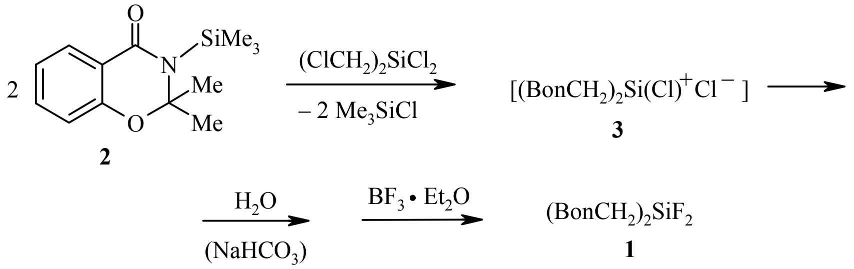


$BonCH_2$

It should be noted that only mono-chelate derivatives with this ligand have been reported until now, these being $BonCH_2SiMe_2Cl$ chloride and $(BonCH_2SiMe_2)_2O$ disiloxane [9].

The route used by us for the preparation of difluoride **1** was based on the reaction discussed above for lactam and amide TMS derivatives with $(ClCH_2)_2SiCl_2$ in the ratio 2 : 1. The use of the TMS derivative of **2** in this reaction gave the unstable bis-chelate $[(BonCH_2)_2Si(Cl)]^+Cl^-$ dichloride (**3**) which was subsequently hydrolyzed in the presence of $NaHCO_3$. The hydrolysis product was then treated without separation with boron trifluoride etherate to give the difluoride **1** in 45% yield (Scheme 1).

Scheme 1



The structure of the difluoride **1** was confirmed from its IR spectrum and from ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectroscopy. The intramolecular O→Si interaction, and consequently the hexacoordination of the Si atom in the bis-chelate **1** was indicated by the observation in its IR spectrum of characteristic absorption bands in the region 1700-1500 cm^{-1} and the absence of absorption bands for the non-chelated amide fragments [8]. We have carried out a comparison of the IR spectra of the difluoride **1** and the 2,2-dimethylbenzo[2H]-1,3-oxazin-4-one (BonH, **4**) [10] which was used as the starting compound in the synthesis of the trimethylsilyl derivative **2**. Spectra were obtained for samples pressed with KBr and in CH_2Cl_2 solution. In the spectroscopic range studied (1700-1500 cm^{-1}) the accumulated spectra seemed virtually identical under both conditions.

The spectrum of compound **4** shows absorption bands at 1680 (strong, C=O, amide I), 1615, and 1584 cm^{-1} (medium intensity, Ar). In the spectrum of bis-chelate **1** the band at 1680 cm^{-1} disappears and strong bands with frequencies at 1620, 1615, 1565, and an additional strong band at 1520 cm^{-1} appear. The change in spectrum of bis-chelate **1** observed is the result of hexacoordination of the Si atom with two equivalent bis-chelated ligands which leads to electron delocalization in the amide fragments NCO and the appearance of characteristic absorption bands for the two mixed vibrations. As a result, the C=O band at 1680 cm^{-1} is shifted to lower frequency to 1620 cm^{-1} which virtually coincides with the benzene ring band and the second band at 1520 cm^{-1} can also be assigned to a vibration of the NCO fragment. Assignment of the bands at 1620 and 1615 cm^{-1} to specific NCO and Ar vibrations did not prove possible as they are close together in frequency and intensity.

With a view to refining the assignment of the absorption bands in the IR spectrum of compound **1** we have carried out a quantum-chemical calculation of the spectroscopic vibrational frequencies of its free molecule (using MPW1PW91/6-31G(d)) in a conformation close to that achieved in the crystal (see below). In the calculated spectrum, five pairs of frequencies in the range 1620-1460 cm^{-1} are observed. All of the vibrations in this region (including the vibrations of the NCO fragment) are *syn*-phase and *anti*-phase vibrations of two chelated molecular fragments, strongly associated with vibrations of the conjugated aromatic systems.

In confirmation of the assignment of the values of the experimental frequencies at 1620, 1615, and 1565 cm^{-1} we propose the corresponding calculated frequencies of 1622, 1607, and 1573 cm^{-1}. The actual band at 1520 cm^{-1} appears 25 cm^{-1} higher than the calculated value. The difference between the actual and calculated frequencies is likely a consequence of the difference in geometry of the free molecule **1** and the crystal and needs a further, more detailed theoretical analysis.

The hexacoordination of the central atom in the difluoride **1** in solution is indicated by the high field position of the corresponding ^{29}Si NMR signal (-124.3 ppm) when compared with the chemical shifts of signals for both tetra (~ 5 to 40 ppm) and also for pentacoordinated (~ 0 to -70 ppm) silicon atoms [2, 11]. The value found for the δ_{Si} of compound **1** is close to that published previously for the bis(O→Si)-chelated bis{[N-(1-phenylethyl)]acetamidomethyl}difluorosilane at about -129.1 ppm [8].

As in the case of the hexacoordinated dihalogermanes and –stannanes $(LCH_2)_2MHal_2$ (where L is a monoanionic bidentate C,O-chelated ligand) [11] studied by us, the diastereotopic NCH_2 methylene group protons appear in the ^{1}H NMR spectrum as an AB-system multiplet. Increase in temperature causes a reversible broadening of the AB-system components and this suggests a stereodynamic process is occurring which includes exchange of the ligands at the silicon atom. A detailed discussion of the results of examining this process by dynamic NMR will be published by us later.

The structure of the difluoride **1** was shown using precision X-ray diffraction investigation. The molecule **1** occupies the main position in the crystal. The crystal packing of compound **1** also includes two molecules of solvated benzene which occupy a partial position in the crystallographic centre of inversion. The structure of the 2,2-dimethylbenzo[2H]-1,3-oxazine fragments in molecule **1** is close to that for the previously described $BonCH_2SiMe_2Cl$ with a pentacoordinated silicon atom [9, 12].

In the crystal the difluoride **1** is characterized by a distortion of the octahedral configuration of the Si atom (Fig. 1, Table 1). The carbon atoms are positioned in the axial positions of the octahedron with a C(8)–Si(1)–C(8') angle of 165.8°. The atoms O and F appear in equatorial positions, the angle between the O–Si–F fragments being 85°. The coordinated O(1)–Si(1) and O(1')–Si(1) bond lengths are virtually identical (1.967 and 1.968 Å) and this exceeds the standard Si–O bond length [13] by 0.3 Å. In their turn, the Si–F bonds exceed standard values by 0.04 Å. The angles O(1)–Si(1)–F(1) and O(1')–Si–F(1') are almost linear (174.1 and 173.3°). The Si–C bonds are somewhat longer (0.03 Å) than standard values [13].

The mutual placing of the two $BonCH_2$ ligands may be described as synclinal with an angle between the mean planes of the pentacyclic silicon-containing rings of 82°. The conformation of the five-membered ring Si(1)O(1)C(7)N(1)C(8) is a flattened envelope with an excursion of the Si atom from the base plane of 0.18 Å The five-membered ring Si(1)O(1')C(7')N(1')C(8') is virtually planar, the deviation from the mean plane not

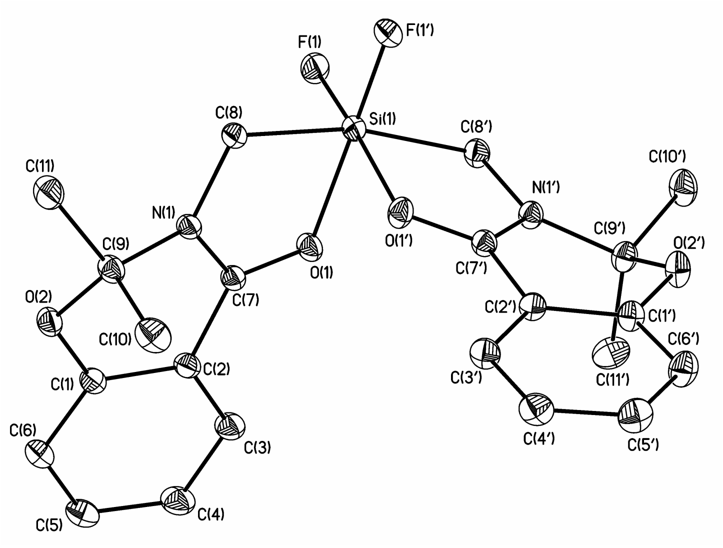


Figure 1. General view of molecule **1** with 50% probability thermal vibrational ellipsoids. Hydrogen atoms are not shown.

exceeding 0.03 Å. The differences between the conformations of the five-membered silicon-containing rings may be the result of the effect of crystal packing. Bearing in mind the marked lengthening of the covalent Si–C bonds it can be also suggested that the observed differences are due to the presence of steric hindrance at the coordinated polyhedron of the Si atom.

In order to study features of the structure of compound **1** quantum-chemical calculations have been carried for various configurations of its free molecule. The quantum-chemical investigation of the potential energy surface of molecule **1** revealed the two most stable isomers* which differed in the mutual positioning of the BonCH$_2$ ligands and the fluorine atoms (Scheme 2). The most energetically favoured is the *cis* isomer, the structure of which is close to that in the crystal structure **1**.

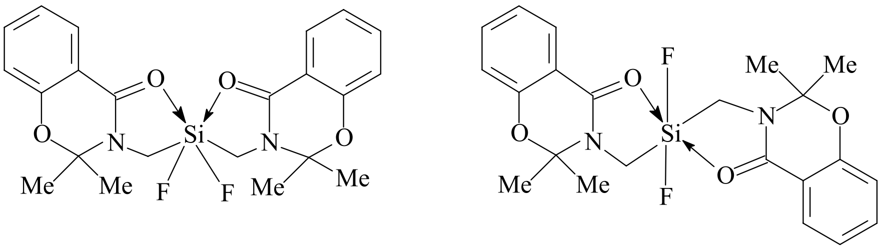
TABLE 1. Basic Bond Lengths (*l*) and Valence Angles (ω) in Structure 1 Obtained Experimentally

Bond	*l*, Å	Angle	ω, deg
Si(1)–F(1)	1.6643(5)	O(1)–Si(1)–F(1')	174.093(18)
Si(1)–F(1')	1.6615(4)	O(1')–Si(1)–F(1)	173.309(18)
Si(1)–O(1)	1.9682(5)	F(1)–Si(1)–F(1')	95.566(19)
Si(1)–O(1')	1.9673(5)	O(1)–Si(1)–O(1')	84.559(18)
Si(1)–C(8)	1.9319(5)	C(8')–Si(1)–C(8)	165.83(2)
Si(1)–C(8')	1.9326(5)	F(1)–Si(1)–O(1)	89.265(18)
O(1)–C(7)	1.2708(6)	F(1')–Si(1)–O(1')	90.756(19)
O(1')–C(7')	1.2716(6)	C(7)–O(1)–Si(1) (cp.)	112.69(3)
N(1)–C(7)	1.3312(6)	C(7)–N(1)–C(8) (cp.)	115.21(4)
N(1')–C(7')	1.3302(6)	O(1)–C(7)–N(1) (cp.)	119.84(4)
N(1)–C(8)	1.4658(6)		
N(1')–C(8')	1.4679(6)		

---

* The quantum-chemical calculations carried out by us revealed 5 isomers of compound in all but the discussion of their structure is governed by the limits of this work and will be published in a separate report.

Scheme 2



cis **1** *all-trans* **1**

The interatomic Si…O distances in the structure of the *cis*-isomer exceed the experimental values by 0.1 Å. In the *all-trans* isomer the interatomic Si…O distances prove even shorter than the experimental (1.906 Å, Si-C bond lengthened by 0.01 Å) but the total energy for this configuration is somewhat higher (2.3 kcal/mol) than for the *cis* isomer. Despite the differences in the interatomic Si…O and Si…C distances the five-membered silicon containing rings are seen with a planar configuration. Evidently the change in the degree of steric strain in the coordinated polyhedron of the silicon atom does not lead to distortion of planarity for these rings. Hence we can deduce that the presence of the envelope conformation in the five-membered Si(1)O(1)C(7)N(1)C(8) ring is a consequence of the crystal packing.

The bond lengths of the coordinated Si atom polyhedron in the free molecule difluoride **1** prove to be very sensitive (Table 2) to change in the relative position of the BonCH$_2$ ligands, in particular regarding the coordinated O→Si bond. A similar behavior for the coordinated Si atom polyhedron in pentacoordinated derivatives has been studied in a series of publications concerned with investigations of different mono-chelate complexes by a structural correlation method and with the help of quantum-chemical calculations [12, 14-16].

In the axial fragment O–Si–X (X = Hal, OTf) of a compound with a pentacoordinated Si atom it was possible to achieve two schemes of chemical bonding. Where the interatomic Si…O distances exceeded 2 Å the chemical bonding in the axial fragment corresponded to a dative bond, i.e. transfer of electron density from the lone electron pair of the O atom to an Si–X bond antibonding orbital. With a decrease in the interatomic Si…O distance to less than 2 Å a three centre, four-electron (3c-4e) bond is most likely in the axial O–Si–X fragment.The geometry of the O–Si–X fragment in compound **1** infers the presence of a 3c-4e bond but the occurrence of the difficultly polarizable Si–F bond and the lability of the coordinated O→Si bond point to the realization of dative bonding. Investigation of the chemical bonding in the O–Si–F fragment in compound **1** on

TABLE 2. Structural Parameters for the *cis*- and *all-trans* Isomers of the Molecule of Compound 1*

Bond	*l*, Å		Angles	ω, deg	
	cis **1**	*all-trans* **1**		*cis* **1**	*all-trans* **1**
Si(1)–F(1)	1.651	1.688	O(1)–Si(1)–F(1')	169.7	89.2
Si(1)–O(1)	2.065	1.907	F(1)–Si(1)–F(1')	99.9	180.0
Si(1)–C(8)	1.930	1.949	F(1)–Si(1)–O(1)	89.9	90.9
O(1)–C(7)	1.255	1.264	O(1)–Si(1)–O(1')	80.5	178.3
N(1)–C(7)	1.337	1.332	C(7)–O(1)–Si(1) (cp.)	111.6	111.7
N(1)–C(8)	1.469	1.472	C(7)–N(1)–C(8) (cp.)	115.6	116.2

---

* Values of some parameters are averaged in agreement with the point group of the molecule (C_i).

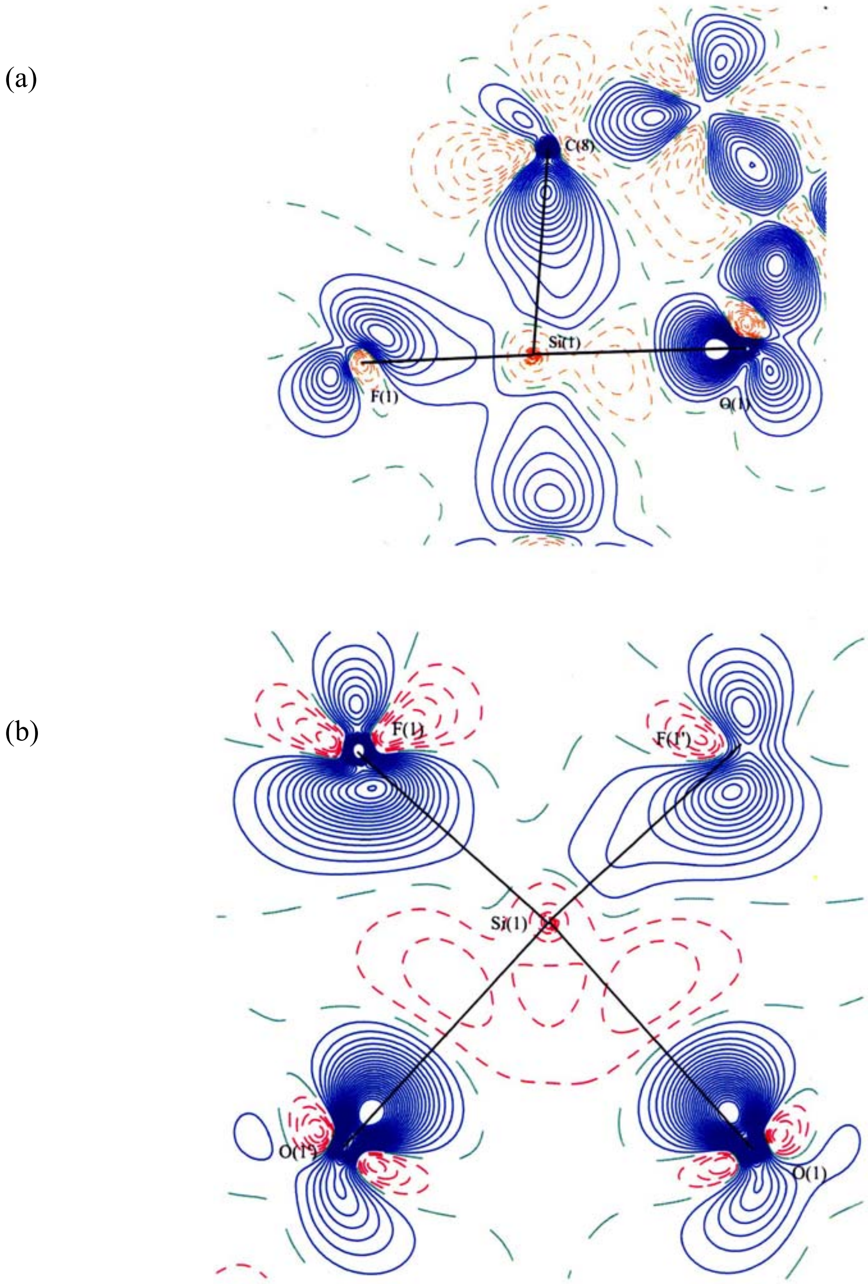
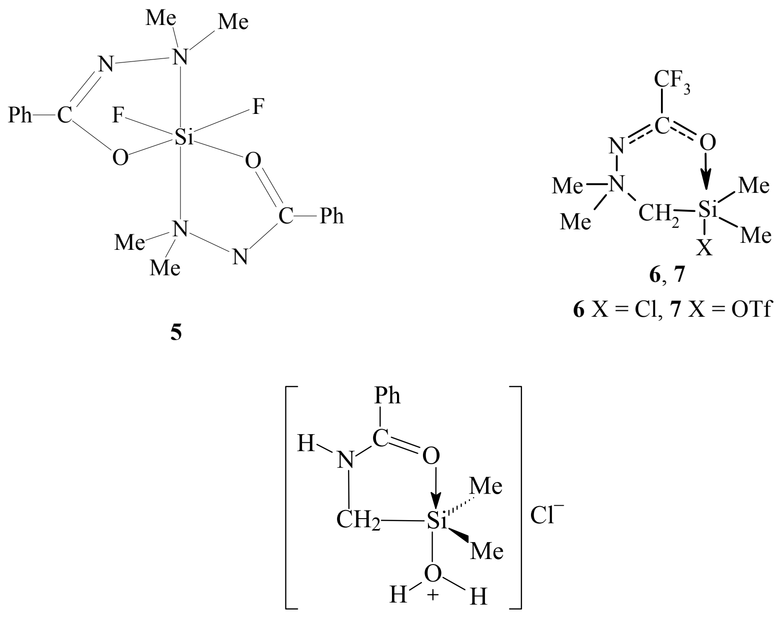


Figure 2. Deformation electron density (DED) in the planes C(8)Si(1)O(1) (a) and O(1)O(1')F(1)F(1') (b).

the basis of only structural data is quite limited hence we have carried out a study of the electron density distribution function ρ(*r*) within the crystal of this compound and its free molecule using the topological theory of R. F. W. Bader in "Atoms and Molecules" (AM) [17].

Qualitative analysis of the profile of deformation electron density (DED) (Fig. 2) showed the presence of maxima in the area of the Si–O and Si–F bonds shifted to the oxygen and fluorine atoms. Thus the position of the electron pair in the O–Si–F fragments corresponds to literature data for the previously studied difluoride **5** [18] with an O,N-chelated ligand (Scheme 3). In the latter case topological analysis of the electron density showed the presence of a marked positive charge on the Si atom (+ 2.78 *e*) and closely similar negative charges on the O and F atoms (-1.21 and - 0.80 *e*, respectively). This allowed the authors of the study [18] to reject the proposal of hypervalent or dative O→Si–F bonds in the corresponding fragments and to suggest that the Si–O and Si–F bonds are principally ionic with an extremely small covalent contribution.

Scheme 3



5

6, **7**

6 X = Cl, **7** X = OTf

8

It can be suggested that in the difluoride **1** the exchange of equatorial nitrogen atoms for the less electronegative carbon atoms leads to a decrease of the silicon atom positive charge and lengthening of the Si–O and Si–F bonds. In fact the Si–F bond length in compound **1** exceeds that in **5** by 0.03 Å while the Si–O bond in

TABLE 3. Topological Parameters of the Molecule 1 Crystal in the c*is* and *all-trans* Isomers*

Bond	Crystal	MPW1PW91/6-31G(d)	
		cis Isomer **1**	*all-trans* Isomer **1**
	$\rho(r)$, e·Å^{-3}		
O(1)→Si(1)	0.41	0.37	0.48
Si(1)–F(1)	0.81	0.76	0.71
Si(1)–C(8)	0.76	0.75	0.72
C(7)–O(1)	2.77	2.54	2.47
	$\nabla^2\rho(r)$, e·Å^{-5}		
O(1)→Si(1)	2.91	2.64	7.09
Si(1)–F(1)	14.62	21.75	18.33
Si(1)–C(8)	0.61	5.97	5.79
C(7)–O(1)	-33.15	-3.07	-3.70
	$E^e(r)$, H·Å^{-3}		
O(1)→Si(1)	-0.11	-0.15	-0.14
Si(1)–F(1)	-0.22	-0.08	-0.12
Si(1)–C(8)	-0.50	-0.43	-0.41
C(7)–O(1)	-1.18	-4.27	-4.13

---

* Values averaged in agreement with the point group of the molecule (C_i).

1 is 0.23 Å longer. This points to an increase in the degree of transfer of electron density from the Si–O bond electron pair to an Si–F antibonding orbital in compound **1** when compared with that in compound **5**.

Topological analysis of the ρ(*r*) function in the crystal and free molecule of **1** has shown the presence of a critical point (CP) (3, -1) in the field of all chemical bonds. The crystal of **1** also showed a CP (3, -1) corresponding to weak C–H…F and C–H…O intermolecular contacts. The C–C, C–N, and C–O bonds are characterized by a negative value of the Laplacian electron density ($\nabla^2\rho(r)$) and local energy density $E^e(r)$ which corresponds to a conventional covalent bond according to AM theory. At the CP (3, -1) of the bonds formed by the Si atom positive values of $\nabla^2\rho(r)$ and negative values of $E^e(r)$ are found (Table 3) and allows us to assign these bonds as intermediate type interatomic interactions.

In the crystal **1** the values of the topological parameters of the Si–F bonds (ρ(*r*), $\nabla\rho^2(r)$, and $E^e(r)$) are close to those for Si–F bonds in compound **5**. Their values in the case of the Si–O bonds prove to be less than in the pentacoordinated silicon derivatives **6-8** [14-16] which contain O–Si–O and O–Si–Cl(OTf) (Si…O interatomic distances close to that in **1**). Comparison of the charge values calculated from AM theory with literature data for compound **5** has shown that the electron density in the O→Si–F fragments is redistributed such that the value of the silicon atom positive charge (+ 2.48 *e*) and negative O and F atom charges (-1.12 and -0.76 *e*) are decreased somewhat (Table 4).

In the free molecule (*cis* and *all-trans* isomers) the charge distribution is rather different. The positive charge on the Si atom in the *cis* isomer markedly exceeds that in the crystal. Shortening of the Si–O bond to 1.907 Å in the *all-trans* isomer (linear O→Si-F fragment absent) leads to a further increase in the Si positive charge and negative charges on the atoms of its coordinated polyhedron. This leads us to deduce an increase in the ionic component of the bonds formed by the Si atom with shortening of the interatomic Si(1)…O(1) distance and this is in good agreement with literature data for compound **5** [18].

Confirmation of this deduction came from the energy values for the Si–O bonds. Topological analysis allowed a semi-quantitative assessment of the Si–O bond energy by the Espinosa, Mollins, and Lecomte method [19]. The energy of the Si–O bond in the crystal of **1** averages at 20.1 kcal/mol while for the analogous bonds in **6-8** these values are 37.7, 30.4, and 22.3 kcal/mol. In the free molecule of **1** the mean values of the Si–O bond energy for the *cis* and *all-trans* isomers differ little (17.6 and 22.4 kcal/mol) The values obtained are close to those for the dative Si…N bond in crystals of 1-methyl- and 1-fluoroazasilatrane [20, 21].

The data obtained for the atomic charges in the coordination polyhedron of the silicon atom is evidence that the O→Si, Si–F, and Si–C bonds show a marked ionic contribution. In the *all-trans* isomer of **1** the linear O→Si–F fragment is absent and a dative O→Si–F bonding is not achieved, hence the Si–O, Si–F, and Si–C have the greatest ionic contribution.

On the other hand, the combined topological analysis for the nature of these bonds and the assessment of the energy of the O→Si bonds allows to conclude that the chemical bonding in the O→Si–F fragments in the crystal of compound **1** and in the *cis* isomer of **1** its free molecule corresponds principally to dative bonding, i.e. with transfer of electron density from the unshared O atom electron pair to an antibonding Si–F orbital.

TABLE 4. Atomic Charges Calculated from AM Theory*

Atom	Crystal	MPW1PW91/6-31G(d)	
		cis Isomer **1**	*all-trans* Isomer **1**
Si(1)	2.48	3.15	3.20
O(1)	-1.12	-1.27	-1.29
F(1)	-0.76	-0.88	-0.90
C(8)	-0.19	-0.23	-0.25

---

* Values averaged in agreement with the point group of the molecule

TABLE 5. Basic X-ray Diffraction Experiment and Crystal Structure Data for Compound 1

Parameters	**1**	Parameters	**1**
Empirical formula	$C_{13}H_{20}BF_2NO_3Si_2$	Space group	$P\bar{1}$
Molecular weight	524.63	$2\theta_{max}$, deg	100
T, K	110(2)	$F(000)$	552
a, Å	9.6258(16)	Scanning	ω
b, Å	12.153(3)	Number of reflections gathered	58 471
c, Å	12.259(2)	independent (R_{int})	26 095 (0.028)
α, deg.	80.669(3)	observed with $I>2\sigma(I)$	17 739
β, deg.	73.162(5)	Number of refinement parameters	454
γ, deg.	74.810(3)	Absorption coefficient, cm^{-1}	2.45
V, $Å^3$	1318.8(4)	R_1 ($I>2\sigma(I)$)	0.0453
d_{calc}, $g\cdot cm^{-3}$	1.321	wR_2	0.1366

EXPERIMENTAL

IR spectra for compound solutions in CH_2Cl_2 (~ 3% by weight, NaCl cuvet, $d = 0.078$ mm) and pressed in KBr (1/200 mg) were recorded on a Specord M82 instrument. ^1H, ^{13}C, ^{19}F, and ^{29}Si spectra were taken for solutions in $CDCl_3$ on a Varian XL-400 instrument (400, 100, 396, and 79 MHz, respectively). The ^1H, ^{13}C, and ^{29}Si chemical shifts were measured relative to TMS internal standard. ^{19}F Chemical shifts were recorded relative to an external boron trifluoride etherate standard.

The starting compounds 2,2-dimethyl-3-trimethylsilylbenzo[2H]-1,3-oxazin-4-one (**2**) [9] and bis(chloromethyl)dichlorosilane [22] were synthesized by the previously reported methods.

Bis(O→Si)-chelated bis(2,2-dimethylbenzo[2H]-4-oxo-1,3-oxazino-3-methyl)difluorosilane (1). A mixture of compound **2** (2.49 g, 10 mmol), bis(chloromethyl)dichlorosilane (0.98 g, 5 mmol), and heptane (15 ml) was refluxed for 2 h. The precipitate was filtered off to give the dichloride **3** (2.3 g, 97%) with mp 182-184°C (from *o*-xylene and acetonitrile, 1: 1). A solution of the unpurified dichloride **3** (8 g, 16 mmol) in $CHCl_3$ (100 ml) was stirred for 1 day with a solution of $NaHCO_3$ (18 g) in water (200 ml) and the layers formed were separated. The organic layer was dried over ignited $CaCl_2$ and the chloroform was evaporated. The remaining bulky, amorphous powder was dissolved in CH_2Cl_2 (5 ml). $BF_3.Et_2O$ (2.3 g, 0.016 mol) was added to the solution obtained and the mixture was heated to complete distillation of CH_2Cl_2 and Et_2O (8 ml). The solidified crystalline mass was refluxed with benzene (15 ml) and the solution was filtered off. The mother liquor gave the difluoride **1** (3.2 g, 45%) with mp 247-250°C (benzene). IR spectrum (CH_2Cl_2), ν, cm^{-1}: 1620, 1615 (NCO, Ar); 1565 (Ar); 1520 (NCO). IR spectrum (KBr), ν, cm^{-1}: 1619, 1612 (NCO, Ar); 1563 (Ar); 1520 (NCO). ^1H NMR spectrum, ν, ppm (*J*, Hz): 7.65 (2H, $^3J_{H,H} = 8.3$, H-8); 7.44 (2H, t, $^3J_{H,H} = 8.3$, H-6); 7.00 (2H, t, $^3J_{H,H} = 8.3$, H-7);6.90 (2H, d, $^3J_{H,H} = 8.3$, H-5); 3.52 (2H, t, $^2J_{H,H} = {}^3J_{H,F} = 12.3$, NCH_2) 3.01 (2H, d, $^2J_{H,H} = 12.3$, NCH_2); 1.69 (12H, $C(CH_3)_2$). ^{13}C NMR spectrum, ν, ppm: 24.59, 24.93 ($2CH_3$); 36.19 (NCH_2, t, $^3J_{CF} = 5.9$); 91.76 ($\underline{C}Me_2$); 112,87 (C-8a); 117.24 (C-5); 122.14 (C-7); 127.93 (C-8); 135.82 (C-6); 155.00 (C-5a); 163.06 (C-4). ^{19}F NMR spectrum, ν, ppm: -112.1. ^{29}Si NMR spectrum, ν, ppm (*J*, Hz): -124.3 (t, $^1J_{SiF} = 253.4$). Found, %: C 59.30; H 5.44; N 6.02. $C_{22}H_{24}F_2N_2O_4Si$. Calculated, %: C 59.17; H 5.42; N 6.27.

X-ray structural investigation of compound 1. The crystallographic parameters and basic characteristics of the X-ray diffraction experiments for compound **1** are given in Table 5. The experiment was carried out using a Bruker Smart CCD 1000 diffractometer. The structure of **1** was solved by a direct method and refined using an F^2 full matrix least squares analysis in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were localized in Fourier difference synthesis and refined isotropically. All of the calculations were performed using the SHELXTL PLUS program package (version 5.10) [23].

Method for the treatment of precise X-ray analysis and quantum-chemical calculation data. The experimental distribution of electron density in the crystal of compound **1** was determined by a multipolar refinement of the body of the X-ray diffraction data using the XD program package [24]. Refinement was carried out for F for 18,229 reflections (I>4 $\sigma(I)$, $\theta_{max} = 50^o$) For all of the non-hydrogen atoms the coordinates, thermal, and multipolar parameters were refined to the octupole level (l = 3). C_i Local symmetry was assigned to all of the five-membered ring atoms of the silicon containing rings (besides the Si). Before refinement the C–H distances were normalized to a value of 1.08 Å in agreement with neutron diffraction data [13]. For the H atoms only the dipole population density (l = 1) and the coordinates and thermal parameters were fixed. The maximum number of refined parameters in the multipolar refinement was 447. The results of the multipolar refinement were: R = 0.0313, wR = 0.0379, and GOF = 0.925 for 18229 reflections with I>4$\sigma(I)$.

All of the calculations with full optimization of geometry were carried out employing the Gaussian 03W program [25] with the use of the MPW1PW91 hybrid functional and 6-31 G(d) base set. The topological analysis of the electron density distribution was obtained from calculated data carried out using the Morphy 1.0 program [26, 27].

The work was carried out with the financial support of the Russian Fund for Basic Research (projects 04-03-32557, 02-07-90322, and 04-03-32662) and INTAS (project 03-51-4164).

REFERENCES

1. Yu. I. Baukov and S. N. Tandura, in: Z. Rappoport (editor), *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Vol. 2, Wiley, London (2002), p. 961.
2. D. Kost and I. Kalikhman, in: Z. Rappoport, Y. Apeloig (editor), *The Chemistry of Organic Silicon Compounds*, Chichester: J. Wiley and Sons, 1998, p. 1339.
3. C. Breliere, R. J. P. Corriu, G. Royo, W. W. C. Wong Chi Man, and J. Zwecker, *Organometallics*, **9**, 2633 (1990).
4. C. Breliere, F. Carre, R. J. P. Corriu, G. Royo, and J. Zwecker, *Organometallics*, **8**, 1831 (1989).
5. E. P. Kramarova, L. S. Smirnova, O. B. Artamkina, A. G. Shipov, Yu. I. Baukov, Yu. E. Ovchinnikov, A. O. Mozzhukin, and Yu. T. Struchkov, *Zh. Obshch. Khim.*, **63**, 2275 (1993).
6. Yu. E. Ovchinnikov, S. A. Pogozhikh, I. V. Razumovskaya, A. G. Shipov, E. P. Kramarova, S. Yu. Bylikin, Vad. V. Negrebetskii, and Yu. I. Baukov, *Izv. Akad. Nauk, Ser. Khim.*, 997 (1998).
7. E. P. Kramarova, A. A. Korlyukov, S. Yu. Bylikin, A. G. Shipov, Yu. I. Baukov, and D. Kost, *Izv. Akad. Nauk, Ser. Khim,* 1069 (2004).
8. E. P. Kramarova, S. A. Pogozhikh, A. G. Shipov, Vad. V. Negrebetskii, T. P. Nikolaeva, S. Yu. Bylikin, Yu. E. Ovchinnikov, and Yu. I. Baukov, *Izv. Akad. Nauk Ser. Khim.*, 251 (2004).
9. O. B. Artamkina, E. P. Kramarova, A. G. Shipov, Yu. I. Baukov, A. A. Macharashvili, Yu. E. Ovchinnikov, and Yu. T. Struchkov, *Zh. Obshch. Khim.*, **64**, 263 (1994).
10. A. G. Shipov, N. A. Orlova, O. P. Novikova, and Yu. I. Baukov, *Zh. Obshch. Khim.*, **55**, 943 (1985).
11. Vad. V. Negrebetskii and Yu. I. Baukov, *Izv. Akad. Nauk Ser. Khim.*, 1912 (1997).
12. A. A. Macharashvili, V. E. Shklover, Yu. T. Struchkov, G. I. Oleneva, E. P. Kramarova, A. G. Shipov, and Yu. I. Baukov, *J. Chem. Soc., Chem. Commun.*, 683 (1988).
13. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc. Perkin. Trans. 2*, S1 (1987).

14. A. A. Korlyukov, K. A. Lysenko, and M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.*, 1314 (2002).
15. A. A. Korlyukov, K. A. Lysenko, M. Yu. Antipin, A. G. Shipov, O. A. Zamyshlyaeva, E. P. Kramarova, V. V. Negrebetskii, S. A. Pogozhikh, Yu. E. Ovchinnikov, and Yu. I. Baukov, *Izv. Akad. Nauk, Ser. Khim,* 1846 (2004).
16. A. A. Korlyukov, S. A. Pogozhikh, Yu. E. Ovchinnikov, K. A. Lyssenko, M. Yu. Antipin, A. G. Shipov, O. A. Zamyshlyaeva, E. P. Kramarova, Vadim V. Negrebetsky, I. P. Yakovlev, and Yu. I. Baukov, *J. Organomet. Chem.*, **691**, 3962 (2006).
17. R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford (1990).
18. N. Kocher, J. Henn, B. Gostevskii, D. Kost, I. Kalikhman, B. Engels, and D. Stalke, *J. Amer. Chem. Soc.*, **126**, 5563 (2004).
19. E. Espinosa, E. Mollins, and C. Lecomte, *Chem. Phys. Letters*, **285**, 170 (1998).
20. F. Rioux, M. W. Schmidt, and M. S. Gordon, *Organometallics*, **16**, 158 (1997).
21. E. I. Brodskaya and M. G. Voronkov, *Vestn. Akad. Nauk USSR*, 1546 (1986).
22. A. Ya. Yakubovich, S. P. Makarov, I. A. Ginzburg, G. I. Gavrilov, and E. N. Merkyulova, *Dokl. Akad. Nauk*, **72**, 69 (1950).
23. G. M. Sheldrick, SHELXTL-97, **5.10** (1997), Bruker AXS Inc., Madison, WI-53719, USA.
24. T. Koritsansky, S. T. Howard, T. Richter, P. R. Mallinson, Z. Su, and N. K. Hansen, *XD, a Computer Program Package for Multipole Refinement and Analysis of Charge Densities from X-Ray Diffraction Data*, (1995).
25. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT (2004).
26. P. Popelier, *Comp. Phys. Comm.*, **93**, 212 (1996).
27. P. Popelier, *Comp. Phys. Comm.*, **108**, 180 (1998).