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Nature of Intramolecular O→Si Bond in *N*-(Trifluorosilylmethy)succinimide and *N*-(Trifluorosilylmethy)phthalimide

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Abstract—By AIM analysis with application of PBE/TZ2P(SBK-JC) method the O→Si bond in isolated molecules of *N*-(trifluorosilylmethyl)succinimide (**I**) and *N*-(trifluorosilylmethyl)phthalimide (**II**) is shown to be of donor–acceptor type. In crystalline state of compound **I** it also is a weak donor–acceptor bond, while in **II** the interaction between the oxygen and silicon atoms is of electrostatic nature.

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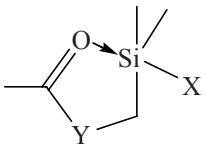
Geometric parameters of coordination node in the intracomplex compounds of hypervalent silicon with an Y→Si bond feature by high sensitivity toward structural effects and external factors (aggregate state, medium polarity, temperature) [1 – 8]. In part, in compounds with pentacoordnated silicon studied in different aggregate states the intramolecular O→Si bond length vary in a wide range, from 1.7 to 2.8 Å. Mechanism of intramolecular O→Si interaction also vary in dependence on the features of structure of the coordination node. This is attested by the results of study of the nature of chemical bonding using "atoms in molecules" (AIM) theory proposed by Bader [9]. Thus, topological analysis of electron density distribution and investigation in the framework of the scheme of natural binding orbitals (NBO) [10] of zwitter-ionic coordination compounds allowed to reveal that interaction in the O→Si–X axial fragment vary from dative to three-center tetraelectronic one (3c4e) [1]. According to AIM analysis, coordination bond in (benzoyloxymethyl)trifluorosilane is suggested to be highly polar covalent one [12]. In Si-substituted dimethyl(diacetylimidomethyl)silanes $(O→Si)(MeCO)_2·NCH_2SiMe_2X$ this bond is weak covalent, therewith electron density transfer from the donor oxygen atom depends on the X substituent in the axial O→Si–X fragment [13].



A special interest concerns pentacoordinated silicon compounds where Si–X bond varies sharply at the change in state of aggregation.

An example of compound with high sensitivity of coordination O→Si bond length to external factors is *N*-(trifluorosilylmethyl)succinimide (**I**) [14]. The O→Si distance in its molecule in condensed state (crystal, polar solvent) is short, while in the isolated state the distance increases. At the phase transition from crystal to gas it grows from 2.095 to 2.493 Å. Anotherr situation occurs in the case of a related compound, *N*-(trifluorosilylmethyl)phthalimide (**II**). In its molecule the coordination O→Si bond length almost the same both in solid (2.654 Å) and in isolated (2.581 Å) states [15, 16]. As far as the O→Si bond lengths in the molecules **I** and **II** in crystal differ significantly, it can be assumed that their different sensitivity tio the effects of medium is defined by the change in the nature of coordination interaction.

We aimed ourselves at the theroretical establishing of the type of chemical bonding between the oxygen

and silicon atoms in the molecules of *N*-(trifluorosilylmethy)succinimide (**I**) and *N*-(trifluorosilylmethy)-phthalimide (**II**) in isolated state and in crystal.

Calculations of the molecules **I** and **II** were carried out with PRIRODA program [17, 18] by PBE/TZ2P (SBK-JC) method [18-22]. We found that in isolated molecules **I** and **II** the carbon and silicon atoms in $F_3Si–CH_3$ group are located in the plane of the heterocyclic ring (Fig. 1).

Due to the coordination O→Si interaction the distance between oxygen and silicon atoms in the molecules **I** and **II** (2.282 and 2.362 Å, respectively) is much shorter than the sum of Van der Waals radii of these atoms (3.44 Å). The surrounding of the silicon atoms in the **I** and **II** molecules is a screwed trigonal bipyramid. In the axial positions are located oxygen and fluorine atoms, two another fluorine atoms and methylene bridge are located in the equatorial plane. At the donor-acceptor interaction between O and Si atoms the Si–F_a bond is elongated as compared with Si–F_e (in molecule **I**: Si–F_a = 1.639 Å, Si–F_e = 1.616 Å; in **II:** Si–F_a = 1.635 Å, Si–F_e = 1.614 Å). Such difference is typical for the compounds with penta-coordinated silcon atom.

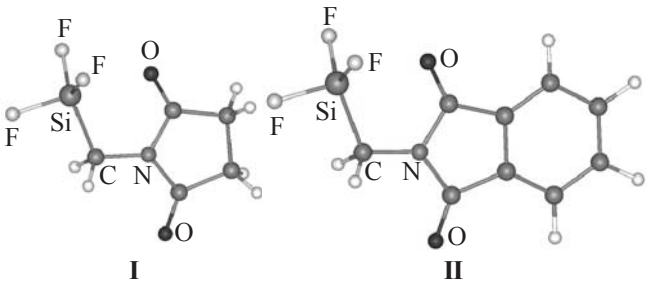


Fig. 1. Molecular structure of *N*-(trifluorosilylmethyl)-succinimide (**I**) and *N*-(trifluorosilylmethyl)phthalimide (**II**).

The coordination of O and Si atoms appears as decrease in the energy of the orbitals corresponding to lone electron pairs of oxygen atom coordinated with silicon (HOMO-2 for **I** and HOMO-4 for **II**, Fig. 2), as compared with those at non-coordinated oxygen atoms (HOMO for **I** and **II**).

Rotation barrier around C–N bond equals to 2.7 and 2.2 kcal mol^{-1} for **I** and **II**, respectively. In both cases, in transition state (TS) groups $F_3Si–CH_2$ are almost orthogonal to the ring plane (Fig. 3). Energy characteristics of molecules **I** and **II** in ground and transition states are listed in Table 1.

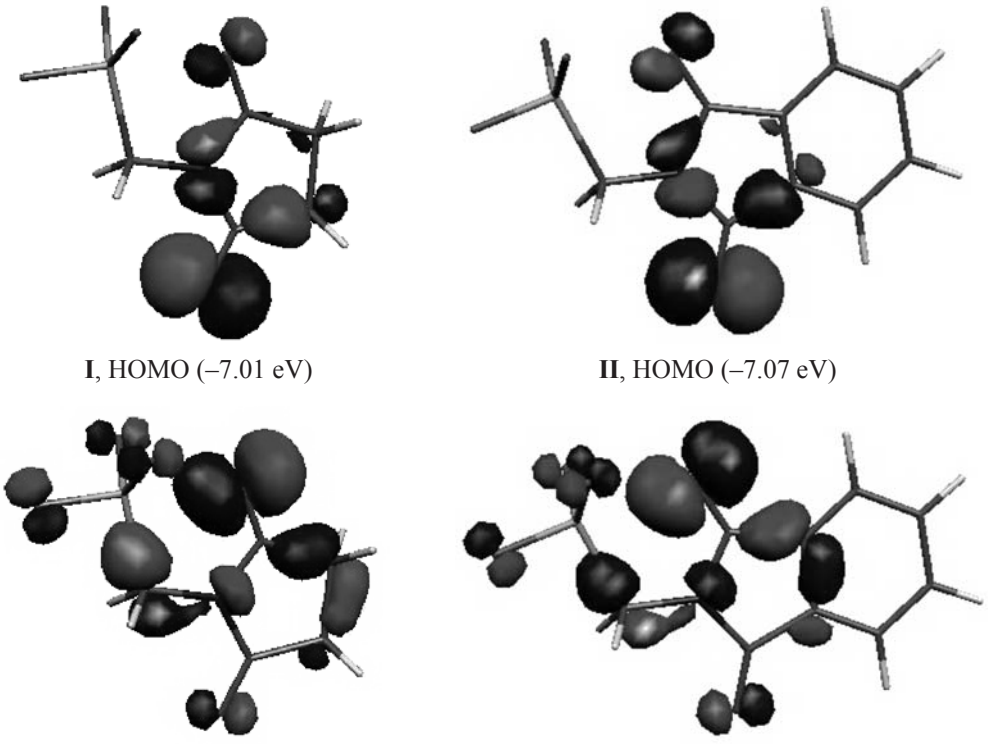


Fig. 2. Frontier orbitals in the molecules **I** and **II**.

Table 1. Energy parameners of *N*-(trifluorosilylmethyl)succinimide (**I**) and *N*-(trifluorosilylmethyl)phthalimide (**II**). [PBE/TZ2P(SBK-JC)]

Molecule	E	E^0	H	G	ΔE	ΔE^0	ΔH^0_{298}	ΔG^0_{298}
	au		kcal mol^{-1}					
I	–150.79046	–150.67429	80.9	48.6	0.0	0.0	0.0	0.0
TS-**I**	–150.78499	–150.66939	80.3	47.9	3.4	3.1	2.8	2.7
II	–173.48609	–173.34645	97.0	61.5	0.0	0.0	0.0	0.0
TS-**II**	–173.48147	–173.34241	96.4	60.8	2.9	2.5	2.2	2.2

Table 2. Properties of the bond critical points (O→Si) of *N*-(trifluorosilylmethyl)succinimide (**I**) and *N*-(trifluorosilylmethyl)phthalimide (**II**) [PBE/TZ2P(SBK-JC)]. Electron density $\rho(r_{av})$, density Laplasian $\nabla^2\rho(r_{av})$, parameters λ_1, λ_2, λ_3, au

Molecule	$\rho(r_{av})$	$\nabla^2\rho(r_{av})$	λ_1	λ_2	λ_3	$\lvert\lambda_1\rvert/\lambda_3$	ε
I	0.042	0.044	–0.040	–0.024	0.109	0.37	0.63
Ia	0.057	0.032	–0.049	–0.025	0.106	0.46	0.98
II	0.036	0.060	–0.034	–0.020	0.114	0.30	0.69

We carried out AIM analysis of **I** and **II** molecules. In both the cases, between oxygen and silicon atoms are located bond critical points (CP) (3, –1) (Fig. 4) that attest interaction between these atoms.

Parameters of O→Si bonds in **I** and **II** molecules by the data of AIM analysis: low $\rho(r_{av})$ ~0.04 au, low positive values of density Laplasian $\nabla^2\rho(r_{av})$ 0.04 and 0.06 au, respectively, and parameter $|\lambda_1|/\lambda_3$, 0.37 and 0.29, respectively, are typical for a weak donor-acceptor interaction (Table 2).

The AIM analysis of molecules **I** and **II** with geometric parameters of crystals **Ia** and **IIa** obtained by X-ray structural analysis [14, 16] showed that bonding CP (O→Si) is found for **Ia** only (Table 2). The CP parameters of O→Si bond of **Ia** in crystal are comparable with those found for isolated molecule **I**. The five-membered coordination cycle of phtalimide derivative **IIa** closed by O→Si bond is not planar, the C–N–C–Si angle is 30°. For this molecule the bonding CP responding to O→Si interaction was not found.

It is typical that ellipsicity (ε) of O→Si bond in **I** and **II** molecules is high (Tabe 2). This fact attests their structural non-rigidity along the coordination bond.

Thus, by the data of AIM analysis, the nature of O→Si bond in isolated **I** and **II** molecules is the same and coordination interaction is weak donor–acceptor one. In molecular crystals **Ia** and **IIa** the nature of O→Si interaction differ significantly. In **Ia** molecule the interaction between oxygen and silicon atoms is of electrostatic nature.

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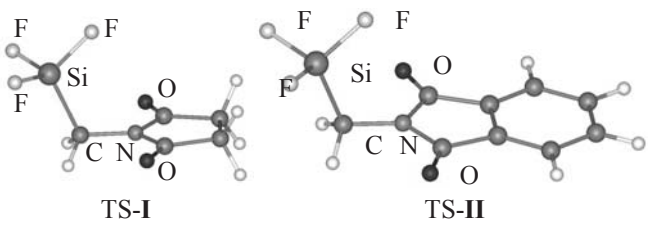

Fig. 3. Molecular structure of transition states of *N*-(trifluorosilylmethyl)succinimide (**I**) and *N*-(trifluorosilylmethyl)phthalimide (**II**).

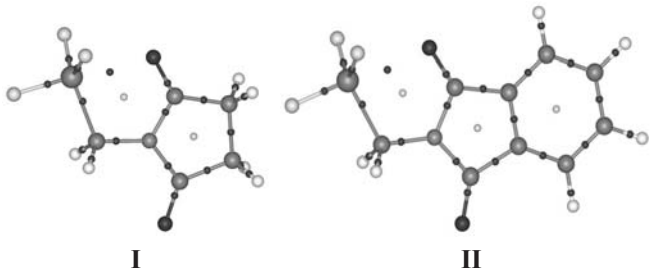

Fig. 4. AIM molecular graphs of isolated molecules **I** and **II**. Dark balls denote bond critical points (3, –1), light balls are ring critical points (3, +1).

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