The nature of hypervalent bonding in compounds of pentacoordinated silicon as found from X-ray diffraction and quantum chemical calculations

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On the basis of high-resolution X-ray analysis and quantum chemical calculations the electron density distribution function ρ(r) in the series of silatranes (Fig. 1, *a*) and monochelated compounds compounds with pentacoordinated silicon atom has been studied (Fig. 1, *b* and *c*).

Topological analys of the ρ(r) has revealed that Si-O and Si-N bonds in silatranes (Fig. 1, *a*) and monochelated compounds with pentacoordinated silicon atom (Fig. 1, *b*) corresponds to interactions of intermediate type in terms of Bader's "Atoms in molecules theory". In the studied silatranes (Fig. 1, *a*) the decreasing of the Si-N distance to 2.0Å (X = Cl) does not lead to weakening of the axial Si-X bond. On the other hand, in the monochelated compounds the decreasing of the Si-O distance to 1.88-1.95Å causes significant changes in the electron density distribution in the region of the Si-X bonds that does not allow to consider these bonds as "ordinary" covalent ones. The special interest attracts the organosilicon derivatives of salicylamide (Fig. 1, *c*) in which the Si…O interatomic distances falls in the range 2.8 ÷ 3.0 Å that is 0.3 ÷ 0.5 Å less than the sum of the van-der-waals radii of silicon and oxygen atoms. Besides, the Si-X bonds is elongated in comparison to its standart values. So, one may expect the presence of Si…O intramolecular interactions in the above mentioned compounds. However, topological analys of the ρ(r) has shown the absense of Si…O interaction. The high value of dipole moment (~ 8.3 D) allow one to conclude that elongation of the Si-Cl bond can be explained by its polarization by influence of strong negatively charged OF_2O moiety. This work was supported by the Russian Foundation for Basic Research (grants 03-03-32214 and 02-07-90169).

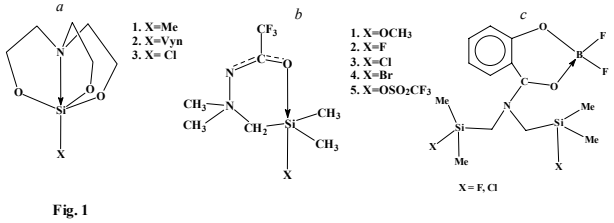

Fig. 1