s2.m9.p2 **Topological information of the electron density distribution in hydrogen bonded systems.** Enrique Espinosa,[a] Ibon Alkorta,[b] José Elguero[b] and Elies Molins[c]. *[a]LIMSAG, UMR 5633, Université de Bourgogne, 6 bd. Gabriel, 21000 Dijon (France). [b]Instituto Química Médica (CSIC), C/ Juan de la Cierva 3, 28006 Madrid (Spain). [c]Institut Ciencia de Materials de Barcelona (CSIC), Campus UAB, 08193 Cerdanyola (Spain). E-mail: Enrique.Espinosa@u-bourgogne.fr*

Keywords: Electron density; Topology; Hydrogen bonding.

Using the topological properties of the experimental electron density distribution $\rho(\mathbf{r})$ observed in 83 hydrogen bonds [X-H···O (X=C,N,O)], we have related the total energy density observed at the bond critical point (H^{CP}) to the H...O interaction potential (U) by means of a proportional relationship $U\propto\cdot H^{CP}$.[1] This function has been successfully checked against several physical and chemical properties and compared to Morse and Buckingham type potentials. Recently,[2] we have undertaken the theoretical study of r(r) calculated for the isolated H···F interaction and for 79 X-H···F-Y complexes. The analysis of all these systems lead to three characteristic $\rho(\mathbf{r})$ regions for distances H···F ranging from weak van der Waals to strong covalent interactions. While the extreme regions are respectively associated to *pure* CS and SS interactions, the middle region is associated to the redistribution of $\rho(\mathbf{r})$ between those electronic states. The analysis carried out with the isolated H···F interaction has permitted to associate this transit region to internuclear geometries involved in the building of the H-F bonding molecular orbital. The interaction energies of X-H···F-Y *pure* CS interactions have been estimated by using the bond degree parameter (B.D. = H^{CP}/ρ^{CP}) and the [F···H···F]-proton transfer geometry has been associated to the local maximum of the electron kinetic energy density (G^{CP})$_{max}$.

References

[1] E.Espinosa and E. Molins *J. Chem. Phys*., 2000, **113**, 5686.
[2] E.Espinosa, I.Alkorta, J.Elguero and E. Molins *J. Chem. Phys*., 2002, **117**, 5529.

s2.m9.p3 **The nature of hypervalent bonding in compounds of pentacoordinated silicon as found from X-ray diffraction and quantum chemical calculations.** Alexander A. Korlyukov, Konstantin A. Lyssenko, Mikhail Yu. Antipin, *A.N. Nesmeyanov Institute of Organoelement Compounds, 119991, 28 Vavilov St, Moscow, Russia. E-mail: alex@xrlab.ineos.ac.ru*

Keywords: Electron density distribution; Quantum chemical calculations

On the basis of high-resolution X-ray analysis and quantum chemical calculations the electron density distribution function $\rho(r)$ 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 $\rho(r)$ 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 $\rho(r)$ 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$_2$O moiety. This work was supported by the Russian Foundation for Basic Research (grants 03-03-32214 and 02-07-90169).
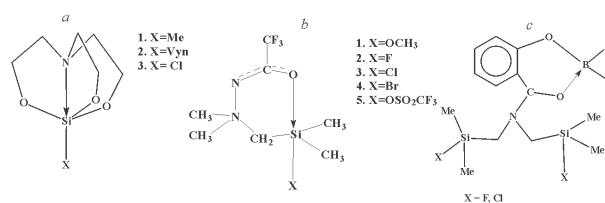

Fig. 1