

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

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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  $U \propto H^{CP}$ .<sup>1</sup> This function has been successfully checked against several physical and chemical properties and compared to Morse and Buckingham type potentials. Recently,<sup>2</sup> 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. =  $H^{CP}/\rho^{CP}$ ) and the [F...H...F]-proton transfer geometry has been associated to the local maximum of the electron kinetic energy density ( $G^{CP}$ )<sub>max</sub>.

#### References

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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

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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 with pentacoordinated silicon atom has been studied (Fig. 1, *b* and *c*).

Topological analysis 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 2.0 Å (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 1.88-1.95 Å 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 analysis of the  $\rho(r)$  has shown the absence 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<sub>2</sub>O moiety. This work was supported by the Russian Foundation for Basic Research (grants 03-03-32214 and 02-07-90169).

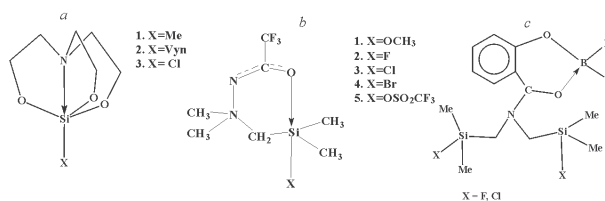


Fig. 1