

Chemical Bonding in Hypervalent Silicon and Germanium Compounds

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On the basis of the analysis of experimental and calculated electron density distribution functions of different atranes and monochelated compounds we have investigated the nature of the chemical bonding in their axial D-M-X (D = O, N; M=Si, Ge; X = Cl, OH, OH₂) fragment.

Both in crystal and isolated molecules the hypervalent D...M bonds are characterized by the intermediate type of interatomic interaction in terms of R. F. Bader's "Atoms in Molecules" theory. The transition of molecules of this type from crystal to isolated state leads to a noticeable decrease of electron density and potential energy density values in critical points (3, -1) of D...M hypervalent bonds that implies the weakening of this bonds. The extent of such weakening depends on the nature of D, M and X atoms.

The usage of the same theoretical background and periodic DFT calculations allow us to reveal the influence of intermolecular interactions on the geometry of M atom coordination centre.

On the basis of topological analysis and NBO population analysis we have estimated the strength of hypervalent bonds in monochelated compounds and atranes. For instance, in a number of six-membered cyclic compounds (X=Hal, OAlk) the strength of D...O bonds (1.96 ÷ 2.45 Å) varies in the range 4 - 29 kcal/mol.

Keywords: charge density distribution, topological properties of charge, theoretical crystal calculations