

Electron density distribution in organic phosphates and phosphonates

Adrian Mermer

Abstract in English

The thesis presents the results of experimental studies on the electron density of organic phosphates and phosphonates: calcium bis(hydromethylphosphonate) and lithium hydrogen methylphosphonate, monopotassium phosphoglycolate, diammonium hydrogenphosphoglycolate, ammonium dihydrogenphosphoenolpyruvate and calcium bis(dihydrogenphosphoenolpyruvate). This was accompanied by calculations of their electronic structure using the DFT method. The topological analyses carried out on this basis showed that the P–O bonds are intermediate interactions in the sense of Bader-Essén, covalent interactions in the sense of Cremer and Kraka, and transit closed-shell interactions in the sense of Espinosa *et al.*, which manifested itself as high values of electron density and its Laplacian at the bond critical point, which was accompanied by negative total energies at this point. Differences between the experimental and theoretical topology, which manifested themselves especially in the area of P–O and C–O bonds, were also found and studied. Based on the collected data, the relationships of these topological parameters vs the length of P–O bonds were also determined. They showed that, despite the growing importance of Pauli-exchange effects for the electron density in the internuclear region, it is nevertheless subject to increasing stabilization, concentration and accumulation when these bonds shorten. Analysis of theoretical results revealed that strong delocalization mechanisms operate in the phosphate and phosphonate groups, which manifest in the NBO analysis as negative hyperconjugations on the part of oxygen atoms. In this respect, the strongest donors were *p*-type orbitals of lone electron pairs located on terminal oxygen atoms, while the strongest acceptors were those of σ -antibonding type, associated with bridging bonds, i.e. the ester and hydroxyl ones. Analysis of the origin of the Gibbs free energy of hydrolysis of organic phosphates was also undertaken, which revealed the key importance of the orbitals located within the bridging P–O–C fragment; in particular, the σ -type orbitals of the bonds forming it and the transversal electron lone pair located at the ester oxygen atom. The involvement of the latter in delocalizations with the acceptor orbitals of the organic residue determined the magnitude of this free energy. In addition, in the spaces between the geminal P–O bonds, domains with low RDG and high DORI values were found. Their potential relationship with delocalization mechanisms operating within the phosphate group and their possible genesis are discussed.