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Experimental versus theoretical electron density in the crystals of $\beta$-aminophosphonic acids

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Investigated compounds are novel $\alpha$-substituted-$\beta$-aminophosphonic acids which are similar to herbicides used in agriculture [1]. X-ray analysis accompanied by the ab initio B3LYP and MP2 calculations showed high level of electron density delocalizations in all investigated structures and antiperiplanar arrangement around the central C$_a$-$C_\beta$ bond. The phosphorus atom is located within the center of distorted tetrahedron. The largest distortions follow from the Coulombic repulsion interactions between the oxygen atoms bearing the negative charge. This effect was further investigated with the natural bond orbital methodology. Wavefunctions were calculated at the B3LYP/6-31G$+$+(d,p) level for the X-ray coordinates. In all compounds the main electron density delocalizations involve back-donation from the $n_\pi$ lone pairs of the phosphonic oxygen atoms to the $\sigma^*$ orbital of the adjacent P-$C_\beta$ bond. Those interactions act against the depletion of electron density in the phosphorus originated by the neighboring electronegative oxygen atoms. The molecular conformation is stabilized by the mutual anti $\alpha$-$\sigma^*$ stereoelectronic interactions of the P-$C_\alpha$ and N-$C_\beta$ bonds. In all crystals N atom of the terminal amine group is protonated and adopts virtually tetrahedral geometry with all three hydrogen atoms involved in the intermolecular hydrogen bonding. The crystal structure of 1-(aminomethyl)vinylphosphonic was further examined using the high resolution low temperature X-ray data and the multipole atom model. Experimental electron density was carefully examined and compared with the densities calculated at the MP2 and B3LYP levels of theory. The Bader’s theory Atoms in Molecules was applied. [1] Krawczyk H., Albrecht L., Wójciecekowski J., Wolf W.M. Tetrahedron, 2008, in press.

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Lessons from a decade of X-ray crystallographic work on N-(hydroxy)thiazole-2(3H)-thione derivatives

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