

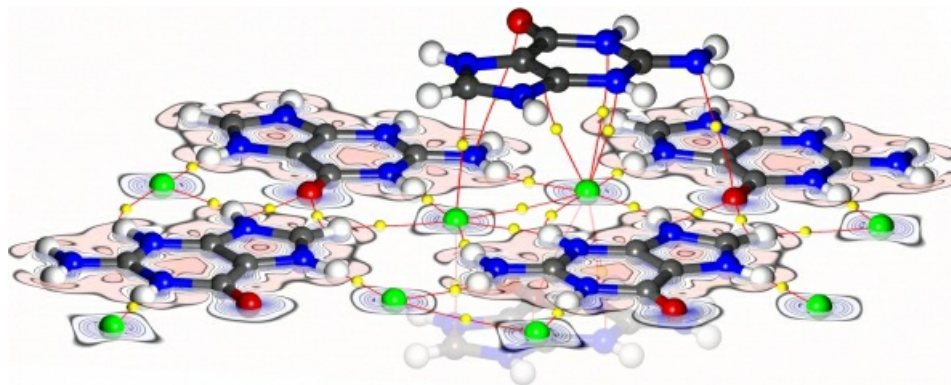
Experimental charge densities of nucleobase chlorides from intermolecular interaction perspective

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Nucleobases are one of the basic building blocks of nucleic acids, the most important molecules for every living organism. The richness of possibilities of how nucleobases may interact with themselves and with other molecules, yet still maintaining specificity of an interaction, makes them a key contributor to the 3D structure and function of DNA, and even more of RNA. The presented work contributes to our understanding of intermolecular interactions among protonated nucleobases and surrounding them chloride counter ions in the solid state. For cytosinium chloride, adeninium chloride hemihydrate and guaninedium dichloride we collected high-resolution X-ray diffraction data to determine crystal charge densities. Experimental results we further supported by extensive theoretical calculations: UBDB charge density modelling, EPMM electrostatic interaction energy calculations, QTAIM analysis, dimer interaction energy from perturbation theory (PIXEL, DFT-SAPT) and periodic quantum mechanics based on variational principle.

We found that cohesive energies of studied systems are dominated by electrostatic interaction energy (Ees) contributions - as expected for ionic crystals. Ees contributions from pairs of neighboring ions are big in magnitude, much bigger than for pairs of neutral molecules of the same type. However, Ees computed from experimental charge densities are not as big in magnitude as theoretical calculations based on perturbation theory suggest. This is because studied molecules are not fully ionized in crystal state according to experiment and periodic quantum calculations. Because of that and because of charge density polarization, some pairs of single protonated bases exhibit attractive interactions (negative Ees) despite same molecular charge. In addition, these pairs, but also other pairs of ions show that the values of Ees cannot be predicted only from interactions between monopole moments (point charges) of studied molecules. The higher electric moments and the overlap of molecular charge densities matters.

On the other hand we found, that despite their overall repulsive character of interactions, there are bond critical points (BCP) and bonding lines between many nucleobases in studied crystals according to QTAIM analysis of crystal electron densities (experimental, UBDB derived and from periodic quantum mechanics). Moreover, interaction energies computed from electron density and its Laplacian at BCPs according to Espinosa-Lecomte-Molins approach are negative pointing to attractive interaction. Although there is no correlation between the sum of these energies for particular pair of ions (regardless their charge) and Ees of this pair, there is strong correlation of these energies with charge penetration contribution to the Ees. We found it to be one of the most significant results of the presented work. Indeed, BCPs are very important single point descriptors of interactions between the whole molecules as they bear the information about molecular charge densities overlap and its contribution to interaction energy.



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