Poster Presentation

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Influence of the electrostatic environment on I3-····I3- and related I–M–I···I–M–I interactions

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Non-covalent interactions in crystals are notoriously difficult to calculate accurately [1], due to the poor computational description of dispersion, which is often an important component of such interactions. This is particularly true for I3-•••I3- interactions, which are observed in crystal structures despite the strong electrostatic repulsion between two negatively charged species [2]. Similarly, related metal-iodides exhibit I–M–I•••I–M–I interactions. In an effort to explain this phenomenon a thorough Cambridge Structural Database (CSD) analysis and theoretical study of the triiodide ion, metal-iodides and I•••I interactions within dimers of these species in a variety of environments is presented here.   Optimisations in the gas phase and in an implicit polarisable continuum solvent model with several different solvents show that there is a significant dependence of the I3-•••I3- interaction energy on the dielectric constant. The MP2/cc-pVTZ-pp level of theory comes closest to reproducing the I3- bondlength and the I3-•••I3-intermolecular distance averages obtained from the Cambridge Structural Database (CSD). DFT methods are in general not as successful since they do not correctly model dispersion, however, the PBE method used in conjunction with Grimme's D2 dispersion correction [3] yields an interaction energy which is less than 2% from the CCSD/aug-cc-pVTZ-pp// MP2/cc-pVTZ-pp result.   The Electrostatic Surface Potential (ESP) of the I3- ion in the gas phase, chloroform, ethanol, water and n-methyl-formamide-mixture can be used as a gauge of the influence of the electrostatic environment on the properties of both the I3- ion and the I3-•••I3- interaction, or similarly I-M-I•••I-M-I interactions. This information can then be used to extrapolate to obtain a value for the strength of the I•••I inter-ion interaction energy in the solid state in a variety of complexes.

[1] K. E. Riley, P. Hobza, WIREs Computational Moleclar Science, 2011, 1, 3–17., [2] F. Groenewald, C. Esterhuysen, J. Dillen, Theoretical Chemistry Accounts, 2012, 131, 1281., [3] S. Grimme, Journal of Computational Chemistry, 2006, 27, 1787-99.

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