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Investigation of I ...S interactions by Charge Density Studies

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Crystals of S_2I_4 (AsF_6)₂ and CHI_3 (S_8)₃ have been examined with charge density studies. The conventional structure of S_2I_4 (AsF_6)₂ and the theory of the bonding of the $S_2I_4^{2+}$ cation has already been published [1]. Here the S-S bond order of 2.4 was claimed to be the highest bond order known between heavy main-group elements and the structure of the cation was constructed to maximise (bonding). There are also a multitude of I ...F and S ...F weak-interaction contacts in S_2I_4 (AsF_6)₂. The topological analysis largely confirms the theoretical studies on the $S_2I_4^{2+}$ cation and examines and categorises the long range contacts to F. The structure of CHI_3 (S_8)₃ was examined [2] many years ago, the structure is in the trigonal space group $R\bar{3}m$ with the CHI_3 group on the three-fold axis (C_{3v}) and the S_8 rings across the respective three mirror planes so that the structure actually contains only 8 unique atoms (C, H, I and five sulfur atoms). It was originally claimed that in the weak I ...S interactions that hold the structure together, the sulfur was the donor, the iodine the acceptor. The topological analysis suggests differently with the bond critical points (BCP) suggesting that the iodine is the donor. All the BCPs for the weak interactions, and the ring BCP for the S_8 ring have been detected and characterised. They fall within the expected range of locations and values.

[1] Scott Brownridge, T. Stanley Cameron, Hongbin Du, Carsten Knapp, Ralf Köppe, Jack Passmore, J. Mikko Rautianen and Hansgeorg Schnöcke *Inorg Chem.*, 2005 44, 1660-1671.

[2] T. Bjorvatten, *Acta Chem. Scand.* 1962 16, 749; T. Bjorvatten, O. Hassel and A. Lindhem, *Acta Chem. Scand.* 1963 17, 689-702.

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The nature of the C-H...F interaction found in molecular crystals evaluated by *ab initio* calculations

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The nature of C-H...F interactions has been controversial. While some authors consider them as weak hydrogen bonds, other suggested that they are not hydrogen bonds (therefore, they should be considered as van der Waals interactions). Based on MP2 calculations of all short intermolecular C-H...F interactions found in the crystals deposited in the Cambridge Crystallographic Database we found that the C-H...F interaction energy fit in the range -163.1 up to 50.1 kcal/mol. An analysis of the components of the interaction energy, done using Stone's IMPT method, shows that the reason for this wide range of energies is the electrostatic component, which strongly depends on the net charge sitting on the two fragments that host the C-H and F parts of the C-H...F interaction. Therefore, short contact C-H...F interactions can be much more important in defining the crystal packing than expected up to now.