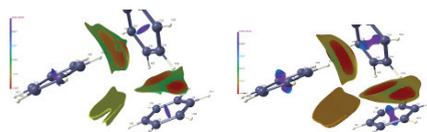


Università degli Studi, Milano (Italy). ^bCNR-ISTM, Istituto di Scienze e Tecnologie Molecolari, Milano (Italy). ^cCMC, Center for Materials Crystallography, Aarhus (Denmark). ^dDept. of Chemistry, Duke University, Durham NC (USA). E-mail: gabriele.saleh@unimi.it

Non covalent interactions (NCI) play a crucial role in biology (protein-drug recognition) and in the design of new materials (self-assembly). A novel electron density (ED) based descriptor of non covalent interaction was proposed in 2010 by Johnson *et al.*[1]. It exploits a key quantity in DFT, the reduced density gradient $s \propto |\nabla\rho|/\rho^{4/3}$, and reveals NCI in terms of low s -value isosurfaces, defined in low-ED regions and on which the ED is mapped with a colour related to the sign of the local density curvature along the second largest variation direction and to the magnitude of the ED itself. Though directly obtainable from experimental EDs, up to now such descriptor has been applied only to theoretical EDs or to independent atom model (IAM) densities.

In this work, we explore the application of this new descriptor to NCI in the bulk, using X-ray derived EDs. In particular, molecular crystals represent ideal supramolecular entities for studying non covalent interactions and the global effect that the crystal field has on them. Austdiol [2], benzene [3] and the two polymorphs of the anti-ulcer drug famotidine [4] were chosen as representative case studies. Atom-centred multipole expansions (XD2006 package [5]) were adopted in the refinement against the experimental structure factors and the grid files for implementing the NCI descriptor were obtained with an *ad-hoc* code. The NCI isosurfaces obtained from experiment have been also compared with those calculated using *ab-initio* periodic wavefunctions and the IAM densities.

On the basis of the experience gained on the investigated systems, it turns out that when applied to experimental EDs the NCI descriptor gives essentially similar information to that found for theoretical EDs. For instance, as shown in the figure below for benzene crystal, we find that interactions having a presumably delocalized nature, such as π - π stackings or C-H... π contacts, are indeed seen as extended surfaces, at variance with the localized and discontinuous picture unavoidably provided by the bond path analysis. Moreover, we confirm that mapping the ED on the s isosurface highlights the strength of the various interactions, while the sign of the curvature helps to distinguish true stabilizing interactions from simple steric repulsions. The visible difference between the NCI isosurfaces portrait found in benzene crystal on passing from the multipolar to the IAM density corroborates the stabilizing and not simply steric nature of the π - π stacking and C-H... π interactions.



NCI isosurfaces [1] ($s=0.3$) in the molecular crystal of benzene. *Left:* multipolar ED. *Right:* IAM-ED

[1] E.R. Johnson *et al.*, *JACS* **2010**, *132*, 6498-6506. [2] L. Lo Presti *et al.* *J. Chem Phys. B* **2006**, *110*, 6405-6414 [3] H.-B. Bürgi *et al.* *Chem. Eur. J.* **2002**, *8*, 3512-3521 [4] J. Overgaard *et al.* *Acta Cryst.* **2004**, *A60*, 480-487 [5] <http://xd.chem.buffalo.edu/>

Keywords: non covalent interactions, electron density

MS34.P15

Acta Cryst. (2011) **A67**, C449

Structural and charge density studies of organic-inorganic [ArBF₃]⁻X⁺ compounds

Radosław Kamiński,^a Marek Dąbrowski,^b Krzysztof Durka,^{a,b} Janusz Serwatowski,^b Krzysztof Woźniak,^a ^aDepartment of Chemistry, University of Warsaw, Warszawa (Poland). ^bDepartment of Chemistry, Warsaw University of Technology, Warszawa (Poland). E-mail: rkaminski.rk@gmail.com

Boron-based hybrid compounds are very attractive due to their numerous applications in modern synthetic chemistry as well as in materials chemistry. Our recent investigations show that experimental charge density studies (combined with computations) can be successfully utilized to explain reactivity and behavior of arylboronic azaesters.[1] Therefore, further search for compounds which could serve as possible optical devices lead us to the hybrid organic-inorganic complexes of [ArBF₃]⁻X⁺ type (Ar = aryl, X⁺ = positively charged organic or inorganic species). The fact that they have an aromatic easily substituted moiety and changeable cation, makes them excellent model systems to investigate various phenomena that occur in the solid state (*e.g.* fluorescence or light-induced structural changes). Hence, we will present in this contribution our preliminary charge density studies of model hybrid organic-inorganic boron complex, PhBF₃K, and similar compounds in terms of the Hansen-Coppens multipole model [2] followed by QTAIM analysis [3] and theoretical calculations. This compound will also serve as a model example in our recent developments of charge-density-based Hirshfeld surfaces.

[1] K. Durka, R. Kamiński, S. Luliński, J. Serwatowski, K. Woźniak, *Phys. Chem. Chem. Phys.* **2010**, *12*, 13126. [2] N. K. Hansen, P. Coppens, *Acta Cryst.* **1978**, *A34*, 909. [3] R.F.W. Bader. *Atoms in Molecules - A Quantum Theory*. **1990**, Oxford: Oxford University Press.

Keywords: hybrid compounds, charge density, structural analysis

MS34.P16

Acta Cryst. (2011) **A67**, C449-C450

Electronic structure and bonding interactions in FeS₂ and FeP₂

Simone Cenedese,^{a,b,c} Carlo Gatti,^{b,c} Bo B. Iversen,^{c,d} ^aDept. of Physical Chemistry and Electrochemistry, Università degli Studi, Milano (Italy). ^bCNR-ISTM, Institute of Molecular Sciences and Technology, Milano (Italy). ^cCMC, Center for Materials Crystallography, Aarhus University (Denmark). ^dDepartment of Chemistry and iNANO, Aarhus University, Denmark. E-mail: simo@chem.au.dk

The crystallographic structures of marcasite-type compounds have been extensively scrutinized in a series of studies around 1970. [1-5] The most successful attempt to establish a link between the electronic and geometrical structure is probably the one due to Goodenough, [6] whose picture is still employed nowadays after 40 years from its proposal. However, as pointed out by Hoffmann for FeSb₂ almost ten years ago, [7] even if the proposed picture seems to be successful at explaining some of the physical properties of these compounds, it appears, instead, to be at odd with well known chemical concepts.

In this work the proposed electronic structure for marcasite-type compounds is reviewed and light is shed on the interplay among geometry, electronic structure and bonding interactions in FeS₂ and FeP₂, taken as suitable reference test cases. Our analysis compares the predictions of ligand field theory with the *ab-initio* orbital-based view of both the anisotropy of the iron *d*-electrons distribution and the composition (DOS analysis) of bonding and antibonding states close to the Fermi level in the two compounds.

Even if the results obtained for the electronic structure are in accordance with the proposed molecular orbital scheme, the thorough analysis of orbital populations allowed us to disentangle and rationalize the differences due to the geometrical and electronic structure of FeS₂ and FeP₂.