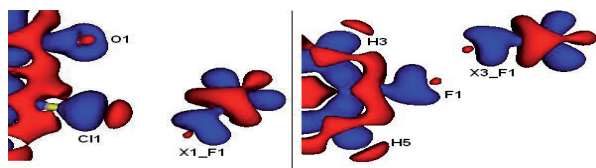


nature of F...F interactions in 4-fluorobenzamide show indication of a minor decrease in repulsion (type I interaction), though the extent of polarization on the fluorine atom is limited [4].



[1] (a) T.T.T. Bui, S. Dahaoui, C. Lecomte, G.R. Desiraju, E. Espinosa, *Angew. Chem. Int. Ed.* **2009**, *48*, 3838-3841. (b) V.R. Hathwar, T.N.G. Row, *J. Phys. Chem. A* **2010**, *114*, 13434-13441. [2] (a) K. Reichenbacher, H.I. Süss, J. Hulliger, *Chem. Soc. Rev.* **2005**, *34*, 22-30. (b) D. Chopra, T.N.G. Row, *CrystEngComm* **2011**, *13*, 2175-2186. [3] R.F.W. Bader, *Atoms in Molecules-A Quantum Theory*, Oxford: Clarendon, **1990**. [4] V.R. Hathwar, T.N.G. Row, *Cryst. Growth Des.* **2011**, DOI: 10.1021/cg1015862.

**Keywords:** charge density, halogen interaction, organic fluorine

### MS34.P12

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#### Experimental and theoretical charge density studies and topological analysis of 2-methyl-4-nitro-1-phenyl-1H-imidazole-5-carbonitrile: case of antiparallel cyano-cyano interaction

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High resolution diffraction data were collected on laboratories diffractometers for 2-methyl-4-nitro-1-phenyl-1H-imidazole-5-carbonitrile, as part of our studies on intermolecular interactions in 4-nitro-1H-imidazole derivatives series.

The standard data processing within the Independent Atom Model (IAM) approximation, where the atoms are treated as 'spherical balls' in their ground state ie free, neutral and non interacting with neighbors does not take into account the density moved to the bonding regions and the charge transfer related to intermolecular interactions.

More realistic picture of the charge density distribution in crystals, which allows for inter- and intramolecular analysis can be derived from the Hansen-Coppens formalism [1] and Atoms-In-Molecule approach topological analysis [2]. The multipole model implemented in MoPro program suite [3] allows electrostatic and topological calculations either for small molecules or biological molecules at subatomic resolution.

The communication presents the experimental charge density analysis of the title compound, supported with the theoretical calculations. The standard resolution crystal structure was published some time ago [4], however no detailed analysis of the substituent's effect on the imidazole ring was performed. 2-methyl-4-nitro-1-phenyl-1H-imidazole-5-carbonitrile consists of two strongly electronegative and withdrawing groups, and the main interactions in its crystal structure are four weak hydrogen bonds (C-H...N; C-H...O) and interesting antiparallel cyano-cyano interactions. This dipole dipole interaction is found to be the most common type of C≡N...C≡N contacts (which in fact are similar to C=O...C=O interaction), and will be analyzed in details by means of experimental data and theoretical calculations.

[1] P. Coppens, T.S. Koritsanszky, *Chem. Rev.* **2001**, *101*, 1583-1627. [2] R.F.W. Bader **1990**. *Atoms in Molecules: A Quantum Theory*. Oxford University Press. [3] C. Jelsch, B. Guillot, A. Lagoutte, C. Lecomte *J. Applied Crystallography* **2005**, *38*, 38-54. [4] M. Kubicki *Acta Cryst.* **2004**. *C60*, o255-o257.

**Keywords:** 4-nitro-1H-imidazole derivatives, multipole, refinement, antiparallel cyano interactions

### MS34.P13

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#### Observation of a conserved "selenium bond synthon" involving Se...O interaction

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Organoselenium compounds have gained extreme importance in recent years due to their diverse biological, medicinal and catalytic activities which essentially stem from the presence of a seemingly divalent selenium atom. An in depth understanding of the non bonded Se...X interactions (X=heteroatom like N, O etc) becomes essential as they play crucial role in enzyme-mimetic reactions and protein engineering [1,2]. Three polymorphs of the organoselenium antioxidant drug *m-Ebselenol*, 2-(3-hydroxyphenyl)-1,2-benzisoxazolo-3(2H)-one [3] have been generated by tuning the solvent polarity and their crystal structures have been analyzed. Polymorph I, which crystallizes in a noncentrosymmetric space group *Pna2<sub>1</sub>* has O-H...O hydrogen bond chains propagating in a catemeric fashion whereas polymorphs II and III which crystallize in centrosymmetric space groups, *Pbcn* and *P2<sub>1</sub>/c* respectively form centrosymmetric O-H...O hydrogen bond dimers. In all polymorphic forms as well as in the original drug *Ebselen* [4] and its derivatives we have identified a new conserved "selenium bond synthon". This is formed by strong Se...O and a surrogate C-H...O interaction which is conserved in all the structures as shown in Figure 1. The intricate nature of the Se...O interactions analyzed by both experimental and theoretical charge density analysis will be presented[5].

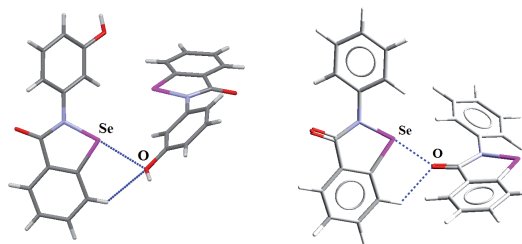


Figure1. Conserved "selenium bond" interactions in m-ebselenol and ebselen

[1] A.J. Mukherjee, S.S. Zade, H.B. Singh, R.B. Sunoj, *Chemical Reviews* **2010**, *110*, 4357-4416.[2] B.K. Sarma, G. Mugesh, *ChemPhysChem* **2009**, *10*, 3013-3020.[3] K.P. Bhabak, G. Mugesh, *Chemistry: A European Journal* **2007**, *13*, 4594-4601.[4] P.L. Dupont, O.Dideberg, *Acta Cryst.* **1990**, *C46*, 484-486. [5] R.F.W. Bader, *Atoms in Molecules-A Quantum Theory*, Oxford: Clarendon, **1990**.

**Keywords:** Se...O interaction, Selenium bond synthon, crystal engineering

### MS34.P14

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#### Non-Covalent Interactions descriptor using experimental electron densities

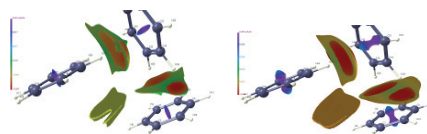
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Non covalent interactions (NCI) play a crucial role in biology (protein-drug recognition) and in the design of new materials (self-assembly). A novel electron density (ED) based descriptor of non covalent interaction was proposed in 2010 by Johnson *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  $\pi$ - $\pi$  stackings or C-H... $\pi$  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  $\pi$ - $\pi$  stacking and C-H... $\pi$  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

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**Structural and charge density studies of organic-inorganic [ArBF<sub>3</sub>]<sup>-</sup>X<sup>+</sup> compounds**

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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 [ArBF<sub>3</sub>]<sup>-</sup>X<sup>+</sup> type (Ar = aryl, X<sup>+</sup> = 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, PhBF<sub>3</sub>K, 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.

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**Keywords:** hybrid compounds, charge density, structural analysis

## MS34.P16

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**Electronic structure and bonding interactions in FeS<sub>2</sub> and FeP<sub>2</sub>**

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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 FeSb<sub>2</sub> 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 FeS<sub>2</sub> and FeP<sub>2</sub>, 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 FeS<sub>2</sub> and FeP<sub>2</sub>.