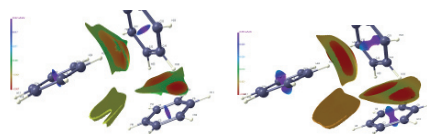


Università degli Studi, Milano (Italy). ^bCNR-ISTM, Istituto di Scienze e Tecnologie Molecolari, Milano (Italy). ^cCMC, Center for Materials Crystallography, Aarhus (Denmark). ^dDept. of Chemistry, Duke University, Durham NC (USA). E-mail: gabriele.saleh@unimi.it

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

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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.

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Keywords: hybrid compounds, charge density, structural analysis

MS34.P16

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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.

To verify and support these findings, the Quantum Theory of Atoms In Molecules (QTAIM), [8] has been applied to two observables, the electron density, ρ , and its Laplacian, $\nabla^2\rho$. This allowed us to analyze the charge transfer, the nature of bonding interactions and the valence anisotropy of iron directly from the topology of these observables. Independently from the adopted partitioning scheme, a mainly covalent rather than a fully ionic description emerges for the bonding interactions in the two systems. In accordance with the atomic electronegativities, a higher degree of covalency is found for the Fe-P interaction.

Besides supporting and confirming the orbital-based view, the topological analysis and the examination of the Valence Shell Charge Concentration (VSCC) regions provides a rigorous link among such a view, the VSEPR theory and the structural modifications (namely the compression along the *c* crystallographic axis) that occurs when substituting S with P in the marcasite structure.

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Keywords: quantum theory of atoms in molecules, marcasite

MS34.P17

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Structural analysis and DFT calculations of (*Z*)-4-methyl-N-(2-((2-oxonaphthalen-1(2*H*)-ylidene)-methylamino)ethyl)benzenesulfonamide

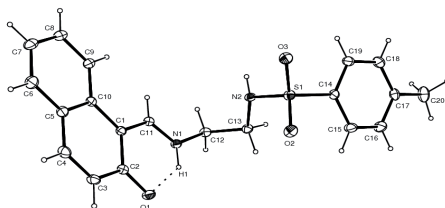
Ahmet Erdönmez,^a Gökhan Alpaslan,^a Mustafa Macit,^b Orhan Büyükgüngör,^a ^aOndokuz Mayıs Univ., Department of Physics, Samsun-Turkey. ^bOndokuz Mayıs Univ., Department of Chemistry, Samsun-Turkey. E-mail: erdonmez@omu.edu.tr

The molecular and crystal structure of the title compound, C₂₀H₂₀N₂O₃S, has been determined by X-ray single crystal diffraction technique. The compound crystallizes in the monoclinic, space group *Pc* with unit cell dimensions

$a=13.2967(7)$ Å, $b=6.9654(5)$ Å, $c=9.9714(6)$ Å, $\beta=99.907(4)^\circ$, $V=909.75(10)$ Å³, $Z=2$, $R_1=0.042$ and $wR_2=0.109$. The molecule adopts a keto-amine form, stabilized by an intramolecular N-H...O type hydrogen bond.

Molecular geometry of the title compound in the ground state have been calculated using the density functional method (DFT) with 6-31G(d,p) basis set and compared with the experimental data. The calculated results show that the optimized geometry can well reproduce the crystal structure.

In addition, DFT calculations of the compound, total energy, molecular electrostatic potential (MEP) and non-linear optical (NLO) properties were performed at B3LYP/6-31G(d,p) level of theory.



Keywords: X-ray, tautomerism, NLO

MS34.P18

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Electronic properties of noncovalent interactions in [Co(fam)en]Cl complex

Sladjana B. Novaković,^a Goran A. Bogdanović,^a Bojana M. Francuski,^a Djenana Miodragović,^b Bernard Fraisse,^c ^a"VINČA" Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, P.O. Box 522, 11001 Belgrade, (Serbia). ^bFaculty of Chemistry, University of Belgrade, P.O. Box 158, Studentski trg 16, 11000, Belgrade, (Serbia). ^cLaboratoire SPMS, UMR CNRS 8580, Ecole Centrale Paris, Grande Voie des Vignes, 92295 Châtenay-Malabry, (France). E-mail: snovak@vin.bg.ac.rs

It has been found that the cobalt(III) complex with the well-known antiulcer drug famotidine (fam) and ethylenediamine (en) shows higher antimicrobial activity and higher selectivity in comparison to the metal free drug [1]. The electronic structure of this complex was described by Hansen-Coppens multipole model [2] using the data collected in a single-crystal X-ray diffraction experiment at 100 K. As the complex is abundant in atoms, which can be involved in hydrogen bond formation either as hydrogen acceptors or hydrogen donors, the crystal structure is stabilized by numerous interactions of this type. In addition, the extended π -systems give rise to variety of interactions such as C-H... π , N-H... π and π ... π . Our present study is focused on a qualitative and quantitative characterization of the hydrogen bonds and other noncovalent interactions from the aspects of the experimental electron density distribution, electrostatic complementarities [3], and topological analysis (Bader's quantum theory of atoms in molecules, QTAIM) [4]. Energy densities at bond critical points are calculated according to Abramov and virial theorem [5]. The geometrical, topological and energetic properties of 32 noncovalent interactions are analyzed and related with the effects they produce on the deformation density of the interacting atoms. A particular attention has been paid on the sensitivity of the valence electron densities of the various hydrogen bonding acceptors, O, N, S, Cl, to their crystal environment.

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Keywords: cobalt (III) complex, charge density, noncovalent interactions

MS34.P19

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The original crystal structures of hybrid materials and the influences of hydrogen bonds

Fatima Allouche et Tahar Benlecheb *Laboratoire des Structure, Propriétés et Interactions Inter Atomique (LASPIA), Centre Universitaire de Khenchela, 40000 Khenchela, (Algerie)*. E-mail: allouche_f@yahoo.fr

The crystal organic-inorganic hybrid materials have been extensively investigated due to their interest in the filed of new materials, and the number of reported structures is rapidly growing owing to their applications in medicine, material science and their