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P.14.07.4

Interactions in Selected Dicarboxylic Acids Derived from Electron Charge Density

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High-resolution X-ray diffraction data were collected for tartaric acid, malic acid and its adduct with urea at 80 K to obtain accurate crystal data and experimental electron density. The measurements were performed on Nonius KappaCCD difractometer equipped with Oxford Cryosystems 700 Series Cryostream Cooler. The quality of tartaric acid data was compared with that of the data obtained using a point detector at 105 K.

Data was interpreted using the multipole formalism [1] to derive the electron density and related properties such as the electrostatic potential and atomic moments. The electron density and its Laplacian extracted from the data were analyzed in terms of the topological properties of covalent bonds and non-bonded interactions [2].

Charge density and topological properties for the studied crystal structures were carried out to explore the character and role of both inter- and intra-molecular hydrogen bonds.

The interesting features related to the differences of electron density distribution were found for the same functional groups (hydroxyl and/or carboxyl). The differences caused by molecular interactions have influence on the molecular symmetry. The results are compared to those obtained for analogous molecules.

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P.14.07.5

Experimental Electron Density Distribution of Bis(thiosemicarbazide)-Zinc(II) Dinitrate

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Over three hundred transition metal complexes with thiosemicarbazide-based (TSC) ligand have been characterized by classical X-ray diffraction and seem to play a role in supramolecular chemistry [1]. In addition, a great number of TSC derivates present a very wide of potent pharmacological application [2, 3], while two of them (3-AP) and (5-HP) are used in clinical phase I or II against ribonucleotide reductase [4]. Understanding the interactions between the organic part and the divalent cation is essential in that case, since the mechanism involves a chelate compound with a divalent cation. Here, we present the electronic and electrostatic properties of the most simple TSC ligand coordinated with zinc(II). Cation behavior will be discussed in comparison with a zinc aspirinate compound [5].

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P.14.07.6

Electron Density, the Driving Tool towards Dynamics and Reactivity of Systems ?

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The fast development of photo-induced and time resolved diffraction leads to fundamental questioning about the proper modelisation of systems out of equilibrium.

Based on the role of Hellmann-Feynman force and its impact onto molecular dynamics, we have modelled the evolution of the charge density of simple molecules along a reaction path. Moreover, we have addressed the change of charge density in a molecular chain undergoing strong distortions, such as those initiating na soft mode transition.

The planned developments are strongly connected with the Cluster Partitioning Model recently developed in our group [1,2] which allows for a description of one particle density matrix of complex systems through a superposition of local contributions taking into account realistic environmental effects.

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P.14.07.7

Estimating ADP's of Hydrogen Nuclei for Charge Density Analysis

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Charge density analysis of X-ray diffraction data requires accurate treatment of the motion of all nuclei in order to deconvolute nuclear motion from the electron distribution. Presently, nearly 80% of charge density studies on molecular crystals assume isotropic motion of hydrogen nuclei, in large part due to the difficulty of performing accurate neutron diffraction studies on all systems of interest. However, failure to model the motion correctly not only alters the topology of the electron density close to the nuclei where the thermal motion has been simplified, but also in the vicinity of neighbouring nuclei [1].

Methods for approximating hydrogen atom ADP's based on a combination of rigid-body analysis and allowances for internal modes have been shown to be quite successful [1,2]. We have recently developed a new method for estimating hydrogen atom ADP's from first principles, using two layer "ONIOM" calculations [3] which mimic the effects of the crystal field and yield internal (high frequency) and external (low frequency) contributions to the nuclear motion. Results obtained for small molecules are consistent with neutron experiments at a variety of temperatures.

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P.14.07.8

Bonding in 5-Membered Cyclic Alkynes: Charge Density in 1-Zirconacyclopent-3-yne

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Small cyclic alkynes are, in general, unstable because of ring strain. Recently, 1-zirconacyclopent-3-yne complexes, *viz* 5-membered cyclic alkynes, were synthesized.[1] The bonding nature

of the complexes has been investigated by theoretical calculations[2], but is still in controversy. Here we show the bonding nature of the 1-zirconacyclopent-3-yne complex by means of experimental charge density analysis.

Diffraction data were collected using synchrotron radiations at KEK PF-AR NW2 beam line by Rigaku Mercury CCD diffractometer up to $\sin\theta / \lambda = 1.0$ Å^{-1}. Multipole expansion method was applied for modeling of atoms. Final R was 0.027 for reflections with $I > 1.5\sigma(I)$.

The 1-zirconacyclopent-3-yne moiety is planar. Valence shell charge concentrating region on each of the C atoms on the α positions extends toward the charge depressing regions on the Zr atom. Bond critical points and bond paths were found on the Zr-C(α) bonds. The bond paths curve inwardly near the C(α) atoms. These suggest that both of the η^2-σ, σ and η^4-π, π structures contribute to the bonding. No bond paths, in contrast, were found on the Zr-C(β) bonds. In conclusion, bonding of 1-zirconacyclopent-3-yne is in resonance between η^2-σ, σ and η^4-π, π structures.

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Keywords: charge density, chemical bonding, zirconium compounds

P.14.07.9
Different Approaches to Absorption Corrections for Charge Density Analyses
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In order to increase the accuracy of high-angle diffraction data for multipole refinement with XD, crystals with diameters of up to 0.5 mm were measured. Bigger crystals give intensity data with higher signal-to-noise ratios, especially for high-angle reflections, but large crystals also make accurate absorption and extinction corrections a necessity, especially for crystals of *3d*-coordination compounds. Extinction corrections require values of TBAR, the absorption-weighted mean sum of incident and diffracted beam path lengths through the crystal, and anisotropic extinction corrections require also the direction cosines of the incident and diffracted beams [1].

Several absorption correction methods were compared based on crystallographic R-values, maximum and minimum values of residual densities, and the *d*-orbital populations from the experimental electron density studies of several *3d*-coordination compounds [2-3]. Valuable additional information was obtained from quantum chemical calculations and subsequent topological analysis of both experimental and theoretical electron densities [4].

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Keywords: charge density, copper compounds, properties

P.14.07.10
Chemical Bonding Based on Charge Density Calculations for Solids
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We calculate the electronic structure of solids within density functional theory (DFT) and use the WIEN2k code [1] that is based on the full-potential augmented plane wave (APW) method. The key quantity is the electron density, which can be decomposed into contributions according to core and valence regions or even a small energy region (an energy sub band) that gives more insight into the chemical bonding than the total density. The partial densities of states (DOS) partitioned into atomic ℓ- and m-like contributions provide further details in chemical bonding.

Recently the experimental determination of the electronic charge density has been greatly improved, e.g. due to synchrotron radiation which allows to obtain structure factors with high accuracy [2]. Although the comparison between theory and experiment is made difficult by T=0 calculations vs. finite temperature experiments with absorption and extinction, fine details can be extracted that often agree well and lead to a better understanding of chemical bonding.

Such comparisons will be shown for a selected class of materials from oxides, SiO_2, silicates to highly correlated systems as the high-temperature superconductor $YBa_2Cu_3O_7$ [2] or the pyrochlore compound $Y_2Nb_2O_7$ [3]. A special feature appears in $BaCoO_3$ for which orbital is found to occur along the Co chains.

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Keywords: DFT, charge density distribution, chemical bonding

P.14.07.11
Electron-density Properties of the Functionally-substituted Hydropyrimidines
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This work reports the results of the study of electron density and electronic energy density in the new functionally substituted hydropyrimidines. We performed the accurate X-ray diffraction measurements at 110 K and reconstructed the electron density and electronic energy density for three compounds of this series. *Ab initio* calculations were performed for different molecular conformations as well. In this work, we shall focus on the study of ethyl 4,6-dimethyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate. The topological analysis of the experimental and theoretical electron densities was fulfilled for all the conformations and the bonding network was quantitative described in terms of the electron density and energy density topological features. In addition, the analysis of critical points of molecular orbitals (i.e. HOMO, LUMO) has been performed. Similar considerations were done for the other functionally substituted hydropyrimidines. New electron-localization/delocalization indices like the exchange energy density and correlation energy density and its Laplacians are introduced. The electron-density-based similarity of the pharmacophoric parts of the conformers of the hydropyrimidines studied has been estimated using new original algorithm.
Keywords: electron density, accurate measurements, ab initio calculations

P.14.07.12
Electron Density Study of 2,5-Dimethyl-3,4-trimethylene-6a-thiathiophthene Using XRD, XAS and DFT Calculations
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Thiathiophthene, a planar molecule with two fused heterocyclic five-membered rings and essentially a linear S-S-S bond, is a molecule of great interest due to the unusual bonding characters and the possible aromatic properties of the two five-memberd rings. In order to understand the remarkable bonding properties, the electron density distribution of one of the derivatives, i.e. 2,5-dimethyl-3,4-trimethylene-6a-thiathiophthene ($C_{10}H_{12}S_3$), was investigated both by