Chemistry Unit, Indian Institute of Science, Bangalore-560012, India. E-mail: munshi@sscu.iisc.ernet.in

Detailed investigation of the charge density distribution in concomitant polymorphs of 3-acetylcoumarin [1] in terms of experimental and theoretical densities show significant differences in the intermolecular features when analyzed based on the topological properties via the quantum theory of atoms in molecules [2]. The two forms, triclinic (form **A**) and monoclinic (form **B**) crystallize in centrosymmetric space group, form **A** in $P\bar{1}$ ($Z'=2$) and form **B** in $P2_1/n$ ($Z'=1$) and pack in the crystal lattice via weak C-H…O and C-H…π interactions. The electron density maps in two forms demonstrate the differences in the nature of the charge density distribution in general. The net charges derived based on the population analysis via multipole refinement and also the charges evaluated via integration over the atomic basins and the molecular dipole moments show significant differences between the two forms. The lattice energies evaluated at the HF and DFT (B3LYP) methods with 6-31G** basis set for the two forms clearly suggest that form **A** is thermodynamically stable compared to form **B**. Mapping of electrostatic potential over the molecular surface showing dominant variations in the electronegative region bring out the differences between the two forms.

[1] Munshi P., Venugopala K. N., Jayashree B. S., Guru Row T. N., *Cryst. Growth Des.*, 2004, **4(6)**, 1105. [2] BaderR. F. W., *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, UK, 1990.
**Keywords: charge density distribution, polymorphs, lattice energy calculations**

P.14.06.2
Experimental and Theoretical Charge Densities of Fe(CO)$_3$(η^4-C$_4$H$_6$)
Cameron Evans, Louis J. Farrugia. *Chemistry Department, University of Glasgow,Glasgow, G12 8QQ, United Kingdom.* E-mail: cevans@chem.gla.ac.uk

Topological analysis of the experimental charge density of Fe(CO)$_3$(η^4-C$_4$H$_6$) (1) based on high resolution X-ray diffraction data collected at 100K is presented. The nature of the metal-ligand interaction is examined using the Atoms in Molecules (AIM) approach. The interaction between the iron atom and the carbon atoms of the trimethylenemethane ligand has been explored in depth. Theoretical DFT studies on the molecule calculated at the B3LYP/6-311++G(2p,2d) level show close agreement with the experimental results.
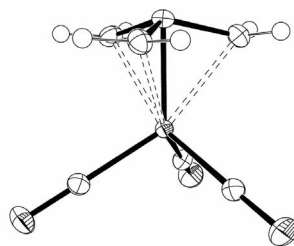
ORTEP diagram of Fe(CO)$_3$(η^4-C$_4$H$_6$)
Keywords: experimental charge density, DFT, carbonyl

P.14.06.3
Multipole-Refined Charge Density Study of Diopside
Riccardo Bianchi[a], Alessandra Forni[a], Roberta Oberti[b], [a]*ISTM-CNR, Milan, Italy.* [b]*IGG-CNR, Pavia, Italy.* E-mail: r.bianchi@istm.cnr.it

The electron density distribution of diopside at ambient conditions has been determined by X-ray diffraction and refined through the multipole model of electron density, following the formalism of Stewart [1].

The final multipole refinement includes two extinction parameters, according to the Sabine model, and two kappa expansion/contraction parameters (one for O and the other for Si, Ca and Mg valence monopoles). The expansions over the spherical harmonics were truncated at the octopole level.

Topological analyses of the electron density and its Laplacian distributions [2] reveal that the bonding character of the four Si–O bonds is intermediate between ionic and covalent, as previously found for stishovite and coesite. As expected, the Mg–O and Ca–O bonds are definitely ionic. Determination of the atomic basins results in charges of +3.2(2) *e* for Si and −1.6(1) *e*, on average, for the oxygen atoms. The charges calculated for Mg and Ca are very close to the formal values. Our atomic charges are then more ionic than the corresponding ones determined by Sasaki et al. [3].

The program VALTOPO [4] was used for refinements and topological analysis of the experimental density.

[1] Stewart R. F., *Acta Crystallogr. Sect. A*, 1976, **32**, 565. [2] Bader R. F. W., *Atoms in Molecules - A Quantum Theory*, Oxford University Press, Oxford, 1994. [3] Sasaki S., Fujino K., Takéuchi Y., Sadanaga R., *Acta Cryst. Sect. A*, 1980, **36**, 904. [4] Bianchi R., Forni A., *J. Appl. Crystallogr.*, 2005, **38**, 232.
Keywords: charge density distribution, topological properties of charge distribution, silicates

P.14.06.4
Topological Analysis of Bio-molecules
Chi-Rung Lee[a], Ching-Yi Lee[a], Andrew H.-J. Wang[b], [a]*Department of Chemical Engineering, Minghsin University of Science and Technology, Taiwan.* [b]*Institute of Biological Chemistry, Academia Sinica, Taipei, Taiwan.* E-mail: crlee@must.edu.tw

Intra and intermolecular interactions of bio-molecules are investigated in terms of topological analyses. Ultra high resolution data helped us to determine the more accurate positions of atoms in protein and nucleic acid. We could find the hydrogen atoms in the difference Fourier maps. We also introduce the bio-molecule databank to the macromolecule and describe the more exact electron density of the structures. The electron density could be transferred to macromolecules as a multipole model which may be used to derive some physical properties including bond orders, electrostatic potential, hydrogen bond energies, bond paths, and atomic domains, atomic or fragment charges and their possible delocalization. When we build an adequate databank of the electron densities, it will useful to refine more accurately the lower resolution crystal structures. The electron densities are obtained both from X-ray diffraction data at low temperature and from a periodic density functional theory calculation. The features of the deformation densities, Laplacian distributions, bond pathes, and atomic domains are shown to describe the variety bonding. All the interactions are verified by the location of the bond critical point and its associated topological properties.
Keywords: charge density studies, multipole model, topological properties of charge density

P.14.06.5
Charge Density and Topological Properties of Chosen Aromatic Nitramines
Jacek Zaleski[a], B. Zarychta[a], Z. Daszkiewicz[a], C. Jelsch[b], C. Lecomte[b], [a]*Department of Chemistry, University of Opole, ul. Oleska 48, 45-052 Opole, Poland.* [b]*Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques,CNRS UMR 7036, Université H. Poincaré, BP 239, 54506 Vandœuvre-les-Nancy, Cedex, France.* E-mail: zaleski@uni.opole.pl

Aromatic nitramines rearranges under the influence of elevated temperature or diluted mineral acids. The migration is entirely intramolecular, *i.e.* the *N*-nitro group shifts three or five atoms from its original position, still remaining bound to the aromatic residue [1]. The mechanism of the nitramine rearrangement remains still unclear. Analysis of charge density distribution in aromatic nitramines could bring the grounds for electron reasons of their interesting properties *viz.* structure–reactivity relationships and the role of an acidic catalyst. Charge density of chosen aromatic nitramines have been studied to understand those special properties. Conjugation between π-electron systems should divert the charge distribution within the *NNO$_2$* group and give rise to some observable changes in its geometry and