

[1] M.A. Spackman, P. Munshi, D. Jayatilaka, *Chem. Phys. Lett.*, **2007**, *443*, 87-91.

**Keywords:** host-guest systems, electrostatic potential, charge density analysis

## MS41.P06

*Acta Cryst.* (2011) **A67**, C509

### Polymorphism studied with invariom-derived cluster dipole moments

Birger Dittrich, Jens Lübben, Kevin Pröpper, *Institut für Anorganische Chemie, Tammannstr. 4, Georg-August-Universität Göttingen, 37077 Göttingen, (Germany)*. E-mail: bdittri@gwdg.de

Polymorphism, the phenomenon that a compound occurs in more than one form in the solid state, is commonplace, but not well understood. While the research area of crystal structure prediction is most successful in predicting polymorphism for relatively small and rigid structures at high computational cost [1], to date no simple way of predicting polymorphism exists. Energetic considerations of packing energies as for example those obtained from the PIXEL approach [2] share computational requirements to some degree.

Our approach towards attempting an understanding of polymorphism is to exploit the benefits of invariom refinement [3]. First of all accurate molecular structures as obtained after invariom refinement [4] make subsequent energetic considerations from experimental coordinates generally more reliable. Furthermore, going beyond molecular properties in the gas-phase is required for understanding solid-state phenomena. We therefore look at dipole moments and electrostatics of clusters of molecules of a number of polymorphic structures. Cluster sizes are chosen as to grant successful optimization of a central molecule within a two-layer ONIOM approach [5]. We assume that such clusters are a suitable model for a molecular packing environment. Quantum chemical results for such clusters are compared to results from a superposition of isolated molecules, where the invariom approach is used to generate the non-spherical density of the isolated molecule. We look at trends that emerge from this comparison.

Polymorphic molecules investigated include glycine, dihydro-carbamazepine, the new case of hydroxylysine hydrochloride, and a number of other published cases, where intensities for invariom refinement were available from the IUCr webpage.

[1] G.M. Day, T.G. Cooper, A.J. Cruz-Cabeza, K.E. Hejczyk, H. L. Ammon, S.X.M. Boerrigter, J. S. Tan, R.G. Della Valle, E. Venuti, J. Jose, S. R. Gadre, G.R. Desiraju, T.S. Thakur, B.P. van Eijck, J.C. Facelli, V.E. Bazterra, M.B. Ferraro, D.W.M. Hofmann, M.A. Neumann, F.J.J. Leusen, J. Kendrick, S.L. Price, A.J. Misquitta, P.G. Karamertzanis, G.W.A. Welch, H.A. Scheraga, Y.A. Arnautova, M.U. Schmidt, J. van de Streek, A.K. Wolf, B. Schweizer, *Acta Cryst. B*, **2009**, *65*, 107-125. [2] A. Gavezzotti, *CrystEngComm* **2003**, *5*, 429-438. [3] B. Dittrich, T. Koritsanszky, P. Luger, *Angew. Chem. Int. ed. Engl.* **2004**, *43*, 2718-2721. [4] B. Dittrich, C.B. Hübschle, M. Messerschmidt, R. Kalinowski, D. Girt, P. Luger, *Acta Cryst. A*, **2005**, *61*, 314-320. [5] M. Svensson, S. Humbel, R.D.J. Froese, T. Matsubara, S. Sieber, K. Morokuma, *J. Phys. Chem.* **1996**, *100*, 19357-19363.

**Keywords:** polymorphism, charge density, electrostatics

## MS41.P07

*Acta Cryst.* (2011) **A67**, C509

### Charge density analysis of the [RhCp\*(N-Me-L-Pro)Cl] rhodium complex

Pilar García-Orduña, M. Pilar Lamata, Daniel Carmona, Fernando J. Lahoz, *Inorganic Chemistry Department, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza (Spain)*. E-mail: mpgaor@unizar.es

Organometallic chiral-at-metal rhodium or iridium complexes are commonly used in homogeneous catalysis as they lower the energy barrier and improve the selectivity in cycloaddition reactions [1]. Due to the presence of a second or third-row transition metal (with a large number of core electrons) the overwhelming majority of their structural studies have been carried on "in a classical way", using the independent atom model (IAM). However, a more accurate description of the metal bonding, as well as the most common ligands, becomes necessary as it may help in the understanding of their catalytic activity.

Here we present the analysis of the charge density of the rhodium complex [RhCp\*(N-Me-L-Pro)Cl] obtained from high-resolution X-ray diffraction. Special features of the multipolar model refinement, as the choice of the electronic configuration and the radial function of the metal; the anharmonic nuclear motion, and the anisotropic thermal refinement of hydrogen atoms will be discussed. The electronic bonding distribution in the proline ligand will be compared to those in other proline derivatives. The deformation density has been interpreted according to the Quantum Theory of Atoms in Molecules [2]. Topological analysis allows for a description of the nature of the bonding involving the metal atom, in terms of charge density, laplacian and energy density at bond critical points.

[1] D. Carmona, M.P. Lamata, F. Viguri, R. Rodríguez, F.J. Lahoz, M.J. Fabra, L.A. Oro, *Tetrahedron* **2009**, *20*, 1197-1205. [2] R.F.W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**.

**Keywords:** Organometallic complexes, charge density, topology.

## MS41.P08

*Acta Cryst.* (2011) **A67**, C509-C510

### A qualitative and quantitative analysis of dynamic charge densities

Siriyara Jagannatha Prathapa, Swastik Mondal, Sander van Smaalen, *Laboratory of Crystallography, University of Bayreuth, Bayreuth (Germany)*. E-mail: prathap@uni-bayreuth.de

The dynamic electron densities of the amino acids  $\alpha$ -Glycine and D, L-serine have been determined to understand the nature of the chemical bonds. Multi-temperature data sets of serine have been used to analyze the effect of thermal vibrations on the charge density distribution. Diffraction data of  $\alpha$ -Glycine have been kindly supplied by Destro et al [1] and of D L-Serine by Dittrich et al [2]. Multipole refinements have been performed for both compounds, employing the computer program XD [3]. The dynamic densities have been obtained by an inverse fast Fourier transform (FFT) of the structure factors calculated from these models, employing the computer program PRIOR. Absence of series termination effects has been established for grid sizes smaller than 0.05 Å. The resulting densities are free of spurious critical points, and they exhibit maxima and bond critical points (BCPs) at expected positions. Topological analyses of these dynamic charge densities have been carried out according to Bader's quantum theory of atoms in molecules (QTAIM) [4], using the computer program EDMA [5]. The density and Laplacian at the bond critical point are obtained. The effects of thermal vibrations are clearly visible, especially in the values of the Laplacian at BCPs.

[1] R. Destro, P. Roversi, M. Barzaghi, R. E. Marsh *the Journal of Physical Chemistry A* **2000**, *104*, 1047-1054. [2] B. Dittrich, C.B. Hübschle, M. Messerschmidt, R. Kalinowski, D. Girt, P. Luger *Acta Crystallographica*

section A **2005**, 61, 314-320. [3] A. Volkov, P. Macchi, L.J. Farrugia, C. Gatti, P.R. Mallinson, T. Richter, T. Koritsanszky *XD* **2006**. [4] R.F.W. Bader, *Atoms in Molecules Oxford University Press* **1994**. [5] L. Palatinus, S.J. Prathapa, S. van Smaalen, *to be published*.

**Keywords:** X-ray\_diffraction, serine, dynamic\_charge\_density

## MS41.P09

*Acta Cryst.* (2011) **A67**, C510

### The Transferability of Atomic Multipoles in Amino Acids and Peptides

Magdalena Woińska, Paulina M. Dominiak, *Chemistry Department, University of Warsaw, (Poland)*. E-mail: mwoinska@chem.uw.edu.pl

Popular force fields usually employ point charges. Supplementing atomic charges with higher electrostatic multipole moments leads to more accurate charge distribution models. New generation force fields based on multipole models require high level of transferability of atomic multipoles. The aim of this work was to analyze the level of transferability achievable with the use of different methods of molecular density partitioning.

Molecular densities (MDs) were calculated for selected natural amino acids as well as di- and tripeptides in geometries as observed in X-ray diffraction experiment. The MDs were obtained through Fourier space fitting of pseudoatom model to the electron densities resulting from *ab initio* DFT calculations at B3LYP/6-31G\*\* level. Such procedure was selected in order to be compatible with the idea of building a pseudoatom database [1-3] pursued in the charge density crystallography. Atomic multipole moments expressed in local coordinate system were calculated on the basis of three density partitions: directly from pseudoatoms, from atomic densities computed via stockholder partitioning and from atomic basins derived via topological analysis. Standard deviations from averaging over multipole moment components of atoms that are considered equal in their chemical environments (atoms representing the same atom type) were chosen as a measure of transferability.

The advantage of stockholder partition as yielding the best transferability within considered atom types was observed. The results were compared to the calculations of atomic multipoles directly from molecular wave functions (in atomic basins partition).

[1] B. Zarychta, V. Pichon-Pesme, B. Guillot, C. Lecomte, Ch. Jelsch, *Acta Cryst.* **2007**, *A63*, 108. [2] P.M. Dominiak, A. Volkov, X. Li, M. Messerschmidt, P. Coppens, *J. Chem. Theory Comput.* **2007**, *3*, 232. [3] B. Dittrich, C.B. Hübschle, P. Luger, M.A. Spackman, *Acta Cryst.* **2006**, *D62*, 1325.

**Keywords:** multipole moments, amino acids, transferability

## MS41.P10

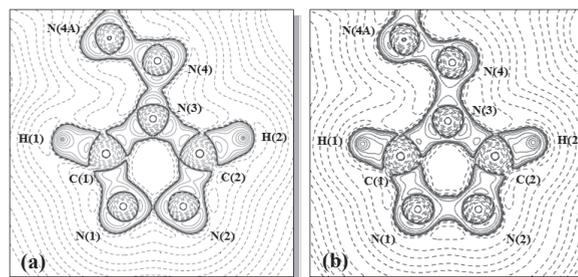
*Acta Cryst.* (2011) **A67**, C510

### Bond Characterization of trans-4,4'-azo-1,2,4-triazole: A Combined Experimental and Theoretical Charge Density Study

Wen-Chun Chung,<sup>a</sup> Lai-Chin Wu,<sup>a</sup> Yu Wang,<sup>a</sup> Gene-Hsiang Lee,<sup>c</sup> Chih-Chieh Wang,<sup>b</sup> <sup>a</sup>*Department of Chemistry, National Taiwan University.* <sup>b</sup>*Department of Chemistry, Soochow University.* <sup>c</sup>*Instrumentation Center, National Taiwan University, Taipei, (Taiwan)*. E-mail: r99223144@ntu.edu.tw; wangyu@ntu.edu.tw

The experimental charge density distribution of a planar centrosymmetric molecule, trans-4,4'-azo-1,2,4-triazole, has been investigated in terms of a pseudo-atomic multipolar expansion

(Hansen-Coppens formalism) using high resolution single-crystal X-ray diffraction data at 100K. A parallel computation based on DFT calculation at the B3LYP level using 6-31G(d,p) basis set was performed on the molecule in gas phase. The electron density will be presented in terms of deformation density as well as the Laplacian distribution. Bond characterizations are expressed in terms of topological properties at the bond critical points; typical covalent character on N–N, N–C bonds are observed. The  $\pi$  bonding-delocalization of the molecule will be further illustrated by the Fermi-hole distribution. A  $\pi$ – $\pi$  interaction with the inter-planar distance of 3.2 Å is allocated through the BCP and the associated bond paths. The agreement between experiment and theory is good on all intra-molecular interactions; the atomic charges, molecular electrostatic potentials, and natural bond orbital analyses will also be presented.



**Figure.** Laplacian map,  $\nabla^2\rho(r)$  in the plane of N1-N2-N4 from (a) the experimental (b) the theoretical charge density.

**Keywords:** charge density, multipole model,  $\pi$ – $\pi$  interaction

## MS41.P11

*Acta Cryst.* (2011) **A67**, C510-C511

### New version of UBDB databank and LSDB program, verification and applications

Katarzyna Natalia Jarzemska, Paulina Maria Dominiak, *Department of Chemistry, University of Warsaw, Warsaw, (Poland)*. E-mail: katarzyna.jarzemska@gmail.com

The theoretical databank of aspherical pseudoatoms (UBDB) has been designed as a set of parameters to be used in standard refinement of crystal structures, as a starting point in high-resolution studies, or also in reconstruction of molecular densities and the evaluation of a number of electrostatic properties of studied molecules. The UBDB consists of all atom types found in peptides, proteins and some other biologically relevant molecules [1]. It had been already shown that the databank corresponds very well to the electron density in a number of amino acids, when compared to conventional *ab initio* methods at the B3LYP/6-31G\*\* level, and also, reproduces the electrostatic interaction energies quite well (~1kcal per mole).

The UBDB was recently extended by over 100 new atom types present in RNA, DNA and in other molecules of great importance in biology and pharmacy. The atom types' definitions were modified and new atom keys added to provide more precise description of the atomic charge distribution. H-X bond lengths were updated according to Allen et al. (2010) [2] and implemented in the LSDB program as well as used for modelling the appropriate atom types. The new version of LSDB and databank is available on the website [3].

UBDB databank was extensively tested. Electrostatic interaction energies calculated on the basis of databank of aspherical atom models (EP/MM method) [4] were compared to the corresponding results obtained directly from wave functions at the same level of theory (B3LYP/6-31G\*\*) (SPDFG program) [5] and to some other theoretical methods [6]. Various small complexes were analysed to cover most of different interaction types and to test the newly added