

P.14.01.1*Acta Cryst.* (2005). **A61**, C419**Comparative Charge Density Studies on Tripeptides of the Ala-Xxx-Ala-type**Diana Förster^a, Eva Rödel, Peter Luger^a, ^a*Institute of Chemistry/Crystallography, Free University of Berlin*. E-mail: mng3@chemie.fu-berlin.de

A key concept in Bader's theory of 'Atoms In Molecules' (AIM) [1] is the transferability of topological electronic properties of submolecular fragments to macromolecular systems. In the biologically important class of amino acids and oligopeptides a considerable number of experimental charge density studies have been performed by high resolution X-ray diffraction. Transferability provided, these data can be used to derive electronic properties even for polypeptides or other polymeres, where crystals of sufficient diffraction quality can hardly be obtained.

The analysis of Ala-Xxx-Ala-type tripeptides is one of the steps following the path from small molecules to polymeric structures. Starting from Ala-Ala-Ala, the central amino acid was replaced by glycine, histidine and others. For that study, high resolution data sets ($\sin\theta/\lambda=1.18\text{\AA}$) were collected in our group at 25K, respectively. The multipole refinements were accomplished with the program package XD [2]. The main attention was directed to the two different peptide bonds between Ala and Xxx in the zwitterionic molecules.

The transferability of the electronic properties could be extensively verified, but effects of the crystal packing are not negligible.

[1] Bader R.F.W., *Atoms in Molecules*, Clarendon Press, Oxford, 1994. [2] Koritsánszky T. et al., *XD, Freie Universität Berlin, User Manual*, 2001

Keywords: charge density studies, peptide crystallography, high resolution crystal structures

P.14.01.2*Acta Cryst.* (2005). **A61**, C419**Charge Density of Amino Acids with Strong Hydrogen Bonds: A Comparative Study**Stefan Mebs^a, Christian Hübschle^a, Peter Luger^a, ^a*Institute of Chemistry/Crystallography, Free University of Berlin*. E-mail: stebs@chemie.fu-berlin.de

Submolecular electronic properties of functional groups in natural products are of particular interest for the pharmaceutical chemistry. The solid-state electron density, which can be obtained experimentally by high-resolution X-ray diffraction, is a main source to gain these informations. During the last years, experimental charge density studies on 15 of the 20 natural amino acids have been performed and the results were compared with those obtained from various calculations [1].

Since the remaining ones are hard to crystallize in sufficient quality, we directed our interest to cocrystals with various solvents and we were able to measure high resolution X-ray data sets of L-phenylalanine and DL- and L-tryptophan-formic acid complexes [2],[3] which have the further interesting property to exhibit strong Speakman-type hydrogen bonds with D...A-distances $<2.5\text{\AA}$.

The results of all so far known charge density studies of the natural amino acids are compared in terms of topological properties with special focus on the strong hydrogen bonds in the noted mixed complexes.

[1] Metta C.F., Bader R.F.W., *Proteins*, 2003, **52**, 360. [2] Görbitz C.H., Etter M.C., *Acta Cryst.*, 1992, **C48**, 1317. [3] Scheins S., Dittrich B., Messerschmidt M., Paulmann C., Luger P., *Acta Cryst.*, 2004, **B60**, 184.

Keywords: charge density studies, amino-acid complexes, hydrogen bonds

P.14.01.3*Acta Cryst.* (2005). **A61**, C419**Experimental Charge Density Study on Vitamin B12**Tibor Koritsánszky^a, Birger Dittrich^b, Stefan Nebs^c, Peter Luger^c, ^a*Department of Chemistry, MTSU Box 0395, Murfreesboro, TN, USA*. ^b*M313, University of Western Australia, WA 6009 Nedlands*,Australia. ^c*Institut für Chemie/Kristallographie, Freie Universität Berlin, 14195 Berlin, Germany*. E-mail: tkoritsa@mtsu.edu

A high resolution X-ray diffraction dataset ($\sin\theta/\lambda=1.2\text{\AA}^{-1}$, 100K MoK α CCD, Rint 3.6% for 98 205 unique reflections) of vitamin B12 propanol solvate was interpreted in terms of the multipole formalism [1,2]. The structure was refined to full convergence, first using a fixed model density composed of invariom pseudoatoms [3] with standard radial functions, followed by a fit of all parameters including multipole populations restricted by local site symmetries and chemical equivalencies. This model was modified, in subsequent refinement cycles, by implementing bound-atom radial functions projected from theoretical molecular densities [4]. The results of the two refinements and DFT calculations were compared in terms of local topological properties and d-orbital populations of the Co site.

[1] Hansen N. K., Coppens P., *Acta Cryst.*, 1978, **A34**, 909. [2] Koritsánszky T., Richter T., Macci P., Volkov A. Gatti C., Howard S., Mallinson P.R., Farrugia L., Su Z.W., Hansen N.K., *XD*, 2003. [3] Dittrich B., Koritsánszky T., Luger P., *Angew. Chem. Int. Ed.*, 2004, **43**, 2718. [4] Koritsánszky T., Volkov A., *Chem. Phys. Lett.*, 2004, **385**, 431.

Keywords: charge density, vitamin B12, bioactive compounds

P.14.01.4*Acta Cryst.* (2005). **A61**, C419**Determination of 'Experimental' Wavefunctions from X-ray Diffraction Data**Michael Turner^a, Judith Howard^a, Dimitri Yufit^a, Dylan Jayatilaka^b, ^a*Department of Chemistry, University of Durham, DH1 3LE, UK*. ^b*School of Biomedical & Chemical Sciences, The University of Western Australia*. E-mail: m.j.turner@durham.ac.uk

Wavefunction fitting experiments aim to build an 'experimental' wavefunction by combining traditional quantum mechanical calculations with experimental measurements according to some well defined procedure. One such approach developed by Jayatilaka [1] and implemented in the program Tonto, attempts to minimise a function based on the sum of the quantum mechanical energy and a weighted chi-squared function, in order to determine the wavefunction.

Using Tonto, experimental wavefunctions and related properties have been determined for a series of organic NLO materials [2] using high resolution X-ray diffraction data. The results of which have been compared with those derived from Charge Density analyses of high resolution, low temperature X-ray data collected at Durham University.

[1] Jayatilaka D., Grimwood D.J., *Acta Cryst.*, 2001, **A57**, 76. [2] Cole J.M., Howard J.A.K.H., McIntyre G.J., Copley R.C.B., Goeta A.E., Szablewski M., Cross G.H., *Acta Cryst.*, 1996, **A52**, C-349.

Keywords: charge density, electrostatic properties, semi-empirical calculations

P.14.01.5*Acta Cryst.* (2005). **A61**, C419-C420**Comparing Charge Densities of Opioids: Morphine, Codeine and Dextrometorphane**Stephan Scheins^a, Marc Messerschmidt^b, Peter Luger^a, ^a*Institute of Chemistry/Crystallography, Free University of Berlin*. ^b*Department of Chemistry, State University of New York at Buffalo, USA*. E-mail: stephan.scheins@chemie.fu-berlin.de

Opioids are not only of interest from their biological activity but also because of their unusual chemical structure. They consist of an oligocyclic strained cage structure with different types of rings and bonds. Metta [1] presented a method of reconstruction larger molecules from submolecular fragments based on theoretical calculations. To compare these results with experimental findings, we examined the charge densities of the title compounds obtained from a high resolution X-ray experiment at 25 K and CCD area detection. The datasets were refined with the XD program package [2]. A full topological analysis was performed including a submolecular partitioning making use of the zero flux surfaces of the electron

density gradient vector field according to the "atoms in molecule"-theory of Bader [3]. To evaluate the atomic volumes and charges the program TOPXD [4] was used.

In order to examine the transferability of smaller fragments the topology of submolecular parts of the three molecules were compared with each other and with those of the Matta study.

[1] Matta C.F., *J. Phys. Chem.*, 2001, **A 105**, 11088. [2] Koritsanszky T. *et al.*, *XD, Freie Universitaet Berlin. User Manual*, 2001. [3] Bader R.F.W., *Atoms in Molecules*, Clarendon Press, Oxford, 1994. [4] Volkov A., Gatti C., Abramov Y., Coppens P., *Acta Cryst.*, 2000, **A56**, 332.

Keywords: charge density studies, CCD detectors, low temperature

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Thymidin Invariom Transfer and Multipole Refinement of a 20K Data Set: a Comparison

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Nucleosides play a key role in life. Therefore they are interesting compounds for X-Ray charge density studies, because this would help to understand their biological function in more detail. The invariom approach [1] uses small theoretically calculated model compounds to derive the multipole populations without the need of high resolution data, because they are kept unrefined.

Thymidin, which is one of the DNA nucleosides, was measured at 20K with Mo-K_α radiation up to a resolution of $\sin\theta/\lambda=1.1\text{Å}^{-1}$. After the spherical refinement of the structure a multipole refinement was executed and also the recently developed invariom transfer was applied. A topological analysis was done in both approaches.

The results of the invariom transfer, the multipole refinement and the theoretical calculations were compared to have a better guess about the quality of the new approach.

[1] Dittrich B., Koritsanszky T., Luger P., *Angew. Chem. Int. Ed.*, 2004, **38**, 1397.

Keywords: charge density studies, nucleosides, high resolution

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Experimental Electron Density and Topological Analysis of D- and DL- Camphoric Anhydride

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Parameter indeterminacies often encountered during pseudoatom modeling of non-centrosymmetric structures unavoidably bias the results of experimental charge density studies [1,2]. A comparative analysis of high-resolution X-ray data of both crystal forms of Camphoric Anhydride C₁₀H₁₄O₃ was performed to learn about model restrictions applicable to reduce correlations between least-squares parameter estimates and the transferability of experimental pseudoatoms. The title compound is an ideal candidate for such a study, since the two enantiomers have very similar crystal packing and thus density differences due to different intermolecular forces are expected to be negligible. All intensity data were collected at 100K using SMART 1K CCD area detector with Mo K_α radiation up to a resolution corresponding to $(\sin\theta/\lambda)_{\max} = 1.1\text{Å}^{-1}$. The multipole refinement and the analysis of the static densities were performed using the XD program suite. The results obtained by different constrained models will be presented in terms of local and integrated topological properties of the densities.

[1] Spackman M.A., Byrom P.G., *Acta Cryst.*, 1997, **B53**, 553. [2] El Haouzi A., Hansen N.K., Le Hènaff, C., Portas L., *Acta Cryst.*, 1996, **A52**, 291. [3] Koritsanszky T., Richter T., Macchi P., Volkov A., Gatti C., Howard S., Mallinson P.R., Farrugia L., Su Z., Hansen N.K., *XD: a Computer Program Package for Multipole Refinement and Topological Analysis of Electron Densities from Diffraction Data*, 2003.

Keywords: charge density, non-centrosymmetry, multipole model

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Light on Phase IV in Ce_{0.7}La_{0.3}B₆

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The Γ₈ ground state of CeB₆, which may support, dipole, quadrupole and octupole moments, is responsible for its complex low temperature phase diagram. On cooling from the paramagnetic phase (Phase I), antiferroquadrupole (AFQ) order occurs below T_Q=3.3K (Phase II). Upon further cooling, antiferromagnetic order (AFM) additionally sets in below T_N=2.2K (Phase III). The substitution La ions for Ce, gives rise to a recently discovered new phase (Phase IV) in Ce_xLa_{1-x}B₆. For x~0.7, the ground state condenses from the paramagnetic phase into phase IV, below T_{IV}=1.5K. However, since its discovery, the nature of phase IV has confounded researchers, because the various experimental results are irreconcilable with either AFQ or AFM order [1].

We report on new resonant X-ray scattering (RXS) studies of phase IV, taken at the XMaS beamline of the ESRF. The E2 RXS cross-section can be expressed as a multipole expansion sensitive to dipole, quadrupole, octupole and hexadecapole moments [2]. From our investigation, we have discovered an E2 RXS feature, for which the azimuth dependence can be reconciled with an ordered octupole moment in phase IV. The results give, to our knowledge, the first direct evidence for a new order parameter in the Ce_{0.7}La_{0.3}B₆ ground.

[1] For a review see: Kubo K., Kuramoto Y., *J. Phys. Soc. Jpn.*, 2004, **73**, 216. [2] Hill J.P., McMorro D.F., *Acta Cryst.*, 1996, **A52**, 236.

Keywords: resonant X-ray scattering, multipole order, spin and charge density

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Anisotropic Displacement Parameters (ADPs) of Hydrogen Atoms. Can Invariom Modeling Contribute?

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Recently we have introduced invarioms (intermolecular transferable pseudoatoms) [1] and have shown that invariom modeling improves molecular geometry [2] for all atoms including hydrogens and overcomes the shortcomings of the independent atom model (IAM). Such modeling also improves the description of the thermal motion parameters as quantified with the Hirshfeld test.

To answer the title question we computed for a variety of small molecules hydrogen ADPs as described in [4], implemented in the XD [5] suite. In that procedure the internal displacements for all atoms are calculated by an *ab initio* methods, and then subtracted from the experimental data that also contain the external modes. The molecular C,N,O-skeleton is then fitted as a rigid body to the remains of the experimental ADPs. Finally these contributions are, together with the theoretical internal modes, assigned to the riding hydrogen atoms. These hydrogen ADPs are compared with results from an invariom structure refinement and to room temperature neutron data.

[1] Dittrich B., Koritsanszky T., Luger P., *Angew. Chem. Int. Ed.*, 2004, **43**, 2718. [2] Dittrich B., Huebschle C. B., Kalinowski R., Girtl, D., Luger P., *Acta Cryst. A*, accepted. [3] Hansen N.K., Coppens P., *Acta Cryst.*, 1978, **A34**, 909. [4] Flaig R., Koritsanszky T., Zobel D., Luger P., *J. Am. Chem. Soc.*, 1998, **120**, 2227. [5] Koritsanszky T., Richter T., Macchi P., Gatti C., Howard S., Mallinson P.R., Farrugia L., Su Z.W., Hansen N.K., *XD, Freie Universitaet Berlin, Berlin*, 2003.

Keywords: charge density, thermal parameters, ab initio calculations