

fragHAR: towards *ab initio* quantum crystallographic X-ray structure refinement for polypeptides and proteins

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Keywords: Hydrogen bond, Hirshfeld atom refinement, protein, peptide

We describe the first *ab initio* aspherical X-ray structure refinement for polypeptides and proteins, using a fragmentation approach to break up the protein into residues and solvent, and thereby speed up the quantum-crystallographic Hirshfeld atom refinement (HAR). We find that the geometric and atomic displacement parameters from the new fragHAR method are essentially unchanged from a HAR refinement on the complete unfragmented system when tested on di-, tri- and hexapeptides. The largest changes are for parameters describing hydrogen atoms involved in hydrogen-bond interactions, but we show that these discrepancies can be removed by including the interacting fragments as a single larger fragment in the fragmentation scheme. Significant speedups are observed for the larger systems. With this approach we are able to perform a highly parallelized HAR in reasonable times for large systems. The method is implemented in the TONTO software.

Electronic structure of copper (II) complex



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Keywords: Cu (II) complex, charge density, QTAIM.

The title square planar copper (II) complex [1] has been studied using quantum-chemical DFT treatment (hybrid B3LYP functional). The geometric structure used in quantum-chemical calculations is based on X-ray multipole refinement. The QTAIM (Quantum Theory of Atoms-in-Molecule) topological analysis of electron density has been performed on the theoretical electron density and alternatively on X-ray diffraction experimental data. The main aim of this study is to compare the results of theoretical and experimental approaches and to predict the distribution of spin density at metal atoms of the complex which is unavailable by standard X-ray techniques.

Chemical bonds between relevant atoms are described by the properties at bond critical points (such as electron density, its Laplacian and ellipticity). Our results characterize the coordination bonds between central copper atom and nitrogen atoms in ligands.

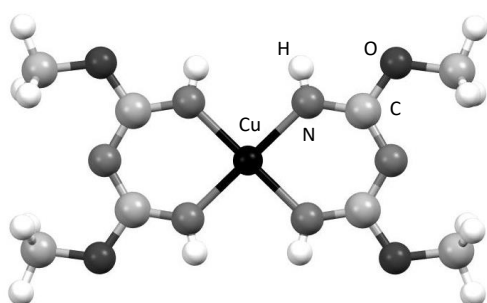


Figure 1: Complex under study with central atom Cu (black) and atoms in ligands: O (dark gray), N (gray), C (light gray) and H (white)

Acknowledgement

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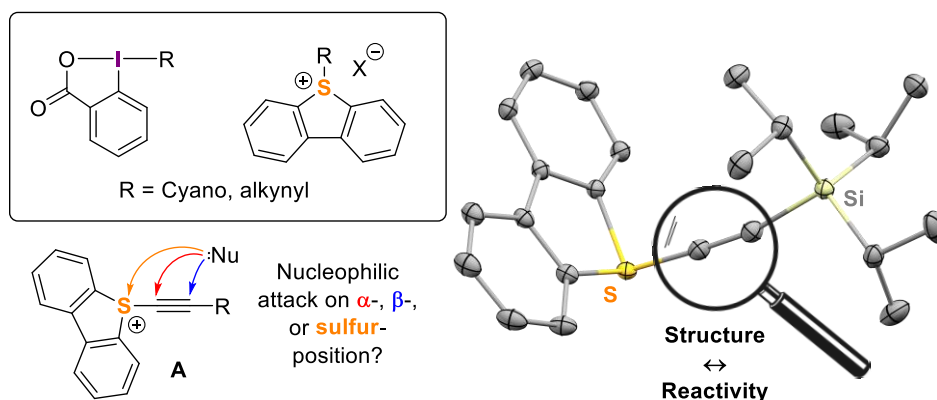
Towards a Better Understanding of the Reactivity of Sulfur-based Electrophilic Group Transfer Reagents

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Keywords: charge density, hypervalent sulfur, transfer reagent, umpolung.

Electrophilic transfer reagents are an important tool for modern synthetic chemists. They allow the *umpolung* of typical nucleophiles, such as an alkynyl- or cyano, and their introduction into the desired substrate at an advanced stage of its synthesis. Current transfer-reagents are either based on platforms containing hypervalent iodine [1] or sulfur [2]. The problem that arises with the transfer of alkynyl- and cyano groups is that their reactivity is often not predictable. In alkynyldibenzothiophenium **A** for example, nucleophilic attack at the α - or β -positions are observed in some cases, in other the attack takes place at the sulfur.[2c] Although those reagents were subject to many experimental and computational studies, so far no model to predict their reactivity was found. We now aim to perform more detailed analyses of solid state structures of the transfer reagents, seeking to enhance our understanding and thus, their synthetic potential. For that purpose, structurally relative sulfur-reagents were studied to identify the key correlations between structure and reactivity.



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TAAM refinements with electron diffraction data

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Keywords: TAAM, electron diffraction, structure refinement

Electron diffraction (ED) is based on scattering of electron beam on electrostatic potential. This recently fast advancing method allows to obtain crystal structures of nanocrystals at atomic resolutions, for both small and macro- molecules [1-2]. However, for this purpose, it is necessary to use scattering factors model which will be refined against measured data. Different models, already known for x-ray diffraction, can be implemented for ED. It should be investigated which of them give the best results at reasonable cost.

In this study, we present comparison of refinements of IAM and TAAM (Transferable Aspherical Atom Model) with parameters of multipolar model with Hansen-Coppens formalism taken from UBDB[3-5]. For both models are used electron scattering factors implemented in DiSCaMB library[6] and interfaced with Olex2[7]. Refinements are performed against experimental electron structure factors[5] and theoretical electron structure factors computed in Crystal14[8-9]. Results (Fig. 1.) show the actual possibilities and limitations of the method and theoretical possibilities in the future. We discuss e.g. improvement of anisotropic displacement parameters and hydrogen atoms positions obtained from refinements of TAAM instead of IAM.

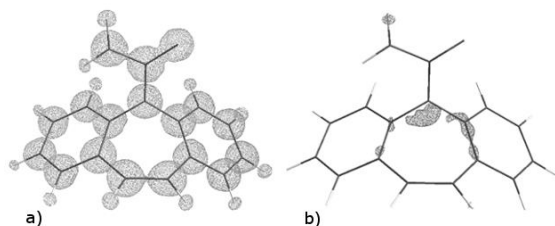


Figure 1. Fourier maps computed from electron theoretical structure factors of carbamazepine crystal with resolution of $\sin\theta/\lambda = 1.3 \text{ \AA}^{-1}$: a) F_{obs} , contour level $0.46 \text{ e\AA}^{-1} = 1\sigma[V(r)]$; b) $F_{\text{obs}} - F_{\text{TAAM}}$, contour level $\pm 0.045 \text{ e\AA}^{-1} = 3\sigma[\Delta V(r)]$

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TAAM: A reliable and user friendly tool for hydrogen atom location using X-Ray diffraction data

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Keywords: IAM, TAAM, HAR, *DiSCaMB*, structure refinement.

The hydrogen is present in most of the molecules in living things.[1] It is very reactive and forms bonds with most of the elements by terminating their valences and enhancing their chemistry. X-ray diffraction being the common method for structure determination depends on scattering from electron density and remains elusive to hydrogens having one electron. Generally, neutron diffraction data is used to determine the accurate position of hydrogens. However, the demands for larger single crystals (>1mm³), the costly maintenance of neutron sources are the bottleneck for every researchers reach.

The use of TAAM (Transferable Aspherical Atom Model) instead of IAM (Independent Atom Model) in the structure refinement against X-ray data seemed to be a possible solution which largely improved the X-H bond lengths and made them comparable to average neutron bond lengths.[2] However, the method was limited to specific users due to complexity in its application. A new method called Hirshfeld Atom Refinement (HAR) was introduced and the general applicability of HAR in accurate and precise estimation of the X-H bond lengths in small molecule was shown by Woinska *et al.*[3]. However, the computation cost for HAR is much higher than the TAAM refinement.

The applicability of TAAM in determining the X-H bond lengths with accuracy comparable to neutron data was reinvestigated on the 81 organic molecule high resolution datasets used by Woinska *et al.* The emphasis was given to make the TAAM refinement user-friendly and provide a general solution for determination of X-H bond lengths for a routine X-ray data at $d_{min} \leq 0.83 \text{ \AA}$. In this line, a new software implementation called *DiSCaMB*, 'densities in structural chemistry and molecular biology', has been developed to facilitate integration of the aspherical atom model into a wide range of refinement programs commonly used in X-ray crystallography for small and macro-molecules.[4] The structures will be refined using TAAM via *DiSCaMB* integrated with *Olex2* and the X-H bond lengths thus obtained will be categorized and compared with the averaged neutron lengths as defined by Allen and Bruno.[5] The model related statistics comparison between IAM, HAR and TAAM will be highlighted.

Support of this work by the National Centre of Science (Poland) through grant OPUS No.UMO-2017/27/B/ST4/02721 is gratefully acknowledged.



Figure 1: *DiSCaMB*.

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The nature of the chemical bond in trichloride Cl_3^- from the viewpoint of experimental electron density

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Keywords: charge density, polyhalide, topological analysis

How would you describe the bonding situation in a polyhalide e.g. Cl_3^- ? Is the molecule linear or bent? What atom do you suspect to carry the charge? Of what nature are the bonds, covalent or electrostatic? Although trihalides are well studied with theoretical methods^[1], many questions remain open. The influence of the cation, by its size and shape, as well as the influence of the crystal packing is not sufficiently clarified. Although the theory predicts linear and symmetric trihalides, about two-thirds iodine and bromine compounds are bent and asymmetrically bond in the solid state. The stability of such compounds decreases descending group 17. The few known chlorine species crystallize in the asymmetric configuration. In this study the experimental electron density distribution of the first centrosymmetric trichloride ion was investigated. High resolution X-ray diffraction data up to 0.45 Å were collected at our home Mo rotating anode source. After structure refinement based on the Hansen-Coppens multipole model^[2] the charge density distribution was analysed according to Bader's Quantum Theory of Atoms in Molecules (QTAIM)^[3]. We discovered that the bond has an ionic and covalent character. Because the bond critical point is shifted to the central Cl-atom and the VSCC (valence shell charge concentration) along the bond is more pronounced at the terminal Cl-atoms, the bond is slightly polarized. Furthermore, the Bader charges shows that the negative charge to be exclusively concentrated at the outer atoms.

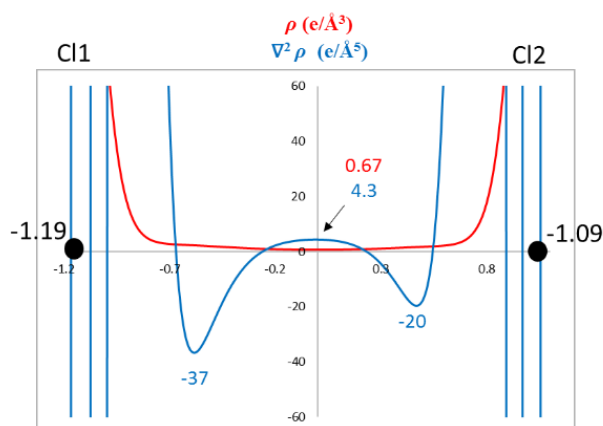


Figure 1. Electron density ρ and the laplacian $\nabla^2\rho$ along the bondpath of the Cl-Cl bond in the trichlorid ion.

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Experimental Charge Density Analysis of $(^t\text{BuNH})_2\text{S}(\text{N}^t\text{Bu})_2$ – the Amido Analog of Sulfuric Acid

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Keywords: charge, density, QTAIM

The title compound is a very appealing starting material on the way to f-metal single-molecule-magnets (SMMs). They show promising behaviours and applications for many modern electronic devices.[1] In 2015 Stalke et al. published a Co(II)-complex of a sulfur-nitrogen centred ligand which makes the present S-N ligand promising for SMMs.[2] A further option for constructing a SMM is using S-N centred ligands to coordinate f-group metals in a special way. The backbone of these complexes is based on $\text{S}(\text{NR})_4^-$ entities, which are well investigated.[3] Now, we have succeeded in isolating the protonated species $(^t\text{BuNH})_2\text{S}(\text{N}^t\text{Bu})_2$ (Fig. 1), which is isoelectronic to sulphuric acid. Herein, we present the first experimental charge density analysis of $(^t\text{BuNH})_2\text{S}(\text{N}^t\text{Bu})_2$. High-resolution single crystal X-ray data were used for a multipole refinement according to the Hansen & Coppens method.[4] The topological analysis based on QTAIM by Bader[5] gives insight to the bonding situation of the S-N-bonding. In particular, we could find the lone pairs at the amine as well as the amide atoms and confirm that there is no S-N double bond present (Fig. 2).

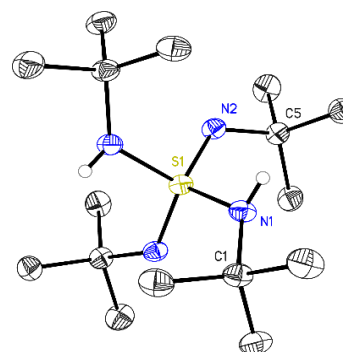


Figure 1 Molecular structure of $(^t\text{BuNH})_2\text{S}(\text{N}^t\text{Bu})_2$. Anisotropic displacement parameter are depicted at the 50% probability

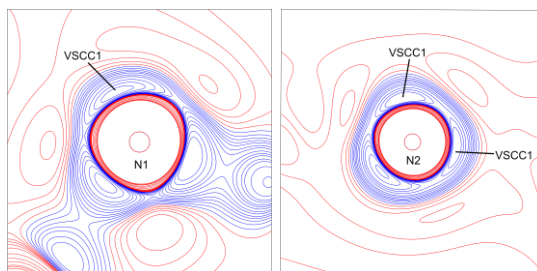


Figure 2 $\nabla^2\rho(r)$ of N1 (left) and N2 (right). Positive values are depicted by red and negative values by blue lines.

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Evaluation of residual bond density in molecules using simplified virtual scattering centers

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Keywords: bond density, virtual scattering center, residual density.

The Independent Atom Model (IAM) provides a good estimate for the most of routine crystallographic research. A charge density approach, which also describes bonding electrons, requires very high quality data in order to obtain meaningful results. Here we address a 'gray area' of good quality datasets with 0.5-0.8 Å resolution, which show visible deviation from IAM but are not satisfactory for experimental charge density calculations. The suggested methodology follows the well-known virtual atom method (see [1-3] and numerous references therein; historically the first one probably was [1]). Virtual scattering centers (VSC) are placed at fixed calculated positions between C, N, and O atoms with 'occupancies' being different for single, double, aromatic, and triple bonds. Scattering is approximated by a single Gaussian which can be justified by a small value of correction. VSCs are treated as isotropic: multiplication of scattering Gaussian by Debye-Waller factor yields another single Gaussian function to describe both effects (no deconvolution of vibrations and charge density). Usual IAM software was employed. The number of introduced parameters can be as low as one (for overall occupancy of the VSC part of the structure).

Introduction of VSCs makes the effect similar to the scattering of one hydrogen atom per 4-5 C-C bonds, which is substantial enough to justify the effort. Alternatively, each bond can be treated separately (number of additional parameters is roughly equal to the number of bonds). This can lead to further improvement. An attempt was made to handle S-C, S-O, and C-H bonds as well as lone pairs in the same fashion. A number of structures of various organic and element-organic molecules were tested. When it was possible, charge density calculations (MoPro) and/or HART calculations [4] were performed using the same experimental data. Visible improvement of fitting characteristics was achieved, especially for molecules with aromatic fragments. After removing most of residual bond density from the Fourier difference map, other sources of deviation such as disorder and experimental and data processing limitations can be addressed. Applicability of this algorithm is limited by Coppens's suitability factor *S* values: compounds with *S* < 0.3 show no or very little improvement. The same procedure was additionally tested at high quality 'benchmark' data sets, for which charge density distributions were experimentally obtained [4,5]. Similar behavior as with 'routine quality' examples was achieved.

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Data processing and Hirshfeld atom refinement for an organo-gold(I) compound

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Keywords: HAR, heavy, elements, charge, density, quantum.

Since long time ago, the heavy element chemistry is firmly concentrated on the relativistic effects, because these effects strongly influence the chemical and physical properties of crystals containing heavy atoms. The well-known macroscopic examples are the yellow color of gold, the low melting point of mercury and high voltage of the lead-acid car battery [1]. These effects appear when the speed of electrons approaches the speed of the light [1] and increase as Z increases. Relativistic effects manifest themselves in three major aspects [2]:

- (a) the radial contraction and decrease of energy of the s and p shells,
- (b) the spin-orbit splitting and the radial expansion,
- (c) increase of the energy of upper d and f shells.

Single crystal X-ray diffraction provides information about the electron distribution in molecules, which can be modeled with the Hansen-Coppens formalism (MM) [3]. Unfortunately, the MM is hardly flexible enough for heavy atoms. An alternative method is the X-ray Wavefunction Refinement (XWR) [4] which consists of two steps: Hirshfeld Atom Refinement (HAR) and XCW fitting. According to Bučinský *et al.* [5] it is possible to perform relativistic XWR, and thus, relativistic, as well as electron correlation effects, can be described.

The data sets for an organo-gold(I) compound were collected by dr. Jakub Wojciechowski (Rigaku) on the XtaLAB Synergy-S diffractometer equipped with the HyPix-6000HE detector using both molybdenum and silver X-ray sources at temperatures of 93K and 90K, respectively. Here, we present the results of data processing and Hirshfeld atom refinements carried out for these data, limited to different resolution ranges. The outcome of DFT-based refinements with the nonrelativistic (NR) and quasi-relativistic (IOTC) approaches will be compared, including refinement of anharmonic thermal motions of the gold atom.

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Electron densities of organic molecular crystals from powder X-ray diffraction

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Detailed knowledge of the nature of the chemical bonding is a prerequisite for understanding the physical and chemical properties of materials. This information is best available in the electron density (ED). Virtually all experimental ED distributions are determined from structure factors extracted from single crystal X-ray diffraction, since this has been regarded the optimal way to obtain data of the highest quality. However, our recent work has shown that data obtained from powder X-ray diffraction (PXRD) can exceed the data quality from single crystal diffraction¹⁻⁴. At the same time PXRD is experimentally less demanding and time-consuming⁵.

Current work shows that it is possible to obtain good descriptions of ED distributions and atomic displacement parameters (ADPs) of molecular materials from highly accurate PXRD data based on multipolar modelling. This critically depends on both the raw data quality but also on robust data reduction and treatment routines. As both sample requirements and systematic errors are different for powders compared to single crystals, PXRD provides a valuable and fast alternative to conventional single crystal electron density determination.

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Regioselective Metalation and Transmetalation of Organosilanes with Heavier Alkali Metals

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Keywords: alkali metal, regioselectivity, transmetalation, single crystal X-ray determination

Studies on the reactivity of organo alkali metal compounds have been of great interest and especially since further investigations on the lithium chemistry in the last decade.^[1] Addressing different reactive positions in one compound can be highly interesting for the organic synthesis. Here in, we report the regioselective metalation

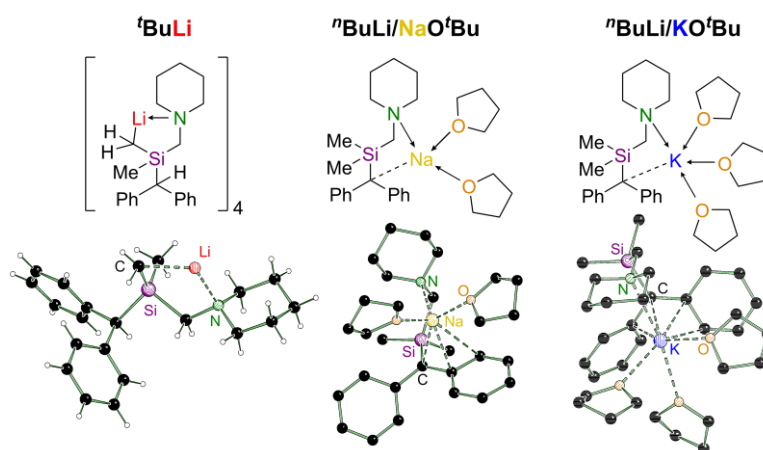


Figure 1 : Different regioselectivities of metalation with various alkali metal compounds.

and transmetalation of organosilanes with the heavier homologues of lithium. The use of different alkali metal compounds can lead to a change in regioselectivity of metalation. Metalation with *tert*-butyllithium results in a hydrogen-metal exchange at one of the methyl groups at silicon, whereas metalation with the Lochmann-Schlösser's base results in a deprotonation in benzylic position.

Nevertheless, it is possible to bypass the regioselective metalation using an α -lithiated organosilane.^[2] Transmetalation of the lithium compound with sodium-*tert*-butoxide leads to a highly reactive sodium compound, metalated at the methyl group.

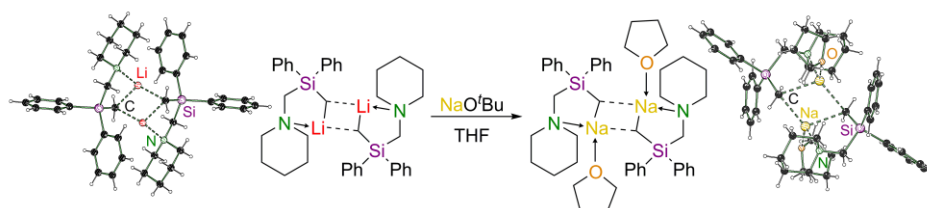


Figure 2 : Transmetalation of an α -lithiated organosilane with sodium-*tert*-butoxide.

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Experimental & Theoretical Charge Density Study of Bonding Interactions in FeSb₂

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Keywords: charge density, multipole model, Bader's topological analysis.

A decade ago FeSb₂ was shown to possess the largest thermoelectric power factor ever observed making it highly interesting for low temperature cooling applications [1]. Unfortunately, the thermal conductivity proved too large to obtain a significantly high thermoelectric figure of merit to initiate commercial applications. However, the diamagnetic FeSb₂ exhibits other exotic physical properties such as Kondo insulating behavior at low temperatures. The origin of the extraordinary transport properties is still not well understood, and the chemical bonding in this archetypical marcasite structure has been debated since the 1960s. The chemical bonding has been described both as mainly ionic and mainly covalent, and neither picture fully explains the measured properties of FeSb₂.

Therefore, an X-ray charge density study has been conducted based on measurements at ~15 K at both SPring8 and APS. So far, only the APS data has been used as basis for multipole modelling and topological analysis of the electron density aided by DFT calculated densities. Neither the extra bond implied by the covalent picture nor the large formal charge on iron from the ionic picture are observed experimentally nor theoretically. In fact, it appears that iron is negatively charged while the octet of antimony is not met contrary to common chemical intuition. Nevertheless, aspects of the ionic model are still valid when reconsidering the *d*-orbitals involved together with the geometrical relation between Fe and Sb.

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'Pancake' bonding in diathiadiazolyl radicals

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Keywords: pancake bonding, radical.

The 1,2,3,5-dithiadiazolyls (R-CNSSN^{*}, hereafter DTDA), are a family of thiazyl radicals that have been the focus of much investigation due to their potential as building blocks for magnetic and conducting materials. [1] These molecules tend to dimerise in the solid state *via* a spin-pairing interaction known as 'pancake bonding' [2], rendering them diamagnetic. This spin-pairing, as well as the geometry of the dimers, indicates that pancake bonds have a covalent component. However, the bond lengths in pancake bonds are too long to be considered conventional covalent bonds. Understanding pancake bonding interactions will aid in controlling them to develop magnetic or conducting materials.

Experimental charge density analysis has been carried out on a number of DTDA homodimers, heterodimers and monomers. [3] We have investigated features of the charge density of covalent bonds, pancake bonds and intermolecular interactions in DTDA radicals in the solid state. These data, as well as various computational results, are assessed to probe the nature of the pancake bonds in DTDA.

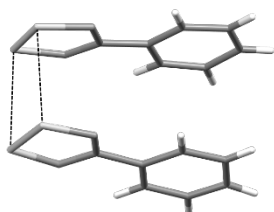


Figure 1: DTDA radical dimer

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Bonding Intramolecular H...H Contacts Forced by Stereoelectronic Interactions

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Keywords: charge density, molecular conformation, DFT, non-covalent interactions.

Despite the low energy, intra- and intermolecular H...H interactions can play an essential role in crystal packing as well as in stabilization or destabilization of a certain molecular conformation. A well-known (but still controversial) example is the biphenyl molecule in a flat conformation. Although this conformation is not an energy minimum on the potential energy surface, the interactions between hydrogen atoms in ortho-positions are generally accepted to be bonding and stabilize the system in general. [1–2]

In the tetracyclic glycoluril derivatives considered in this work, the substituents at the nitrogen atoms are always located in the axial position. In the case of methylene fragments, it leads to the shortened intramolecular H...H contacts (up to 1.827 Å).

A high-resolution X-ray diffraction study of a 2-hydroxyethyl derivative (H...H 2.171 Å, Fig. 1) demonstrates that this interaction is bonding in terms of Atoms in Molecules (AIM) theory. However, the question arises about its nature, as the short distance between the H atoms can be forced by stereoelectronic interactions.

A comprehensive *ab initio* study of model molecules in terms of natural bond orbitals (NBO) theory, AIM theory and interacting quantum atoms (IQA) approach shows that molecular conformation is mainly defined by stereoelectronic interactions of the lone pairs of nitrogen atom. At the same time, the conformation with the shortest intramolecular H...H contact corresponds to the lowest energy. Most important that the interaction between H atoms is bonding in terms of AIM and IQA and stabilizes such conformation.

This work is supported by the Russian Science Foundation (projects Nos. 19-13-00437, 19-13-00238).

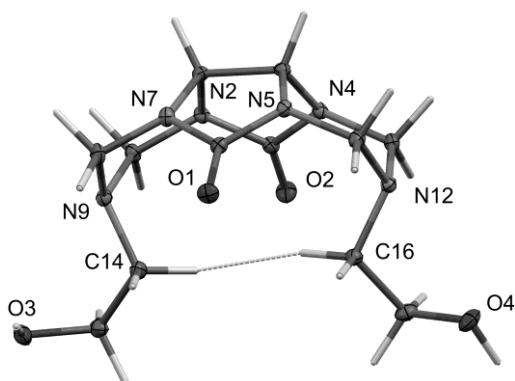


Figure 1: An example of a tetracyclic derivative of glycoluril with bonding

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Using Quantum Crystallography to Rationalise the Formation and Properties of Pharmaceutical Co-Crystals

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Keywords: charge density, quantum crystallography, co-crystal.

Tbd

Co-crystallisation is a viable tool for modulating the physicochemical profile of crystalline active pharmaceutical ingredients (APIs). The introduction of an additional molecular entity into the crystal lattice has the effect of altering the molecular arrangement, 3D packing and intermolecular interactions and thus a range of physicochemical properties.¹

Quantum Crystallography is a relatively recent concept that integrates quantum mechanical methods with the fundamental, underlying principles of crystallography determined by the electron density and its distribution.² Co-crystals provide an ideal vehicle to explore this new methodology through the ability to understand the intricacies of interactions critical for their formation and structure, as well as their effect on various physicochemical properties.

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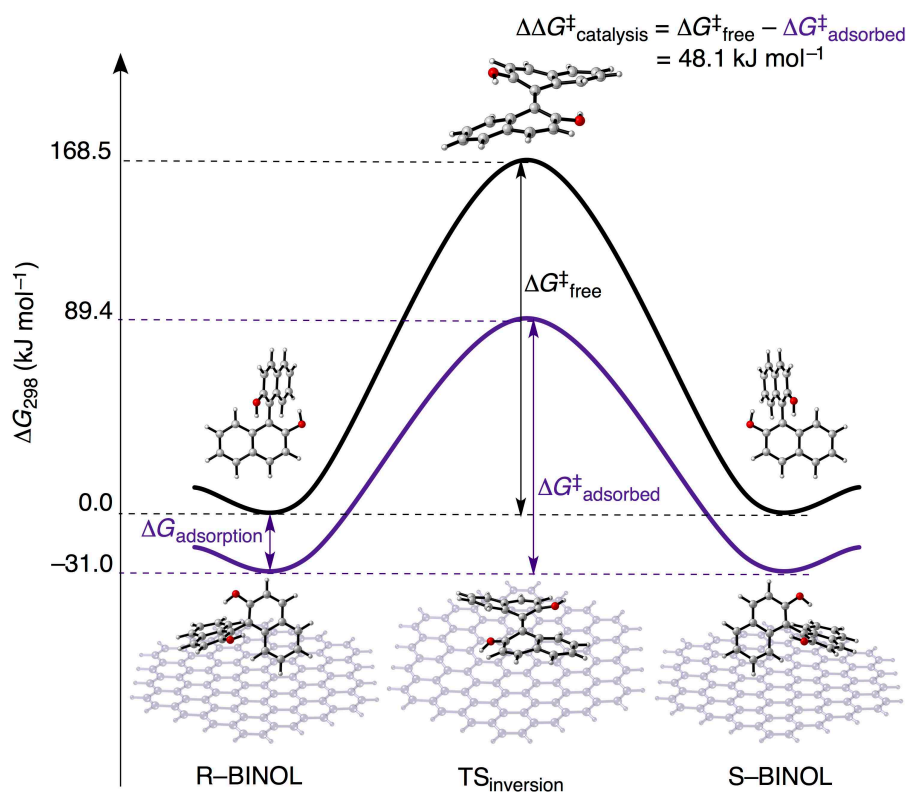
Catalysis by pure graphene - From supporting actor to protagonist through π - π interactions

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Keywords: catalysis, graphene, shape-complementarity, π - π interactions.

Since its first isolation in 2004, graphene has been extensively studied for its numerous exceptional properties such as its conductivity and mechanical strength.^[1] While its ability to non-covalently bind molecules has been well studied for applications in sensors and extraction devices,^[2] this principle remains surprisingly unexplored for the sake of stabilizing transition structures. Given the current interest in metal-free catalysis,^[3] expanding the application of this concept to transition structures has the potential to open up opportunities for applications of graphene as a catalyst. Herein, we explore the possibility to lower the activation energy of a chemical process purely through stabilizing π - π interactions between transition structure and graphene using density functional theory methods. On the simple example of binaphthyl racemizations we find a significant catalytic effect originating purely from π - π interactions and shape-complementarity between catalyst and transition structure indicating the potential for applications of pure graphene in catalysis beyond its use as a catalyst support.



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Intermolecular interactions in pairs of flavanone-chalcone isomers

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Keywords: intermolecular interactions, energy frameworks, global reactivity descriptors,

Chalcones, through a conversion to their isomers – flavanones, are important precursors in the biosynthesis of various flavonoids. In this study, the seven pairs of flavanone-chalcone isomers substituted with electron withdrawing groups (Cl or Br) and electron donating groups (OH, CH₃ and OCH₃) were examined.

We addressed three aspects of the comparison between flavanone and chalcone isomers: the intermolecular interactions in the crystal lattice; the quantification of lattice energy calculations together with energy frameworks visualization^{1,2}; global reactivity descriptors (chemical hardness, chemical potential, electrophilicity index).

The relationships between different noncovalent interactions derived from Hirshfeld surface analysis³, crystal lattice energy and global reactivity descriptors of compounds were discussed.

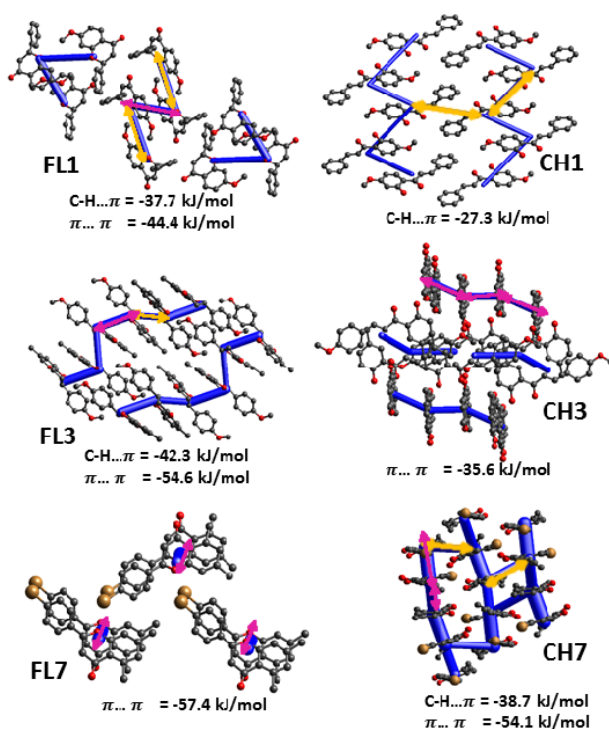


Figure 1: Energy frameworks for pairs of crystals FL1/CH1, FL3/CH3, FL7/CH7 (total energy is presented). Yellow and pink arrows indicate energetically dominant C-H... π and π ... π interactions, respectively. The cut off value is selected individually to show only one/two highest energy if exists.

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2 Mackenzie, C. F.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A. *IUCrJ*. **2017**, *4*, 575-587.

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Evaluation of the reliability of electron density based index, in the study of π - π interactions.

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Keywords: electron, density, intermolecular, DFT, MP2, QTAIM.

In the last years, DFT methods have focused on an accurate energy description of the systems while leaving behind the electron density. In this work we evaluate the accuracy of electron density obtained using DFT methods in a system with π - π intermolecular interactions. The objective is to come closer to a reliable method of study of intermolecular interactions in solids, using the electron density. In order to do that, we calculated the electron density for a Naphtalene and Octofluoronaphtalene system, using various DFT methods and comparing them to MP2.

The methods used in DFT were chosen considering which ones have empirical dispersion or long range correction, in order to get an effective description of the electron density in the intermolecular interaction areas. Once we obtain the electron density we use tools from the Quantum Theory of Atoms in Molecules to study it. Using the reduced density gradient, we map an isosurface of the interaction, in which we can integrate different properties in order to get an idea of the nature of the interaction. We found a significant difference in the values of the integrated density between MP2 and DFT methods, despite having shown very similar energy values.

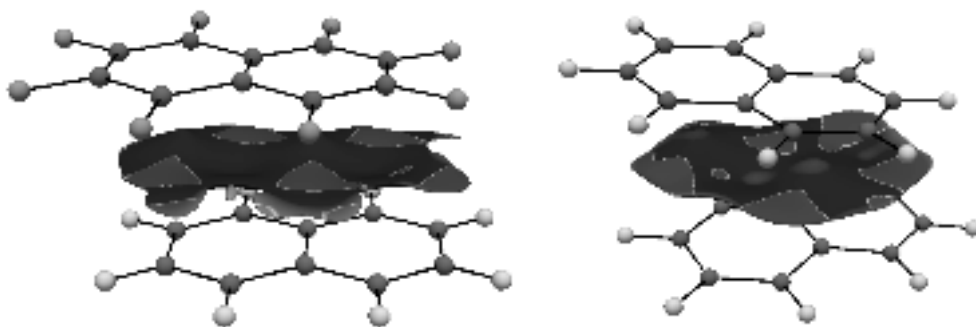


Figure 1: Isosurfaces for the system with 8 Fluor atoms and the one with no Fluor atoms, generated with the electron density from MP2 calculations.

Theory, gas-phase diffraction and high-angle SCXRD

The Trinity of Structural Characterization of Pyrosulfuryl dichloride

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Keywords: polymorphism, gas-phase electron diffraction, in-situ crystallization, solid-state structure, electron density

Structural characterization of small volatile compounds offers a variety of methods to be applied, like high-angle X-ray diffraction on *in-situ* grown crystals and electron diffraction on gas-phase molecules.^[1] With the gained structural information augmented by quantum-chemical calculations the effects of intra- and intermolecular interactions can be estimated. The object of the present investigation is pyrosulfuryl dichloride ClSO₂OSO₂Cl, which is assumed to be present in the Venusian atmosphere^[2] because of high concentrations of chlorine gas. Although the examined substance is known for more than a century^[3] no complete elucidation of the structural features was performed.

We undertook a computational investigation of pyrosulfuryl dichloride for different conformers. The presence of three different conformers in the gas phase was confirmed by vibrational spectroscopy whereas the gas-phase electron diffraction data was refined using a single-conformer model.

In-situ crystallizations of ClSO₂OSO₂Cl on the diffractometer afforded not less than four different modifications, in which the molecular parameters do not differ significantly and are in good agreement with the result of the gas-phase electron diffraction. However, Cl...O contacts of the adjacent molecules build up dimers or tetramers, which are linked in different ways to different molecular networks. The geometrical parameters of Cl...O contacts are in part inconsistent with the halogen bonding concept.

On one modification, the electron density distribution was refined using a multipole model against high-angle X-ray data. The topological parameters give insights into the interaction between two molecules connected by the halogen-bond like Cl...O contact.^[4]

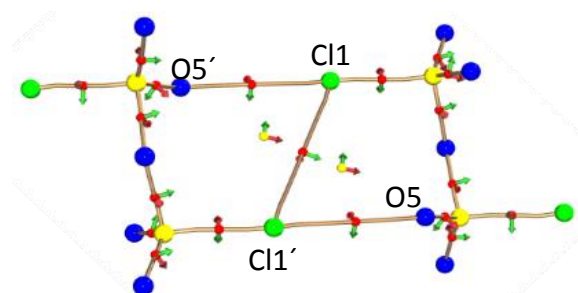


Figure 1: Plot of the atomic interaction lines (AIs) of a dimer of pyrosulfuryl dichloride in the solid state.

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Stabilization of sulfur-substituted lithium compounds

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Keywords: sulfur-substituted lithium compound, negative hyperconjugation, racemisation.

Sulfur-substituted lithium compounds are synthetically of particular interest and are used in various reactions. Due to their increased configurational stability, they are also relevant for asymmetric syntheses. For the configurational stability of these systems the rotation barrier around the C-S-bond is rate-determining. In the example of lithiated benzylphenylsulfide with *N,N,N',N'*-tetramethylethylenediamine (TMEDA) **1** the stabilization of the charge by negative hyperconjugation can be observed in the crystal structure. Based on the coordination of lithiated 2-pyridylbenzylsulfide with TMEDA **2**, the influence of the additional coordination of the metal on the electronic situation can be seen. The hyperconjugation is suppressed by the conformation but the metal is more fixed to the carbon center.^[1]

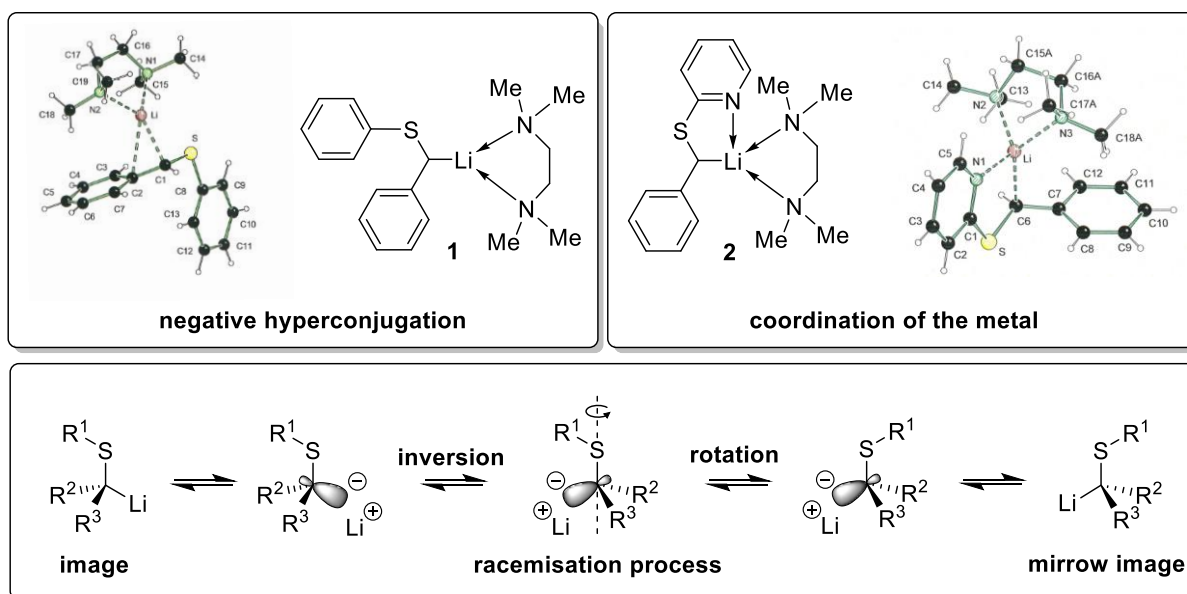


Figure 1: Solid state structure of benzylphenylsulfide with TMEDA and solid state structure of 2-pyridylbenzylsulfide with TMEDA is represented. Below the inversion process of α -sulfur-substituted lithium compounds is shown.^[1, 2]

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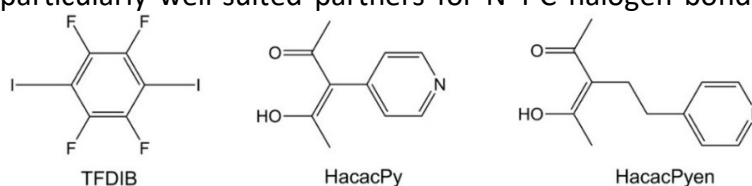
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Halogen bonds involving TFDIB: Answers from experimental electron density

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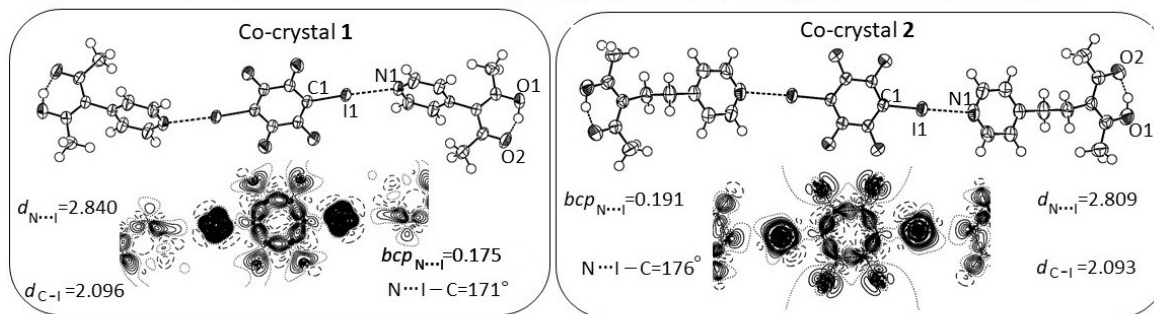
Keywords: charge, density, quantum, Halogen Bond, TFDIB.

A "halogen bond" denotes a short contact between an electron donor D and a halogen atom X as the electrophile [1,2]. The electrophile is usually approached by the donor in a region of depleted electron density opposite to its σ bond, the so-called " σ hole". Tetrafluorodiiodobenzene (TFDIB, Scheme below) and the *N*-donor substituted HacacPy and HacacPyen represent particularly well-suited partners for $N\cdots I-C$ halogen bonds in almost linear geometry.



To understand the halogen bonds involving TFDIB: **1** (HacacPy·TFDIB·HacacPy) and **2** (HacacPyen·TFDIB·HacacPyen), intensity data were accurately measured at low temperature (100K) and up to high resolution. Multipole refinements [3,4] and interpretation of the experimental electron density have been done according to Bader's AIM theory [5]. Our results indicate that the halogen bonds in **1** and **2** are weaker than expected for their distance range: the σ holes are not very pronounced, and the C–I bonds in the TFDIB moiety are not significantly elongated. With respect to these features, they resemble longer contacts [6].

Displacement ellipsoid plots of TFDIB trimolecular cocrystal aggregate in **1** (left) and **2** (right) at the 90% probability level



Deformation density (bottom, contour lines are drawn at $0.1 \text{ e} \cdot \text{\AA}^{-3}$) for **1** and **2**.

Acknowledgement: We gratefully acknowledge financial support by DFG (project EN309/10-1: Experimental electron density of halogen bonds and interhalogen contacts).

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Complementary bonding analysis : a) Organometallic semiconductor Stannole derivatives b) metallic Aluminium

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Keywords: complementary bonding analysis, theoretical structure factors, charge density

Structure, chemical bonding and reactivity are the essence of chemistry.¹ A simultaneous consideration of various bond descriptors in real, orbital and reciprocal spaces reveal different aspects of a chemical bond and thus is essential to analyze and tune its properties.²

In this poster presentation, I will present chemical bonding analysis in two different systems, (i) organometallic semiconductors, particularly stannole derivatives^{3,4} and (ii) metallic aluminium⁵ (Figure 1). A deeper understanding of stannoles would provide fundamental insights into main group chemistry as well as towards its application as optoelectronic devices.

Aluminium is considered as simple metal and its electronic distribution is expected to resemble free electron model. However, tight binding type features have been reported in recent accurate experimental studies on aluminium.^{6,7} Hence, a detailed comparison of experimental data with various levels of theoretical calculations would help us to interpret the electron distribution and chemical bonding scenario in metallic aluminium.

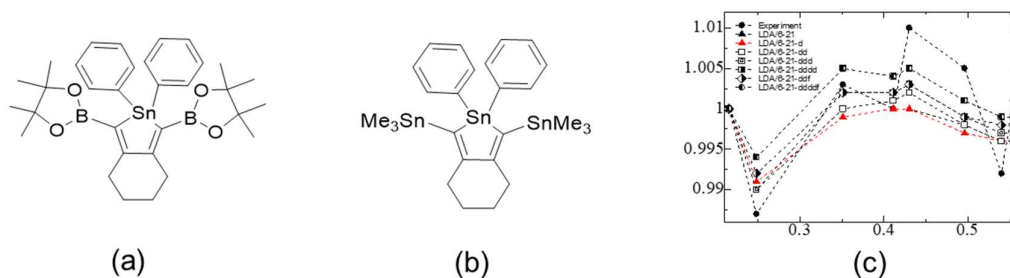


Figure 1: (a) and (b) Molecular structure of two stannole derivatives; (c) Comparison of structure factors for metallic Aluminium (CRYSTAL14 package)

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The charge density study of new Schiff-base titanium (IV) complex derived from 1,2-phenylenediamine with o-vanillin and peroxide.

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Keywords: Ti (IV) complexes, quantum crystallography, Schiff-base, potential anticancer compound

The Titanium complexes stand for a new category of potential anticancer compound. The first studies of titanium complexes copied square-planar arrangement of cis-platin complexes. These complexes show a significant anticancer activity for a wide range of cell lines of cancer [1]. We synthesized a new titanium complex derived from 3-methoxysalicylaldehyde, 1,2-phenylenediamine and Ti (IV) butoxide. This complex was prepared in monocrystal form and suitable crystals were selected for X-ray experiment. The crystal structure for measured compound was solved in OLEX2 software using SHELXT-2015 program *via* Intrinsic Phasing and refined with SHELXL-2016 by least-squares procedure on F^2 [2]. Experiments were performed by means of Stoe STADIVARI diffractometer with a Dectris Pilatus 300K detector and with an Incoatec μ S Ag microfocus source ($\lambda = 0.56083 \text{ \AA}$) at 100 K using a nitrogen gas open-flow cooler Cobra Oxford Cryosystems. Data reduction was processed using X-Area [3], where the value of average redundancy was 10.1, R_{int} of 6.96 % and resolution of 0.40 \AA . Direction cosines were applied for anisotropic secondary extinction correction. The results of multipole refinement and the topological analysis were performed *via* XD2006.

Acknowledgement: This work has been supported by the Ministry of Education, Science, Research, and Sport of the Slovak Republic within the Research and Development Operational Programme for the project “University Science Park of STU Bratislava”, ITMS 26240220084, co-funded by the European Regional Development Fund and also by support of the Research and Development Agency under the contract No. APVV-15-0079 and Scientific Grant Agency of the Slovak Republic VEGA (Project No.1/0718/19).

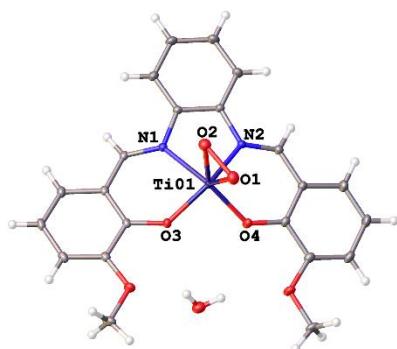


Figure 1: Titanium (IV) complex

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Comparative study of isostructural compounds with potential biological properties by quantum crystallography

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Keywords: NSAIDs complexes, anticancer activity, charge density, quantum crystallography, intercalation, Hirshfeld surface.

Metal complexes containing non-steroidal anti-inflammatory drugs (NSAIDs) have been the subject of many research papers and reviews which report the range of biological activities quite often inaccessible to the original NSAID ligands. Also, substituents as phenanthroline are able to effectively modulate the strength of intercalation of the metal complexes into DNA. Therefore, these complexes have different molecular properties than those of the parent drugs. Our study is focused on newly synthesized NSAIDs metal complexes with phenanthroline and investigation of the correlation between charge density results and biological activity.

The crystal and electronic structure of the two isostructural complexes [C₄₀F₆N₄O₄Cu (**1**) and C₄₀F₆N₄O₄Mn (**2**)] have been determined and analyzed in terms of the connectivity and topological properties. Both compounds crystallize in the monoclinic crystal system in the space group C2/c with four molecules in the unit cell. Least squares calculations for Multipole refinement were based on F² [1]. Data collection was performed on a Stoe STADIVARI diffractometer with a Dectris Pilatus 300K detector and with an Incoatec I μ S Ag microfocus source (Ag-K α , λ = 0.56083 Å) at 100 K using a nitrogen gas open-flow cooler Cobra from Oxford Cryosystems. Data reduction was processed using X-Area [2]. For numerical absorption corrections a crystal-shape model with 12 (**1**) and 6 (**2**) faces was employed. The data sets were merged by symmetry, an average redundancy of 6.78 for **1** and 17.59 for **2** gives R_{int} 3.57 (**1**) and 5.26 (**2**) [3]. A Hirshfeld surface analysis was carried out and two-dimensional (2D) fingerprint plots were generated to visualize the intermolecular interactions and to provide quantitative data for their relative contributions.

Acknowledgement: This work has been supported by the Ministry of Education, Science, Research, and Sport of the Slovak Republic within the Research and Development Operational Programme for the project “University Science Park of STU Bratislava”, ITMS 26240220084, co-funded by the European Regional Development Fund and also by support of the Research and Development Agency under the contract No. APVV-15-0079 and Scientific Grant Agency of the Slovak Republic VEGA (Project No.1/0718/19).

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Inferring a 1-RDM for molecular crystals from expectations values under N-representability conditions

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Keywords: X-ray diffraction and Compton scattering, Molecular Solids

A new method to infer the one-electron reduced density matrix for molecular crystals from position space (**X-ray structure factors**) and momentum space (directional **Compton profiles**) expectation values is presented. The method requires the additionnal assumption on the crystal that the molecules (or groups of them) in the cell can be considered electronically independent.

Given an atomic basis set for the atoms of the molecules, the method solves the least-squares fitting problem on the expectation values with respect to the **population matrix P** under the **N-representability conditions**.

It is shown that this optimization problem, which includes non-trivial conditions on the eigenvalues of P, can be formally addressed by the mathematical framework of **Semidefinite Programming**. This optimization method conveniently addresses the N-representability constraints on the population matrix. Additionally, it belongs to the family of convex optimization. Hence, it inherits nice properties, including not requiring any educated initial starting point.

This method has been applied to the crystal of dry ice. A one-electron reduced density matrix of reference has been obtained by periodic ab-initio calculations. From this one, a limited set of structure factors and directional Compton profiles have been computed. Gaussian noise, with a typical experimental standard deviation, has been added to the set. This constituted our pseudo-experimental data set. Doing so, enabled us to evaluate the inferred one-electron density matrix with respect to the one of reference. For the case of dry ice, it provides very satisfactory results.

Combined electron and spin density study of $(\text{CH}_3\text{P}(\text{Ph})_3)[\text{NibdtCl}_2)_2]$

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and Mohamed Souhassou^b***

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Keywords: charge, spin density, joint refinement.

The aim of this study is to perform a joint refinement of the charge and spin densities of a nickel complex.

The selected complex, $(\text{CH}_3\text{P}(\text{Ph})_3)[\text{NibdtCl}_2)_2]$ (methyl triphenylphosphonium bis (3,6-dichlorobenzene-1,2-dithiolato) nickelate(1-)), is square planar with nickel in oxidation state III. Ligands are of so-called non-innocent type. Crystal structure consists of two anions $(\text{NibdtCl}_2)^-$ in special position and counter cation $(\text{CH}_3\text{P}(\text{Ph})_3)^+$.

In order to perform a joint refinement, different techniques were used: neutron diffraction (ND), high resolution X-ray diffraction (XRD) and polarised neutron diffraction (PND). Data collections for ND and PND were performed at 2 K on D19 and D3 at Institut Laue–Langevin, Grenoble. XRD data were collected with the use of the synchrotron radiation at 10(1) K in order to obtain data at temperature closer to the one used for neutron diffraction experiments. Multipole refinement and the topological analysis of the electron density were performed using XD2006 program package. Joint refinement of the charge and spin densities was performed with Mollynx software package using the very low temperature data sets. We will discuss this model and a comparison with a joint refinement based on a laboratory XRD measurement at 100(1) K will be presented.

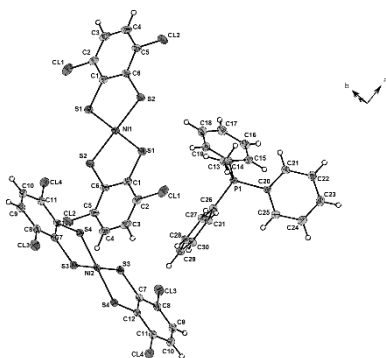


Figure 1: Structure of the studied complex at 100K

Acknowledgement: This study was financially supported by Research and Development Agency of the Slovak Republic under the contracts No. APVV-15-0079, SK-FR-2017-0014, the Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0718/19) and the bilateral program PHC STEFANIK 2018.

It was supported by the Ministry of Education, Science, Research and Sport of the Slovak Republic within the Research and Development Operational Programme for the project “University Science Park of STU Bratislava”, ITMS 26240220084, co-funded by the European Regional Development Fund.

Charge density of α -glycine at the ambient conditions and under 1GPa pressure – consequences of limited completeness of X-ray data

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Keywords: charge density, high-pressure, glycine, full and limited completeness of data.

We will present the results of our experimental charge density refinements performed against single crystal X-ray data collected for α -glycine ($P2_1/n$) at room-temperature under ambient pressure with our in house diffractometer, MoK α ($\lambda = 0.71 \text{ \AA}$), and under 1 GPa pressure with synchrotron X-ray radiation (in Almax wide-angle Diamond Anvil Cell, data collected on the Cristal beamline at Soleil, France, $\lambda = 0.42 \text{ \AA}$). The high-quality charge density measurement yielded a 100% completeness up to the 1.20 \AA^{-1} resolution.

The collected X-ray data were reduced with the use of Apex II¹ program, merged and used for refinement of the multipole model of electron density (MoPro² software). The following parameters were refined: positions, ADPs, multipoles (up to hexadecapoles), κ parameters, extinction and anharmonic thermal parameters for oxygen atoms. For the 1 GPa-pressure experiment, the raw X-ray diffraction data were reduced with the use of CrysAlis Pro³ software and next the same procedure of merging and consecutive steps of refining the electron density model were carried as it was in the case for the ambient condition data. Completeness of the 1 GPa data was 51% up to 1.11 \AA^{-1} resolution.

We will present details of differences between corresponding structural, thermal and electronic parameters obtained in the above two approaches. We have also prepared additional X-ray data sets where the reflections from (a) the full resolution high-quality in house and (b) 1 GPa synchrotron data sets were limited to: (a) only those collected at the Cristal beamline at Soleil (experiment in the wide-angle diamond anvil cell), and (a, b) data restricted even more to simulate X-ray diffraction data collected with applying classical DAC with routine opening angle. Detailed comparison of the results of all refinements allows for estimation of the missing structural, thermal and electronic information when incomplete X-ray data sets are used.

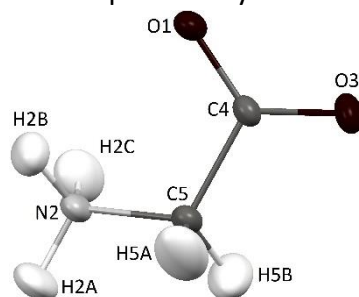


Figure 1: α -Glycine molecular structure under ambient pressure. At room temperature the oxygen atoms exhibit anharmonic motion.

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Electronic Structure, electron density and charge density of (3-(2'-tetrahydropyranyloxy)-4-methylthiazole-2(3H)-thione)

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Keywords: quantum crystallography, Domain averaged Fermi holes, negative Laplacian

We investigate the structurally derived O-ester from the heterocyclic thiohydroxamic acid 3-hydroxy-4-methylthiazole-2(3H)-thione, which name is (3-(2'-tetrahydropyranyloxy)-4-methylthiazole-2(3H)-thione)) (see Figure 1). The theoretical calculations have been performed using the BLYP and B3LYP functionals utilizing different software packages and basis sets. The electronic structure has been analysed in the framework of the orbital and the density representations via Domain averaged Fermi holes (DAFH) [1], localized orbitals, Natural bond orbitals (NBO) [2] and the Quantum Theory of Atoms in Molecules (QTAIM) [2]. QTAIM deformation densities and Laplacian maps have been used to compare theoretical and experimental results. Furthermore, theoretical electronic structure determination in terms of Hirshfeld Atom Refinement (HAR) [4] was used with three different setups for the refinement of position and thermal smearing parameters of hydrogen atoms.

The characterization of the N(1)-O(1) bond showed a controversy between experimental (multipolar refinement) and theoretical results with respect to the Laplacian sign in the bond critical point (BCP). The theoretical assessment of the electronic structure yields a negative value of the Laplacian in the BCP of the N-O bond, in contradiction to the experimentally determined (positive) value. This has been also shown in Laplacian maps. Nevertheless, the Hessian eigenvalues themselves agree well with each other. Further common features as well as the differences between the theoretical and multipolar refinement based charge densities shall be critically highlighted.

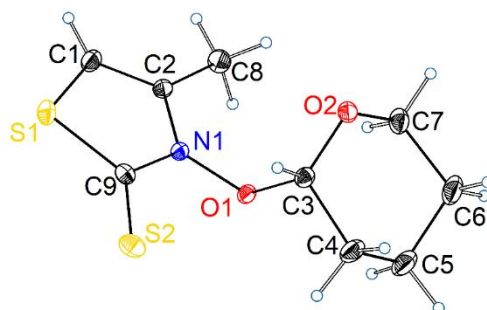


Figure 1: Structure of the molecule studied with atoms numbering

Acknowledgement

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Comparison of Different Strategies for Modeling Hydrogen Atoms in Charge Density Analyses

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Keywords: Hydrogen atoms; anisotropic displacement parameters; neutron data.

The quality of five approximation methods to model anisotropic displacement parameters (ADPs) for hydrogen atoms was investigated in a comparative study based on two model compounds, 9-diphenylthiophosphoranyl anthracene (SPANH) and 9,10-bis-diphenylthiophosphoranyl anthracene (SPANPS).^[1] Hydrogen atom parameters and structural properties derived from our collected neutron data sets of these compounds were compared with those obtained from the *SHADE-server*^[2], the software *APD-Toolkit*^[3], the results from Hirshfeld atom refinement conducted in the *OLEX2 GUI (HART)*^[4], and the results of anisotropic hydrogen refinement within *XD2016*^[5]. Surprisingly, the refinement of anisotropic hydrogen displacement parameters against the X-ray data yielded the smallest deviations from the neutron values. The refinement of bond-directed quadrupole parameters turned out to be vital for the quality of the resulting ADPs^[6]. In both model structures, *SHADE* and, to a lesser extent, *APD-Toolkit* showed problems in dealing with atoms bonded to carbon atoms with refined Gram-Charlier parameters for anharmonic motion.^[7]

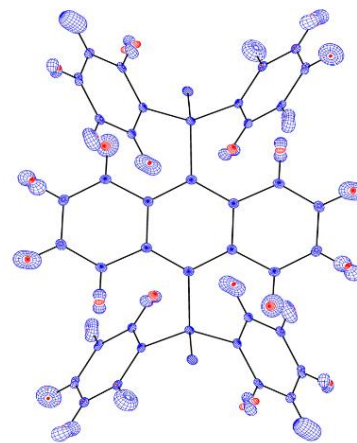


Figure 1: Exemplaric comparison of approximate and neutron ADPs of SPANH using the computer program PEANUT.^[8]

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Measuring accurate single crystal diffraction data using a Pilatus3 CdTe detector

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Keywords: pixel array detector, data quality, experimental charge density.

Pilatus3 detectors were released in 2012 and are widely established in macromolecular crystallography with over 4,000 PDB entries. The specifications of the Pilatus3 CdTe were quickly recognized as promising in charge density investigations, mainly due to the detection efficiency in the high-energy X-ray regime. Moreover, the dynamic range and low noise should overcome the perpetual problem of detecting strong and weak data simultaneously. However, to the best of our knowledge there is no publication available presenting high resolution data collected with a Pilatus3 CdTe detector.

Our experience with this detector family revealed two aspects that lead to systematically underestimated intensities at the two extremes of the detected intensity scale. Herein, Rubrene and FeSb₂ are representatives for the two cases. Additionally, a LaB₆ powder sample was consulted to validate the findings of the single crystal studies where counting statistics and reproducibility are more delicate.

The first aspect is indicated by systematically too low intensities for weak reflections, revealed by a variation of exposure time and beam attenuation. The origin was found in the data processing, specifically in the outlier rejection and data averaging.

The second case affects the most intense reflections and is connected to the maximum flux of the diffracted beam but not the total number of counts. As the widely discussed charge sharing should not affect strong reflections in any systematic manner, we utilized a maximum flux estimation procedure to identify unproblematic flux ranges. Disregarding this issue leads to unreasonably large extinction parameters.

Our results conclude that only the combination of careful data collection and processing can result in high quality data.

Charge density in frozen liquids – Experiment and theory

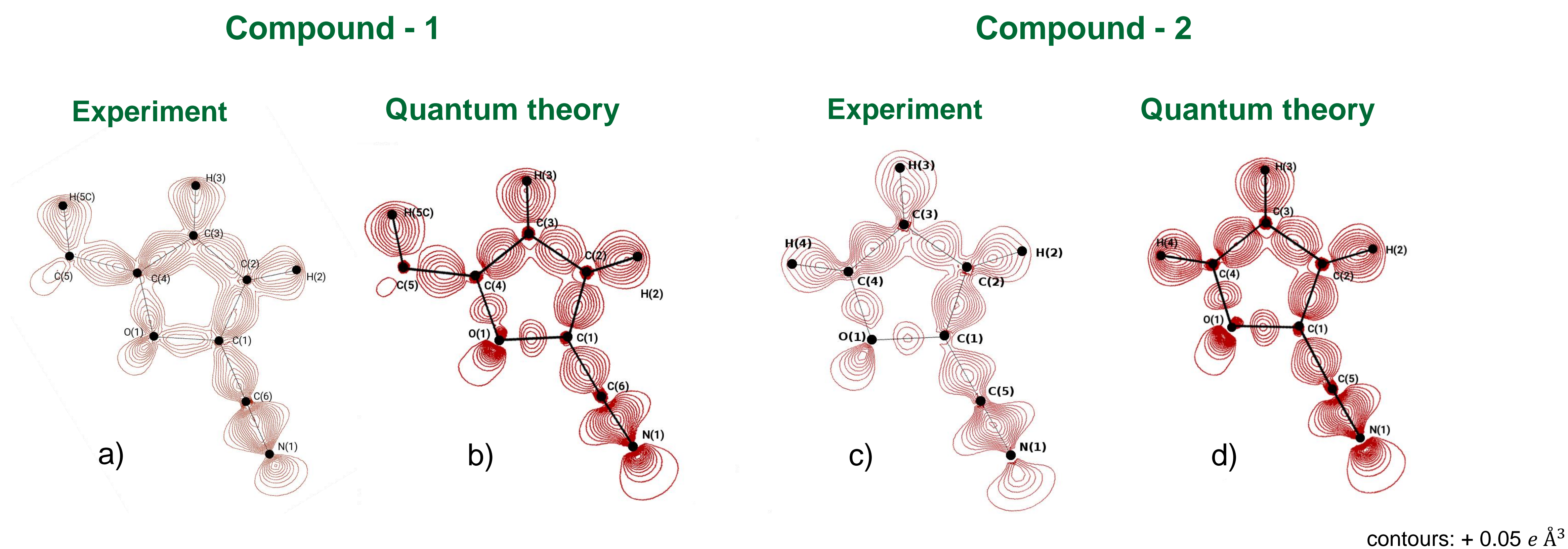


Michael Patzer, Nils Nöthling, Richard Goddard, Christian Lehmann*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, Mülheim (Ruhr), Germany

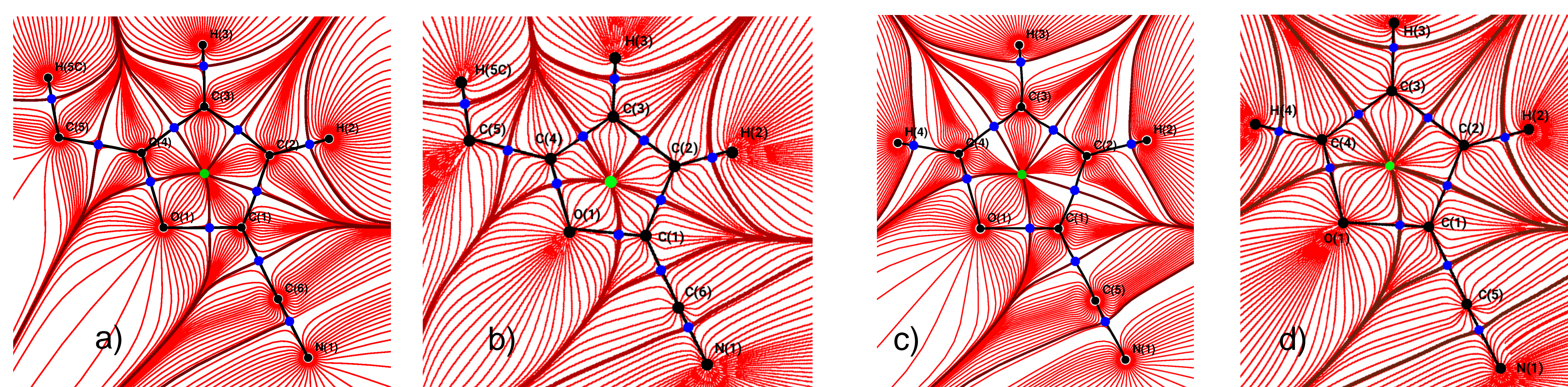
Deformation density

In the following section you can see the deformation density of two molecules derived by X-ray diffraction experiment and by quantum theory. Here you can see how the electron density redistributes when bonds are formed!



Density gradients and bond critical points

Here we can see the gradient of the electron density (red lines). In addition there are critical points ($\nabla\rho = 0$) marked with coloured points.



Bond critical point
Ring critical point

(blue): saddle point (two negative curvatures and one positive); the minimum of the electron density is along the bond
(green): critical point in the centre of a ring; one negative and two positive curvatures; Maximum of density along one axis perpendicular to the plane of the ring

How to get the Charge density of a molecule ?

Experimental point of view

X-rays interact with the electrons in a molecule. We have to find a suitable structure model to fit the experimental data. The Multipole Model derived by Hansen and Coppens [1] is one of the most convenient models to fit the charge density of a molecule.

$$\rho_{at}(r) = P_c \rho_{core}(r) + P_v \kappa^3 \rho_{valence}(\kappa r) + \sum_{l=0}^{l_{max}} \left[\kappa'^3 R_l(\kappa' r) \cdot \sum_{m=0}^l P_{lm\pm} Y_{lm\pm}(\theta, \phi) \right]$$

Here the electronic density around an atom ρ_{at} is separated into a core part and a valence part. The total electronic density $\rho(r_e)$ is given by the sum of all atom densities $\rho_{at}(r)$. After structure solution the electron density was refined with XD2006.

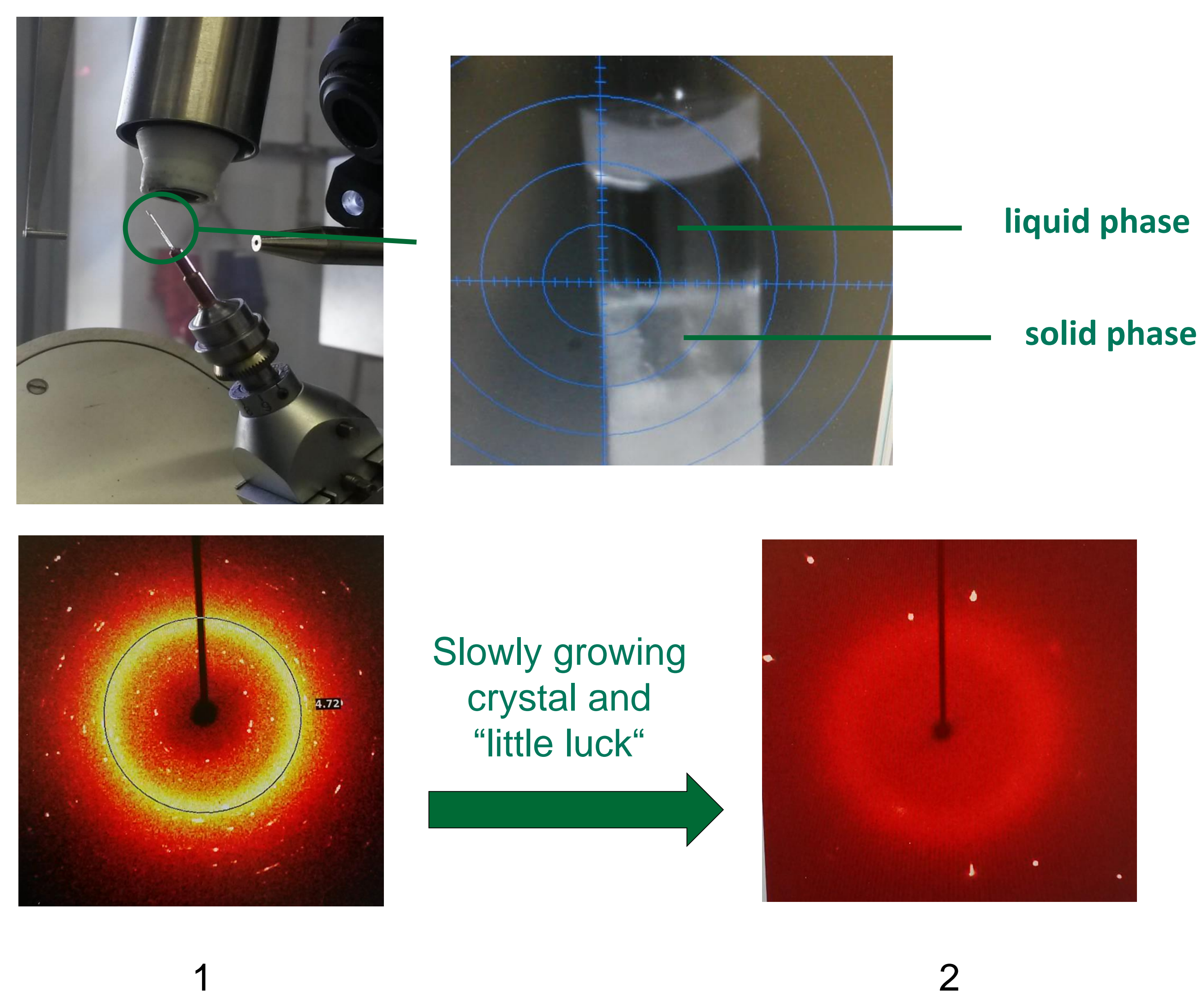
Theoretical point of view

We have to solve the electronic time-independent Schrödinger equation:

$$\hat{H}_e \Psi_e(r_e, R_{fix}) = E \Psi_e(r_e, R_{fix})$$

For a given molecule one can compute the electron density by calculating the modulus square of the electronic wave function. The wavefunction was derived with ORCA [2] (density functional theory, B3LYP, basis-set TZVPP) and the analysis of the wavefunction was done with Multiwfn [3].

In situ cryo crystal growth



1

2

Outlook

In the next step we want to combine theory and experiment as it is already done in the *Invariomtool* and in *Hirshfeld Refinement*. The golden goal is to predict experimental data ab initio. In progress ...

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StructureFinder

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Keywords: Unit cell, structure search, database.

Databases like the Cambridge Structural Database or the Crystallographic Open Database are good at collecting information from crystallographic experiments and making it searchable. But to my knowledge, there is no easy-to-use software to find and present the results of crystallographic experiments for a single workgroup.

Presented is a new computer program called StructureFinder^[1]. It creates a database of crystallographic structures on a computer and makes them searchable. The program can search for various properties: unit cell, free text, included atom types, creation date and space group. To build the database, StructureFinder collects all computer information files (cif file format) or res files (from SHELXL) below certain directories on a hard disk. The containing information is stored into a SQLite database. The database can be accessed by two different interfaces. A stand-alone Qt program (Figure 1) to install on a single computer or a web interface to be accessed by a whole work group.

StructureFinder greatly enhances the ability to find old structures in huge collections of crystallographic datasets. The program can easily handle more than 10.000 structures. It can be downloaded at <https://www.xs3.uni-freiburg.de/research/structurefinder>.

StructureFinder v34

Structures All of values SHELX res file Advanced Search CellCheckCSD

Cell Search: a b c alpha beta gamma More Results Find Superlattices Search text: text in name, path or .res file

Filename	Data Name	Directory
1000000.cif	1000000	D:/GitHub/StructureFinder/test-data/COD
1000001.cif	1000001	D:/GitHub/StructureFinder/test-data/COD
1000002.cif	1000002	D:/GitHub/StructureFinder/test-data/COD
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2004809.cif	2004809	D:/GitHub/StructureFinder/test-data/Archiv2.zip

Unit Cell:
a = 9.899 Å, σ = 103.442°
b = 11.729 Å, β = 96.291°
c = 12.259 Å, γ = 95.560°
Volume = 1364.90 Å³, P

Sum Formula: C₂₉H₃₀O₁₁P₂CU₁

Measured Refl. 4319
Independent Refl. 4319
Data with [I>2σ(I)] 4039
Wavelength [Å] 0.7107

Space Group: P-1 (2)
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Temperature [K] 293(2)
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R1 0.0469
Goof 1.16
Max Shift/esd 0.001
Peak/hole [e-Å⁻³] 1.321 / -1.563
R(int) 0
R(σ) 0.0104

Parameters: 298
data/param 14.5
Restraints 0
θ(max) [°] 25.18
θ(full) [°] 25.18
d [Å] 0.835
complete [%] 88.0
CCDC Num.
Last Modified 2017-07-10
 Grow Structure

Asymmetric unit

Added 252 files (248 cif, 4 res) files (212 in compressed files) to database in: 0 h, 0 m, 1.09 s

Figure 1: Hydrogen bonded sucrose molecules

[1] D. Kratzert, I. Krossing, *J. Appl. Cryst.* **2019**, *52*, 468-471.
<https://doi.org/10.1107/S1600576719001638>.

Metal Jet X-ray source: ^{49}In SCXRD we trust

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Keywords: new technologies, SCXRD

Since the discovery of X-rays in 1885 numerous applications in various fields of science, medicine and safety services emerged. However, the fundamental design of electron-impact home lab X-ray sources has not changed much. Because the sources brightness is proportional to the electron beam power density at the anode, development mainly focused on achieving higher tolerable anode heat loads, for example by rotating anodes or implementation of materials with superb thermal conductivity. This intrinsic thermal limitation was outsmarted with the introduction of the liquid-metal-jet anode [1].

Our Excillum Metal Jet D2 X-ray source in a Bruker D8 Venture setup with a Photon II detector is equipped with multilayer optics made by Incoatec to utilise the indium K_{α} radiation (24.2 keV). Although the use of characteristic gallium radiation (9.2 keV) is more established, we opted for the In K_{α} line. On the one hand because of the (theoretically) achievable high resolution suitable for charge density studies, on the other hand because diffraction data from our typical samples would suffer from absorption when exposed to the comparatively softer Ga K_{α} radiation.

Herein we present our methods and attempts to achieve high quality data from SC-XRD experiments with this setup. Major efforts were made to minimise spectral impurities and to develop alignment routines. Finally experiments on test crystals were performed and compared to results from the same crystals on a silver μS 2.0 setup with an APEX 2 detector.

[1] Hemberg, O; Otendal, M; Hertz, H. M. *Appl. Phys. Lett.* **2003**, *83*, 1483-1485.

InGa Metal-Jet:

Benchmark Charge Density Refinements

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Keywords: Charge Density, Metal-Jet, New methods.

While a conventional anode consists of a solid-state metal, the anode of a Metal-Jet is consists of a liquid metal alloy. This offers a compelling solution to the challenge of heat dissipation within X-ray anodes, allowing for a more focused beam. Currently, a Metal-Jet using gallium radiation presents the strongest commercially available in-house X-ray source.

However, we wanted to tap into the less established indium part of the alloy. While the intensity is considerably lower, the indium radiation still offers a high brilliance and the short wavelength ($\lambda(K_{\alpha,1}) / \lambda(K_{\alpha,2})=0.51212 / 0.51655 \text{ \AA}^{[1]}$). This potentially leads to a high resolution and low absorption, making it well suited for well diffracting crystals, which we aim to study with the Hansen-Coppens multipole model.

In order to set up the instrument optimally for this task, we decided to benchmark our progress with the very aim of our pursuit. We therefore used common quality descriptors of an ylide charge density refinement as the indicator for progress.

Herein, we will present the method as well as the results concerning two alternative mirrors and two different alloys for the machine, which were bot assessed with different thicknesses of aluminium and palladium for attenuation.

The influence of the mirror optics is determined to be small, which confirms the common knowledge of reproducibility in the production of Incoatec mirror optics. The influence of the attenuator is measurable reproducibly, with palladium being superior to aluminium attenuation. While the aluminium is more effective in filtering out low energy (i.e. gallium) contamination, the palladium increases spectral purity, as its absorption edge lies at $\lambda=0.50902 \text{ \AA}^{[1]}$, therefore suppressing higher energy radiation, just above indium emission. However, the difference between a tin containing and a tin-free alloy seems to be negligible.

[1] R. D. Deslattes, E. G. Kessler Jr, P. Indelicato, and E. Lindroth in *International Tables for Crystallography C (Third Ed.)*, Kluwer Academic Publishers, Dordrecht/Boston/London, 2004, p. 207.