Tools for Chemical Bonding 2019

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Contents

Structural studies and hirshfeld surface analysis of tempo radical derivates. [Ethyl-4-methyl-6-(4-nitro-phenyl)-1,4-dihydro-2h-[1,2,4,5]tetrazin-3-one radical]

P1

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The radical compound family commonly known as TEMPO represents a very interesting target for structural analysis. Due to their particular stability and magnetic properties, these compounds exhibit multiple applications in different fields, such as organic synthesis, medical chemistry, biochemistry, crystal engineering, and industrial catalysis [1-3].

In this report we present the crystal structure of a novel TEMPO derivative: 2-Ethyl-4-methyl-6-(4-nitro-phenyl)-1,4-dihydro-2H-[1,2,4,5]tetrazin-3-one radical (Fig. 1). The investigated system crystallizes in the orthorhombic $P2_12_12_1$ space group, with the unit cell parameters: **a**=3.90207(8), **b**=14.9047(4) and **c**=18.8796(4)Å. The analysis of its crystal packing revealed occurrence of particularly interesting π-stacking interactions, in which significant overlapping of adjoining ring-plane areas is observed. In order to gain deeper insight on those interactions and to disclose other intermolecular contacts, a complementary analysis of Hirshfeld surface for investigated system was performed.

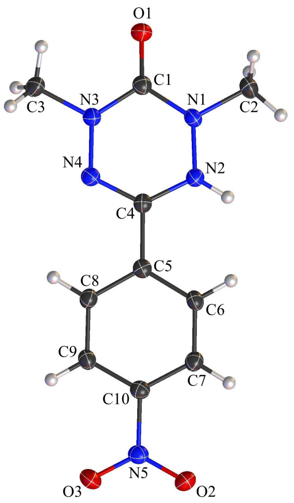

Fig. 1. Asymmetric unit of the crystal lattice of investigated TEMPO radical derivative with crystallographic atom numbering. Displacement ellipsoids are drawn at the 50% probability level and the H-atoms are shown as small spheres of arbitrary radius.

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P2

Revealing the source of color in the crystals of violuric acid with amino acids

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Nowadays, chromic phenomena attract a lot of attention since the colored materials find enormous applications in modern technologies, e.g. thermal printing, optical data storage or biosensor development.[1] Several chromic effects, such as termochromism, piezochromism or crystallochromism, can be observed in crystalline phases.

Crystallochromy phenomenon is often related to the presence of $\pi \cdots \pi$ interactions between molecules in a single-component crystal.[2] The source of color in materials which consist of more than one building block are even more complicated in nature and cannot be described only in terms of $\pi \cdots \pi$ interactions. Other factors such as changes in molecular structure of building blocks related to the presence of second component can also influence color in crystalline state. Violuric acid (VA) is an organic building block which is known to form colored salts with alkali metals.[3] Recently, we have shown that combination of VA with tyramine results in formation of red and violet crystals (pseudopolymorphs) in which $\pi \cdots \pi$ interactions are absent.[4] Those results focused our attention on other chromic phenomena in crystals containing violuric acid. The purpose is to examine the source of color in the presence and absence of $\pi \cdots \pi$ interactions. Promising class of compounds for our study proved to be amino acids due to the possibility to obtain co-crystals as well as salts. Moreover, due to variety of interactions formed by amino acids we can investigate color changes analyzing possible $\pi \cdots \pi$ interactions as well as hydrogen bonds.

Here we present a series of crystal structures of violuric acid and amino acids. The color phenomenon for those materials is studied using experimental and theoretical methods including X-Ray diffraction, UV-Vis spectroscopy, Hirshfeld surface analysis/Fingerprint plots[5,6] and Non-Covalent Interaction index[7]. This study enables us to correlate crystal packing features with absorption properties of obtained crystalline phases.

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Analyzing residual bond density in organic molecules with simplified virtual scattering centers

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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. We employ SHELXL-201X. The methodology follows (see [1-4] and numerous references therein; historically the first one [5]) virtual atom method. Virtual scattering centers (VSC) are placed at fixed calculated positions between C, N, & 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 one Gaussian function to describe both effects (no deconvolution of vibrations and charge density). Alternatively, each bond can be treated separately (number of additional parameters is roughly equal to the number of bonds). An attempt was made to handle S-C, S-O, & C-H bonds and lone pairs. A number of organic and element-organic molecules were tested. Some examples: Biphenyl, resolution 0.57 Å: IAM R=5.9, VSC 3.6; HARt[6] 3.4. Diphenylacetylene, 0.58Å: IAM: R=4.8, VSC: R=2.6. Dimethyl-3,4,5,6- tetraphenylcyclohexa-3,5-diene-1,2-dicarboxylate, 0.80Å: IAM: R=3.5, S=1.04; VSC 2.6 and 1.03. Ylide, 0.48Å: IAM R=2.7, VSC 1.8, HARt 2.0. Uncertainties of bond distances are also lower. After removing residual bond density from the Fourier difference map, other sources of deviation such as disorder and experimental and data processing errors can be addressed. The same procedure was additionally tested at high quality benchmark data sets, for which charge density distributions were experimentally obtained [6,7]: Rubrene, 0.47Å: IAM: 4.2, VSC 2.7, HARt 2.6, XD 2.45; 1,1-diethyl-2,2- bis(pentafluorophenyl)-4-phenyl-1,2-azoniaboretidin-2-ate, 0.47Å: IAM: 3.0, VSC 2.2, HARt 2.1. Thus benchmark data show similar behavior as the routine quality examples.

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P4

Crystal packing control of a trifluoromethyl-substituted furan-phenylene cooligomers

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Materials combining high luminescence efficiency and efficient charge transport are in strong demand in organic optoelectronics [1]. Furan/phenylene co- oligomer single crystals are considered as future materials for organic optoelectronics. Here, the effects of trifluoromethyl substituents on the crystallization, structure and optical properties of furan/phenylene co-oligomer 1,4-bis{5-[4-(trifluoromethyl)phenyl]furan-2-yl}benzene (CF3-BPFB) are studied systematically (Fig. 1) [2]. Crystallization by different methods leads to appear of polymorphs with different crystal packing notably differing by tilt angle relative to basal crystal plane. All obtained crystals exhibit high photoluminescence efficiency and have optical properties which strongly depend on the crystal packing. Variable-temperature X-ray powder diffraction analysis shows the thermal transition of two forms into a third one.

The introduction of terminal substituents coupled with crystallization by different methods allows a fine tuning of crystal packing being a powerful approach for the morphology and optoelectronic properties control.

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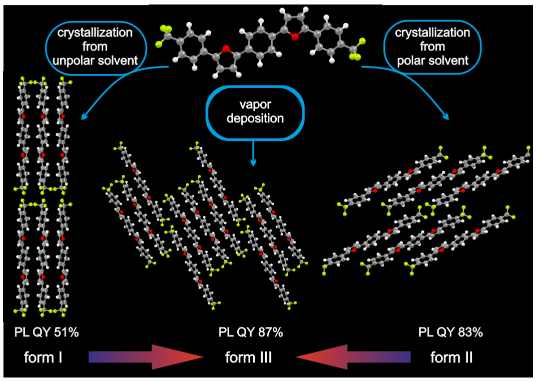

Figure 1. Chemical and crystal structures of polymorphic forms of CF3-BPFB. Top crystallization methods, bottom photoluminescence quantum yields of forms (PL QY) and solid phase transition of forms I and II into form III.

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Contact- and metal-free silyl anions

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Metal-free carbanionic centers were at first synthesized by W. Schlenk in 1916 through a simple salt metathesis of a sodium triphenylmethanide and tetramethylammonium chloride.[1] Since than the scope of metal-free and contact-free carbanions was widely extended through the usage of strongly coordinating ligands like crown ethers or highly stabilizing groups near the carbanion.[2,3,4] By using these known techniques in combination with silyl anions it is possible to examine the decreasing influence of the cation on the electronic structure of the anionic center through the reduction of the cation- anion-interaction and thereby learning more about silicon metal bond.[5]

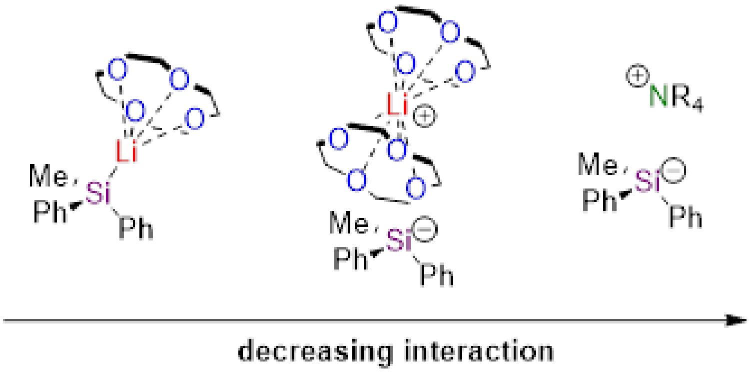

Figure 1: Decreasing interaction from a coordinated to a metal-free silyl anion

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P6

X-ray / XUV superfluorescence and stimulated x-ray emission spectroscopy: correlation function theory and first experiments

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The irradiation of a medium by short intense X-ray or XUV FEL pulses can result in population inversion. Spontaneous emission from one atom in such medium can stimulate emission from other atoms. This self-amplified process can lead to short and intense radiation emission, the process is known as superfluorescence [1]. To describe this process one needs quantum mechanical treatment of both the electromagnetic field and the atomic system, however, due to large number of interacting atoms an exact solution is not possible. In the current contribution within the scope of a few approximations (two level model for resonant atomic transition, 1D model of field propagation, factorization of triple operator products) we formulate a system of integro-differential equations for field and matter correlation functions [2]. The obtained system of equations was used to model the superfluorescence taking place in the Xe gas irradiated by FLASH. As a function of emission yield, we show an increase of the emission linewidth, that taking into account for the instrumental resolution, corresponds to results of our theoretical modeling.
An important application of the derived formalism is stimulated x-ray emission emission spectroscopy. It was experimentally shown that the chemical shift is present for stimulated emission signal for Mn K-alpha1 line in the $MnCl_2$ and $NaMnO_4$ solutions [3]. The measured stimulated emission signal was 6 orders of magnitude stronger than the spontaneous emission. However, at high intensities close to saturation nonlinear effects start to play role. This results in change of peak position and peak width. Hence, theory becomes an essential ingredient in interpreting the measured spectra. Here we will discuss possible explanations of the observed modifications of the spectrum and will outline how to modify the introduced correlation function formalism to describe such kind of effects.

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Hypercoordination and Hypervalency: inseparable companions?

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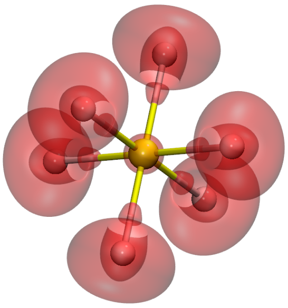
In most textbooks, the terms hypercoordination and hypervalency are used synonymously, the prime example being SF_6. But is this really correct, or do the two terms describe different aspects of chemical bonding?



ELI-D of SF_6 at an isovalue of 1.4. One can clearly see the lonepairs on the fluorine ligands, as well as the disynaptic basins which indicate covalent bonding character.

In this work, we investigate hypercoordinated species for their hypervalent character, taking as an example the aforementioned sulfur hexafluoride [1] and structural analogues like RSF_5 (R = aryl, alkyl) [2] and SH_6 [3]. Combining a variety of state-of-the-art computational bonding analysis techniques like *quantum theory of atoms in molecules*, *electron localizability indicator*, *natural bond orbitals*, and *energy decomposition analysis* with each other, we reconcile the delocalized Rundle-Pimentel ω-3c4e-bond-molecular-orbital [4,5] approach with a localized bonding orbital perspective in the framework of Lewis structures. We will further show how such a complementary bonding analysis can be carried out based on data from high-resolution X-ray diffraction experiments.

The analysis has shown that apart from ω-3c4e-bond stabilization of opposite substituents, electrostatic contributions depicted through resonance as well as steric aspects of the adjacent substituents play a major role in the stabilization of these compounds.

By using this new joint approach of quantum mechanics and crystallography [6], referred to as quantum crystallography, this study deepens our understanding of the chemical bond for hypercoordinated compounds.

In the future, we plan to apply it to central atoms other than sulfur.

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P8

Catalysis by pure graphene - from supporting actor ro protagonist through π-π interactions

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Graphene, a honeycomb lattice consisting purely of carbon, has been extensively studied for its numerous exceptional properties.[1] While its ability to non-covalently bind ground state molecules has been well studied and led to applications in sensors and extraction devices,[2] this principle remains surprisingly unexplored for 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 on the simple example of binaphthyl racemizations. We demonstrate a significant collective catalytic potential of multiple π-π interactions and show up transition structure shape complementarity with a carbon nanomaterial as a potential alternative strategy towards reducing reaction barriers heights.

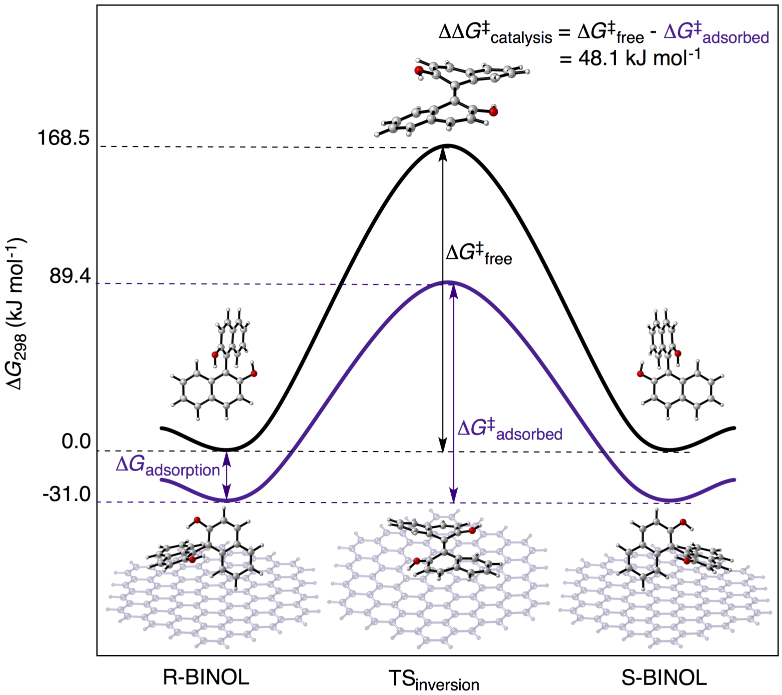

Figure 1: The chiral phosphoric acid catalysed aldehyde addition to hydroxybenzhydryl alcohol derived ortho-quinone methides and its possible mechanisms

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TAAM refinements with electron diffraction data

P9

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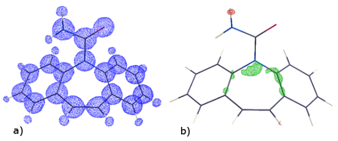

Figure 1: Fourier maps computed from electron theoretical structure factors of carbamazepine crystal with resolution of $\sin\theta/\lambda = 1.3$ Å^{-1}: a) Fobs, contour level 0.46 eÅ^{-1} = 1σ[V(r)]; b) Fobs-F(TAAM), contour level +/- 0.045 eÅ^{-1}=3σ[ΔV(r)], red negative, green positive.

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 (Figure 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.

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

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P10

NNS-Ruthenium complexes for the hydrogenation of α,β-unsaturated esters to allylic alcohols

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The interest in the hydrogenation of carboxylic esters employing homogeneous catalysts has grown vastly in the past decade. Most of the reported catalysts are sophisticated ruthenium based pincer complexes, which hydrogenate a broad range of substrates.[1] However, the selective hydrogenation of α,β-unsaturated esters to the corresponding allylic alcohols remains a major challenge in this field. Only few examples are known and mostly fully saturated alcohols are obtained as major product.[2] To the best of our knowledge, only two complexes exist which enable this transformation with some selectivity towards the unsaturated alcohol utilizing methyl cinnamate as substrate.[3] Here, we report on the development of a versatile NNS ruthenium pincer complex which delivered unprecedented selectivity in the hydrogenation of various α,β- unsaturated esters under mild conditions.[4] Moreover, we observed indications that the selectivity can be switched simply by changing the solvent and the properties of the ligand, respectively.

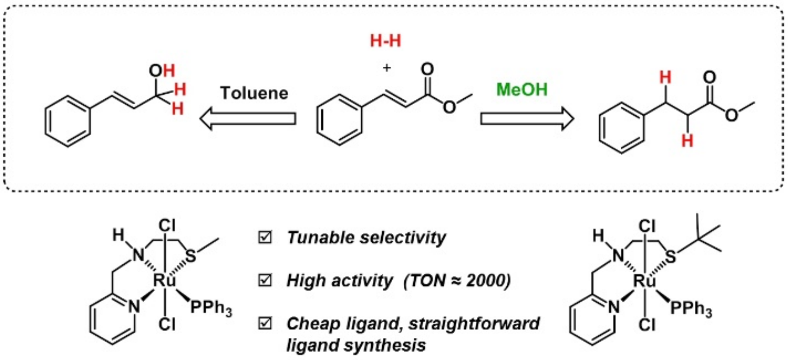

Figure 1: Hydrogenation of methyl cinnamate to the corresponding allylic alcohol or saturated ester

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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 diffraction [1-4]. At the same time PXRD is experimentally less demanding and time-consuming [5]. 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.

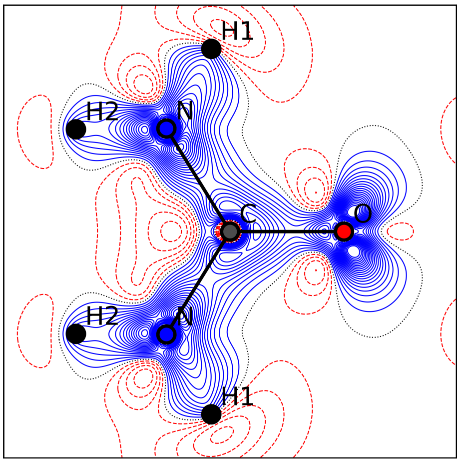

Figure 1: Deformation density of Urea based on powder X-ray Diffraction measurements

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P12

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

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Electrophilic transfer reagents are an important tool for modern synthetic chemists. They allow the umpolung of typical nucleophiles, such as an alkynylor 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 alpha- or beta-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 sulfurreagents were studied to identify the key correlations between structure and reactivity.

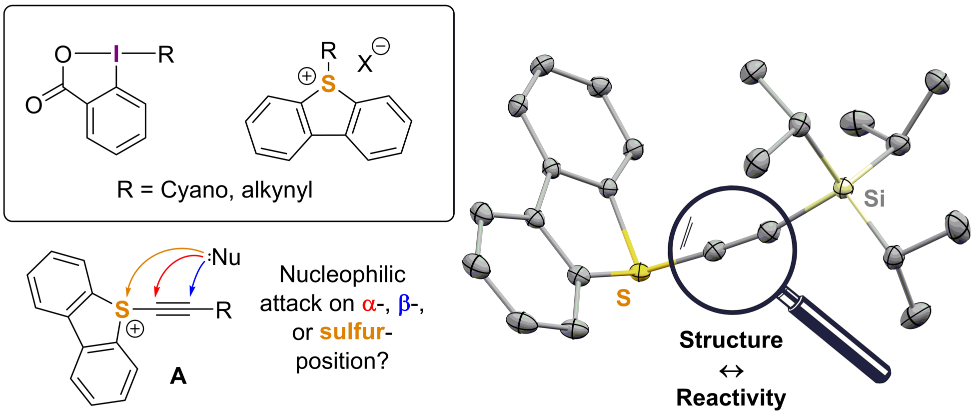

Figure 1: Analysis of high resolution x-ray data should shed some light on the reactivity of electrophilic transfer reagents.

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Silanes with polyfluorinated m-terphenyl substituents

P13

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Silylium ions, the silicon analogs of carbenium ions, are extremely strong Lewis acids due to the six valence electrons at the silicon atom. Because of their high electrophilicity and reactivity, these three-coordinated silicon cations are more difficult to stabilize and isolate than their carbenium analogs.[1,2] It was observed that the m-terphenyl backbone has stabilizing effects through intramolecular interactions between silicon atom and flanking aromatic rings.[1] Besides the π stabilizing effects, lone-pair halogen coordination and solvent adducts formation appear to be efficient in silylium ions stabilization.[3] Recently it was shown that these species are promising reagents in catalyzed C−F activation or C−C bond formation reactions, hydrosilylation reactions and homogeneous catalysis, including polymerization reactions.[4-6] The synthesis and spectroscopic characterization of polyfluorinated silanes 2,6-(4'-n-$BuC_6F_4)_2C_6F_3Si(H)Me_2$ (1) and 2,6-(4'-n-$BuC_6F_4)_2$−4-$MeC_6H_2Si(H)Me_2$ (2) is reported. Both compounds were obtained in a one-pot reaction, via reaction of the in situ generated organolithium derivative with $Me_2Si(H)Cl$. The molecular structure of 2 was determined by single-crystal X-ray diffraction (Figure 1).

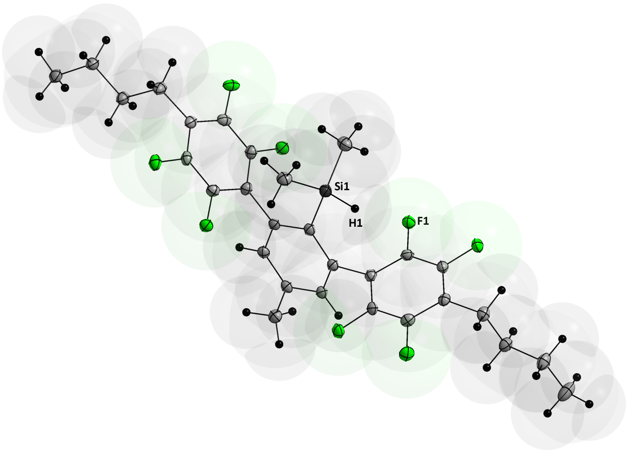

Figure 1: Molecular structure of 2.

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P14

'Pancake' bonding between dithiadiazolyl radicals

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The 1,2,3,5-dithiadiazolyls (R−CNSSN·, hereafter DTDAs), have been the focus of much investigation due to their potential as building blocks for magnetic and conducting materials. [1] However, these molecules tend to dimerise in the solid state via a spin-pairing interaction known as 'pancake bonding' [2], rendering them diamagnetic. Overcoming this dimerisation is important for developing materials with interesting magnetic properties. A more detailed understanding of pancake bonding in DTDAs is thus important.

Pancake bonds are multi-centre two-electron interactions that form between π-radicals, and there is a clear orbital component to this bonding interaction. However, pancake bond distances are too long to be considered conventional covalent bonds, and an equilibrium between radical monomers and pancakebonded dimers can be observed in solution, indicating that these interactions are much weaker than covalent bonds. [2]

In order to probe the nature of the pancake bonds in DTDAs, experimental charge density analysis has been carried out on a number of DTDA homodimers, heterodimers and monomers. [3] An analysis of these results, as well as some of our computational results, reveals how pancake bonds are distinct from both covalent bonds and intermolecular interactions.

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Charge transfer chemistry of novel strong electron acceptor - 5,6-Dicyano-1,2,5-selenadiazolo[3,4-b]pyrazine

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1,2,5-Chalcogenadiazoles are of interest to the fundamental chemistry and its applications in materials science. Their common property is high positive electron affinity (EA) making them effective electron acceptors. The transfer of electron density from the donor onto the heterocycle may be complete, leading to the thermodynamically stable radical anions (RAs), or partial one leading to charge transfer complexes (CTC) [1]. The present contribution covers synthesis and XRD structure of a novel highly acceptor molecule - 5,6-Dicyano-1,2,5-selenadiazolo[3,4-b]pyrazine (1) as well as two examples of the above reactivity of 1.

Compound 1 was synthesized via cyclisation of the corresponding diamine with $SeOCl_2$ and its structure was solved by XRD. Cyclic voltammetry of 1 revealed reversible single-electron reduction at 0.022 V vs. SCE. Reaction of 1 with potassium thiophenolate or sodium dithionite gives RA salts [K(18-crown-6)][1] (2) and [Na(18-crown-6)][1] (3) respectively. Salts 2 and 3 are EPR active in both solution and solid state. The latter is unexpected, because the π-dimerisation of RAs, present in these structures, typically leads to the loss of the EPR signal in the solid state.

Interaction of 1 with KBr or KI gives anionic complexes 4 and 5 respectively, which were isolated and structurally characterized by XRD. Formation of these complexes is a new example of the recently found reaction of anion coordination to chalcogenadiazoles, which was previously observed only for 3,4-dicyano-1,2,5-selena- and telluradiazoles[2]. The length of the Se···X bond in the anions 4 and 5 is by 1 Å longer than the sum of the covalent radii, but by 0.4 Å shorter than the sum of Van Der Waals radii, indicating that these are rather weak complexes. Properties of 2-5 are being investigated. The authors are grateful to the Russian Foundation for Basic Research (project 17-53-12057) and the Russian Science Foundation (project 18-73-00225) for the financial support.

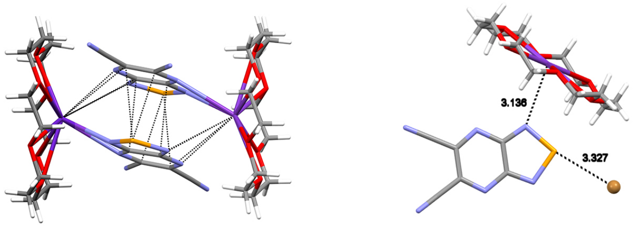

Figure 1: XRD structures of RA salt 2 (left) and CT complex 4 (right).

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P16

Correlated methods for Hirshfeld Atom Refinement: are they necessary?

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Standard structural refinements of X-ray diffraction data exploit the basic Independent Atom Model (IAM), which represents the global electron density of the molecule of interest as a collection of spherical atomic densities. This is an acceptable approximation if one is interested in determining only the positions of non-hydrogen atoms, but it is insufficient if accurate and precise hydrogen bond lengths and bonding features are desired.

The main reason for this shortcoming is the incapability of the IAM model in capturing the asphericity of the atomic electron densities due to the molecular environment. To overcome this drawback different techniques have been proposed [1]. In this context a method that has attracted attention is the Hirshfeld Atom Refinement (HAR) [2,3]. This technique consists in performing tailor-made quantum mechanical calculations on the system of interest followed by a leastsquare refinement. At each iteration the atomic scattering factors are obtained by partitioning the computed molecular electron density into aspherical Hirshfeld atomic densities.

Recent assessments of HAR have shown that the technique is able to determine the positions of hydrogen atoms in organic molecules with the same precision and accuracy that is attained from neutron diffraction measurements, even using data sets of 0.8 resolution [4]. This is remarkable because it means that HAR can be exploited to obtain more accurate crystallographic structures also when only standard in-house data are available.

So far, only quantum mechanical calculations at Hartree-Fock or Density Functional Theory (DFT) level have been performed in HARs, while the performances of correlated methods have not been evaluated yet. We have thus decided to perform a series of HARs using small-molecule X-ray datasets and exploiting MP2 and Coupled-Cluster calculations. The obtained results have been compared to HARs carried out at Hartree-Fock and DFT levels and to neutron data.

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Assessing Atomic and Group Electrostatic Solvation Energies Following the Interacting Quantum Atoms Approach

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The Interacting Quantum Atoms (IQA) approach allows for a decomposition of the global molecular energy into atomic contributions which tend to the energies of isolated atoms at the limit of non interaction. Within a molecule, one can discriminate between the own energy of an atom (ie., the one corresponding to the electron movement, repulsion and attraction to a given nucleus) and its (pair) interaction with the rest of the atoms in the system. It is possible (and many times desirable) to group atomic contributions (such as functional groups when dealing, for example, with organic compounds), giving rise to fragment energies as system descriptors.

A crucial issue to correctly model a molecule is to adequately reproduce its environment. To this end, the use of implicit solvation models in combination with quantum mechanical methods may provide an accurate description while preserving an affordable computational cost for large molecules. It is therefore desirable to include solvation contributions for the group description of molecules in a particular solvent environment. Nevertheless, it is well known that solvation free energy cannot in principle be decomposed into independent contributions, since the proximity of contiguous groups highly influences the solvation sphere of a given atomic group. In this work we aim to assess the goodness of an IQA-like group partition of the electrostatic contribution to the solvation energy.[1] For this purpose, we carry out COSMO-HF/aug-cc-pVTZ calculations followed by IQA analyses on more than 400 neutral and ionic solutes from the MNSol database. Structure-activity trends can be outlined from our results. Overall, the dispersion of the fragment solvation energies for neutral species is moderate, although the reconstructed molecular solvation energies from fragment contributions are not satisfactory. Further improvements shall account for correlation effects, a more adequate fragment selection or the inclusion of extra parameters.

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P18

Computational discovery of new metal nitrides at high pressure

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Oxides are, perhaps, the most studied compounds because they are widely used for many technological applications. On the contrary, metal nitrides are much less investigated. In these systems, the application of pressure leads to the formation of many N−N bonds. Therefore, if one could synthesize these systems at moderate pressure (¡25 GPa), they could become attractive for energy applications. Stimulated by recent state-of-art high pressure experiments, carried out the Advanced Photon Source by collaborators, we focused our research on Y−N system. This system was created at 50 GPa and 2200 K (laserheating) by mixing metallic Y and N_2. Nitrogen, in this case, was used both as a pressure transmission medium and as a reactant. Since the precise refinement of atomic positions from the experimental powder X-Ray diffractograms is very difficult, we performed an unbiased variable composition search of the most stable Y−N polymorphs. To this end, we employed the evolutionary algorithms implemented in the USPEX code[1], coupled with the local-basis code SIESTA[2], in order to reduce the computational cost. We performed the USPEX search at very high pressure (100 GPa) to enhance the variety of the structures. Finally, we relaxed the most stable structures from 100 GPa down to ambient pressure, using the plane-wave code Quantum Espresso[3]. We found for instance that the yttrium cation is always trivalent and as a consequence the YN_2 system is metallic and shows a charge disproportionation. On the contrary, in the case of YN_3, the $[N_3]^{3-}$ moiety is well described by a pair of resonating Lewis structure, and the system is a band-gap insulator. We extended our investigation to other compositions and metastable phases that contain N_x chains of increasing length in order to rationalize the relation between the chemical bonding and thermodynamic stability.

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In-situ crystallization of small molecules

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Small molecules often have low melting points naturally, but they are interesting candidates for the theoretical approach to chemical bonds or other structural issues. In our work, we revived and refined the technique of in-situ crystallization. We grow crystals inside capillaries by manually creating a crystal seed. Then we slowly cool the seed so it grows and the entire capillary is filled with a single crystal - if we are lucky. We do not use lasers [1], but we look at the crystal with a binocular and polarized light. Here we present this technique and two results.
1.) Multipole refinement of Al_2Me_6: The distribution of the charge density of the trimethylaluminum dimer was determined by high-angle X-ray diffraction of a single crystal and analyzed using the quantum theory of atoms in molecules. The data can be interpreted as Al2Me6 being predominantly ionically bonded, with clear indications of topological asymmetry for the bridging Al-C bonds due to delocalized multicenter bonding. The data shed new light on the bonding situation in this basic organometallic molecule, which was previously described by contradicting interpretations of bonding. [2]
2.) Structure determination of $C(NO_2)_4$: After numerous attempts over the last seven decades to obtain a structure for the simple, highly symmetric molecule tetranitromethane ($C(NO_2)_4$, TNM) the structure has now been determined in the gas phase and the solid state. A model describing a highly disordered high-temperature crystalline phase was also established, and the structure of an ordered low-temperature phase was determined by X-ray diffraction of an oligo crystalline material, that was twinned (pseudo)-merohedrically as well as merohedrically. TNM is a prime example of molecular flexibility, bringing structural methods to the limits of their applicability. [3]

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P20

Stimuli Responsive Aggregation-Induced Emission of Bis(4-((9H-fluoren-9-ylidene)methyl)phenyl)thiophene Single Crystals

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Highly-emissive solid-state materials are of a great interest for organic optoelectronics as active layers in organic light-emitting devices, lasers and sensors [1-3]. However, design of materials with specific optical response is still a challenge since several inter- and intramolecular factors should be taken into account. In this work we synthesized and studied 2,5-bis(4-((9H-fluorene-9-ylidene)methyl)phenyl)thiophene (Fig. 1a, BFMPT) as a novel stimuli-responsive Aggregation Induced Emission (AIE) material.

Solvent-antisolvent crystallization of BFMPT resulted in simultaneous formation of two conformational polymorphs (Fig. 1b) with different crystal structure and emission - orange needles and green-yellow plates. The photoluminescence quantum yield (PLQY) for BFMPT solution was lower than 1% whereas both polymorphs are highly emissive with PLQY up to 40%. Moreover, form I was shown to undergo mechano- and thermo-responsive transformation to more thermodynamically stable form II. Despite thermal-induced cracks BFMPT crystals retain high photoluminescence efficiency. The analysis of BFMPT potential energy surface (PES) as a function of twisting angle showed that dihedral angles of BFMPT (Fig. 1c) in the form I are almost coincident to the PES minima, whereas those of form II are farther due to crystal environment effect. Upon twisting S1v and T6v excited states intersect, which might be one of key luminescence quenching channels. Study of reduced density gradient allowed us to analyze key intra- and intermolecular interactions defining its conformational and crystal structure (Fig. 1d).

Due to high intrinsic conformational elasticity BFMPT-related compounds could serve as a basis for further molecular design of novel high performance aggregation induced materials.

This work was supported by RSF (project 18-73-00081).

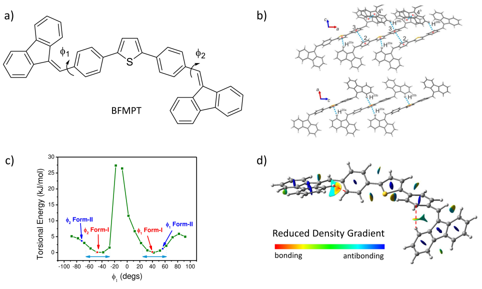

Figure 1: (a) Molecular structure of BFMPT; (b) crystal structure and intermolecular interactions in BFMPT form I and form II; (c) Potential energy surface of BFMPT as a function of Φ1 dihedral angle. Red and blue dots and arrows show the values of Φ1 and Φ2 dihedral angles of form I and form II, respectively. Cyan arrows visualise the intervals of torsional angles around minima for BFMPT molecule at room temperature; (d) RDG analysis of BFMPT, based on the optimized ground state electron density (s = 0.5 a.u. and ared-to-blue color scale from -0.015 a.u. ¡ sign(λ2) ρ(r) ¡ +0.015 a.u.). Blue color stands for repulsion, yellow/orange for attraction.

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Aurophilic Interactions in the Gas Phase

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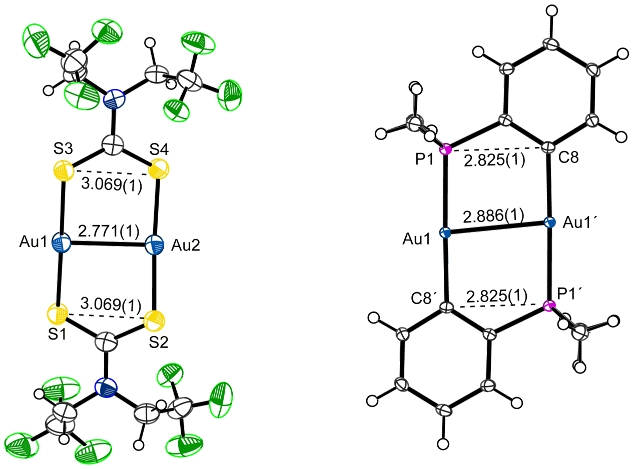
Short contacts among coinage metals in the formal oxidation state +1 are a common phenomenon in molecular organometallic chemistry.[1] Hence structures of molecules containing two metal atoms are experimentally only investigated in the solid state, the metalophilic interactions are biased by solid state contributions, e.g. packing effects. In our work, we attempt to determine the structure experimentally in the gas phase by electron diffraction.[2] Structures of free molecules offer a comparison to quantum-chemical calculations of gasphase molecules and thus it can be investigated which effects cause the small intermetallic distances. It is discussed whether this finding can be attributed to relativistic effects[3] or dispersion interactions[4] or even a mixture of both. The synthesized molecules (Figure 1) exhibiting a difference in the distances of the gold-coordinating framework in the solid state. In the dithiocarbamate 1 the goldgold distance is significantly shorter than the sulphursulphur distance, whereas in the phenylphosphine-comlex 2 the goldgold distance is slightly longer than the distance of the coordinating carbon and phosphorous atom. Our research aims also to understand this phenomenon.



1

2

Figure 1: Two different Digold complexes based on dithiocarbamat 1 and on phenyl phosphine 2.

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P22

Polar vs centrosymmetric arrangment in concomitant polymorphs of 2-aminopyridinium sulfamethoxazole

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Research in materials science focuses more and more on organic crystalline phases as they can possess large and fast responses to electromagnetic field.[1] Organic compounds when in crystalline state can find multiple applications in optoelectronics, nonlinear optics, ferroelectric materials etc. Unfortunately, most of those properties demand certain symmetry of the crystal to be present. Often, the non-centrosymmetricity is a necessary requirement for the non-zero effects, e.g. non-linear optical properties of the even-order, however several properties as pyroelectricity require additional in this case polar symmetry. Having possibility to control packing of organic molecules in acentric three-dimensional structure is a key challenge for design of functional crystalline phases.[2] The understanding of intermolecular interactions promoting non-centrosymmetric space groups over centrosymmetric ones can lead to rational solutions in materials design. The exemplar case for the analysis of differences in chemical bonding between centric and acentric phases is the existence of at least two different crystal structures of the same material. In this work, we present two concomitant polymorphs of 2-aminopyridinium sulfamethoxazole, which crystallize in Pca21 and Pbcn space groups. Intermolecular interactions present in both materials were analysed using Baders QTAIM theory[3] as well as fingerprint plots[4] and NCI index[5]. The differences and similarities between two polymorphs are discussed and compared with respect to intermolecular interactions found in both structures.

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Change of Organolithium Compounds in the Course of Reactions

P23

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Organolithium compounds form aggregates in solution, which can be devided by the use of LEWIS bases. [1] In addition, chemical reactions and reactivities of lithium alkyls are significantly influenced by the proximity of reactants, which is called the Complex-Induced-Proximity effect (CIP-effect). [2,3] Therefore the deaggregation of the tert-butyllithium tetramers (1) [4] with tetrahydrofuran (2) or N,N,N',N'-tetramethylethane-1,2-diamine (3) leads to side reactions with the additives. The cleavage of lithiated 2 to ethene and lithium ethenolate [1] could be observed in aggregates 6 and 7. Lithiated TMEDA (3) undergoes a β-elimination [2] to the lithium dimethylamide observed in aggregate 7.

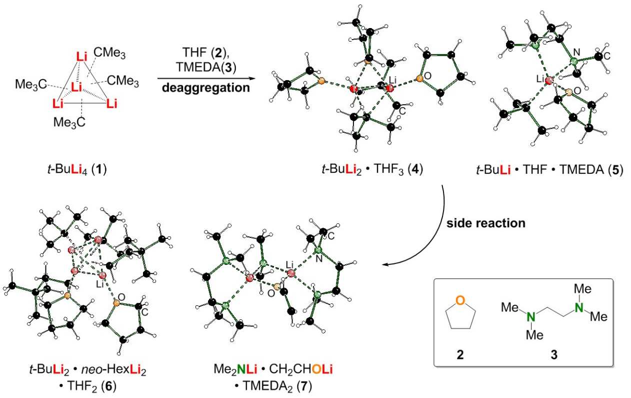

Figure 1: Deaggregation and side reactions of tert-butyllithium (1) with THF (2) and TMEDA (3).

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P24

Combined high resolution X-ray and DFT Bader analysis to reveal a proposed Ru-H $\cdots$ Si interaction in Cp(IPr)Ru(H)$_2$SiH(Ph)Me

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Unusual interactions of hydrogen with transition metal compounds are of great importance in organometallic chemistry. For example, 3 centre 2 electron (3c-2e) agostic bonds are of great importance as they can be seen as a resting state in the hydrogen abstraction reactions for example. They have transitioned from being somehow a bit obscure to meanwhile fully accepted bonding modes of hydrogen. The concept of unusual interactions of hydrogen with transition metal compounds has also been expanded from traditional C-H based agostic bonds to Si-H based ones. Another interesting example of the interaction between a transition metal, silicon and hydrogen was recently published by us, where the original work was conducted by G.I. Nikonov.[1,2] He proposed a Ru-H $\cdots$ Si interaction in Cp(IPr)Ru(H)$_2$SiH(Ph)Me (1) which was mainly based on NMR spectroscopy. We recently performed a low temperature, high resolution x-ray analysis of a similar compound in combination with both experimental and theoretical QTAIM analysis. Our results clearly did not furnish a bond path between the Ru-H and the Si atoms.[3] In this poster we are reporting the new results of a combined, high resolution, low temperature x-ray analysis of 1 in combination of the neutron structure to ascertain the exact location of the Ru-H atoms. Our experimental results will be compared with detailed DFT calculations utilizing different functionals with and without Grimme's dispersion correction. Particular attention is paid whether or not a Ru-H Si interaction does exist but also a rather unusual bond pattern of one of the Ru-H (cf. Figure 2)

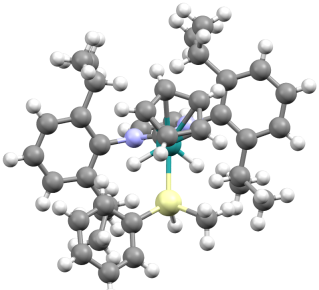

*Figure 1: x-ray structure of **1***

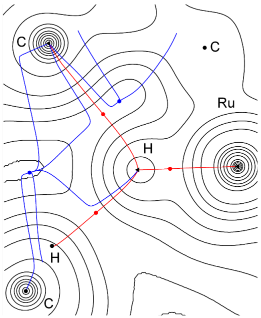

*Figure 2: Electron density plot of **1**, plane through Ru, H and C*

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Experimental Charge Density study of the pharmaceutical cocrystal Isoniazid:5-Fluorocytosine

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In this work is described the experimental charge density (CD) study of a new solid form derived of the combination of two used widely active pharmaceutical ingredients (API): the antimetabolite prodrug 5-Fluorocytosine (5-FC) and the tuberculostatic drug Isoniazid (INH). The result of the combination of these molecules yields the formation of a pharmaceutical cocrystal (5-FC:INH), which is stabilized by the supramolecular synthon held by strong hydrogen bond of NH···N type, between the amine and imine fragments of the 5FC molecule and the hydrazide fragment of INH molecule. The crystal structure of this cocrystal is already known in room temperature, but no charge density study has been published as far.[1] In that vein, we have carried out a single-crystal X-ray diffraction experiment in high resolution ($\sin(\Theta_{max})/\lambda=1.15$ Å^{-1}) at 150 K, in a conventional diffractometer equipped with a X-ray source of Molybdenum rotating anode. After the collection and processing data, Hasen & Coppens aspherical multipolar refinement was proposed,[2] in order to determine the CD distribution of this cocrystal. The good quality of the data allowed to carry out a topological analysis and electron density partitioning using the Quantum Theory of Atoms in Molecules (QTAIM) analysis. Insights about the intermolecular interactions, the presence of fluorine atom, and crystal lattice energy were some of the aspects which were assessed from the multipolar refinement model.

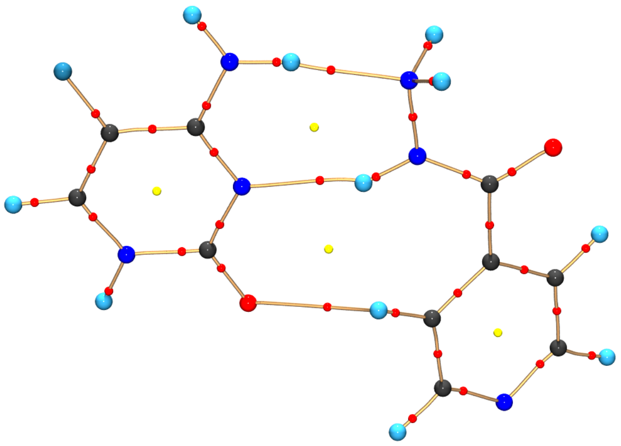

Figure 1: Molecular graph with the bond critical points (BCP) and bond paths (BP) of the 5-FC:INH cocrystal

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P26

Mechanistic Insights into Isomerization Processes of Dinuclear Sulfido Complexes Based on DFT Calculations

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A series of dinuclear tantalum(IV) alkylated sulfur complexes, $[\mathrm{Ta_2}(\eta\mathrm{C_5}-\mathrm{C_5Me_5})_2\mathrm{R_2}(\mu\text{-}\mathrm{S})_2]$ (R = Me 1, CH2Me 2, $\mathrm{CH_2SiMe_3}$ 3, $\mathrm{C_3H_5}$ 4, Ph 5), were synthesized in which the presence of the cyclopentadienyl ligand significantly enhances the synthesis, characterization and further reactivity of the complexes formed. Additionally, the analogous dinuclear titanium(IV) alkylated sulfur complexes $[\mathrm{Ti_2}(\eta\mathrm{C_5}-\mathrm{C_5Me_5})_2\mathrm{R_2}(\mu\text{-}\mathrm{S})_2]$ (R = $\mathrm{NMe_2}$ 6, $\mathrm{CH_2SiMe_3}$ 7, Ph 8, $\mathrm{CH_2Ph}$ 9) have been obtained. All complexes were spectroscopically characterized and, in case of 1 and 5-9, crystallographically as well. Single crystal X-ray diffraction studies showed in all cases a trans disposition of the alkyl/aryl/amido substituents.

Trans-cis isomerization reactions were evidenced in some of the dinuclear complexes, and DFT calculations enabled us to propose mechanisms for these unexpected processes. Thus, for instance, the trans-cis isomerization for $[\mathrm{M_2}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{R_2}(\mathrm{R_2}(\mu\text{-}\mathrm{S})_2)_2]$ complexes occur photochemically in case of 1 and thermally in compounds 2 and 6. The presence of β-hydrogen atoms in 2 were considered and it was evaluated the path through β-elimination.

DISSPK - novel derivative of tempo radical: crystal structure and Hirshfeld surface analysis

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2,2,6,6-Tetramethylpiperidine-1-oxyl radical (TEMPO) and its derivatives belong to a very interesting group of chemicals in terms of their wide variety of applications. Over the years they have gained significant interest due to their functionality as catalysts [1] and their ability to exhibit both ferromagnetism and antiferromagnetism at low temperatures [2]. The TEMPO-related compounds are also interesting object of crystallographic research with a great relevance in organic synthesis [1], quantum computing [3] and polymer synthesis [4].

In this work we focused on the crystal structure of TEMPO radical and its novel derivative DISSPK. In both cases X-ray diffraction measurements using Agilent Technologies SuperNova Dual Source diffractometer with Cuκ_α radiation at 100 K were made.

Although the crystal structure of TEMPO radical is known since 1974 [5] the DISSPK compound has not been characterized yet. In case of both investigated systems the piperidine rings adopt chair conformation with two methyl substituents on each side. Crystallographic studies revealed that their supramolecular architecture in crystal exhibit different structural features. In this presentation those differences will be discussed in details along with detailed characterization of the most significant intermolecular interactions (e.g. hydrogen bonds) occurring in their crystal networks. Above-mentioned characterization includes also complementary Hirschfeld Surface analysis.

As a next step of crystallographic studies of DISSPK radical, high-resolution single crystal data collection will be undertaken in order to receive knowledge about quantitative distribution of electron density in its crystal. We hope to establish more accurate and precise geometry that will allow us to get - using theoretical periodic calculations additional knowledge concerning spin density distribution and occurrence of magnetic interactions in the crystal lattice of investigated system.

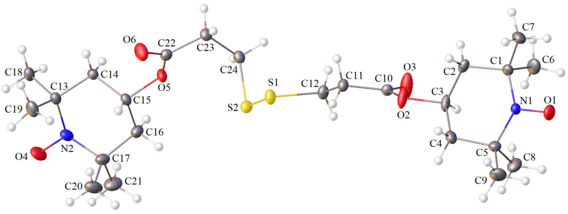

Figure 1: The asymmetric unit of the crystal lattice of DISSPK showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The H-atoms are shown as small spheres of arbitrary radius.

"This research was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by European Union from the European Regional Development Fund under the Operational Programme Innovative Economy, 2007 2013. The data collection was accomplished at the Core Facility for Crystallographic and Biophysical research to support the development of medicinal products sponsored by the Foundation for Polish Science (FNP)."

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P28

Non-Spherical Form Factors and Crystallographic Refinement

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Durham University, OlexSys

Standard crystallographic refinement relies on tabulated form factors[1] carefully calculated and confirmed functions derived from single-atom electron densities. These spherical form factors have been used for decades, but are necessarily an approximation to the true form factors. My recent work has focused on the viability of using alternative form factors of improved accuracy, such as from quantum mechanical calculations.

In its simplest iteration, the form factor is the Fourier transform of the electron density associated with a particular atom. In the standard tables, this electron density is taken as a spherically symmetric function around an atom, leading to a spherically symmetric form factor dependent only on the magnitude of the vector ha*+kb*+lc*. However, in reality, bonding and other factors lead to an electron density which is influenced by its neighbours that is, the all atoms of the whole molecule affect the electron density, and thus, in turn, the form factor.

In this contribution, I cover the theoretical backing behind the use of such form factors, consider the information required, and discuss the adjustments and considerations made to the crystallographic refinement process needed to properly employ this information. Additionally, I will mention further investigations needed into the limits of viability of these form factors, the limits of inaccuracy of the model under which they become less accurate than standard spherical approximations.

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The $(O_2)_4$ tetramer in the light of the Local Spin Analysis

P29

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Phase transition of O_2 under extreme pressure conditions has driven a lot of attention during the last years due to the drastic changes in its magnetic and spectroscopic properties[1]. During the transition from δ to ϵ phase, there is a magnetic collapse and O_2 loses its antiferromagnetic character. Recently [2], the tetrameric model system $(O_2)_4$ has been studied by means of CASSCF ab initio calculations combined with quantum chemical topological analyses, namely Interacting Quantum Atoms (IQA) and electron distribution functions (EDFs). The aim was to evaluate these descriptors along the phase transition in order to rationalize the observed spectroscopic and magnetic behaviour of ϵ-o2. The analysis was performed from CASSCF calculations with minimum active space (8 active orbitals and 8 electrons). In this work we revisit the $(O_2)_4$ tetramer by using CASSCF/DMRG wavefunctions including much larger active space, in order to better capture dynamic correlation effects. In addition, we study the evolution of the spin structure of the O_2 moieties in the light of the so-called local spin analysis [3], which is specifically designed to capture effective local spin moieties within the molecule and their couplings. Such improved analyses are feasible by making use of pySCF in combination with our in-house code APOST-3D, for which appropriate interfaces have been built for the present purpose.

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P30

In-situ single crystal X-ray diffraction studies of proton transfer behaviour under an applied electric field on I19, Diamond Light Source

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Hydrogen atoms (H-atoms) can exhibit the chemical phenomenal of transfer behaviour when part of a hydrogen bond (HB). This behaviour occurs related to the shape of the potential energy for H-atom motion for certain types of hydrogen bonds.[1] Depending on the HB characteristics, this transfer may be static or be susceptible to external stimuli, such as temperature or pressure.[2, 3] For the non-static case, this may be in the form of proton migration,[4] including a gradual shift in H-atom position as a function of temperature, or proton disorder, hopping between sites in the HB.[5] In the solid-state, proton transfer behaviour can lead to a number of potentially useful material properties.[3, 6] In ferroelectrics, proton shuttling may occur under an applied electric field facilitating the reversal of material polarity[7, 8] or transitions between electric (ferro-para) states.[9] Materials such as these are of interest offering applications in sensing and data storage. The electric properties of materials are typically determined from measuring dielectric constants,[10] polarisation-electric field loops,[11] whilst structural effects under applied fields are elucidated using techniques such as small angle neutron scattering,[12] computationally via calculations[13] or by Bragg peak mapping.[14, 15] In this work, we showcase a new electric field set up on beamline I19, Diamond Light Source (U.K.) for in-situ single crystal X-ray diffraction measurements allowing full structure elucidation under an applied field. We describe the set-up and explore its potential in the study of proton transfer behaviour with the aim of discovering new candidates for electric field applications. We investigate a number of polar and non-polar materials containing short hydrogen bonds across which interesting temperature/pressure dependent proton transfer behaviour has previously been found.[3, 16] For each system, we apply fields of ca. 2 kV (600 V/mm) and measure the structural response in-situ.

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Origin-independent energy-based decomposition of nonlinear optical properties

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Great attention has been paid to the materials characterized by a large nonlinear optical response, as they are commonly used in optical communication technology. Historically, there has been great interest in decomposing the global value of the NLOP (e.g. the molecular polarizability) into contributions of individual atoms or functional groups. Transferable group polarizabilities give insight about the value of the NLOP, and also would allow for their prediction. The problem that arises with such decompositions is that the atomic contributions obtained from the straightforward decomposition of the NLOPs are origin-dependent. In 1990, Bader[1] showed that the molecular polarizability can be expressed as a sum of atomic (intrinsic) origin-independent contributions, and a global charge-transfer term. However, a recent study of Mei et al.[2] has shown that, for general molecules, the global charge-transfer term typically represents 60 to 90overall value of the molecular polarizability. Certainly, a better solution to the problem is yet to be found.

In this work, we discuss how the NLOP can be decomposed into one- and two-center contributions (atoms or molecular fragments) in such a way that the origin-independence of the terms is ensured. Thus, the one-center terms are associated to intrinsic contributions, whereas the two-center ones will account for the interplay of the defined fragments to increase or decrease the overall NLOP. The transferability of the terms will be explored for a set of molecules, and the results obtained will be compared with previous decomposition schemes.

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P32

Quantum-chemical study of cytotoxicity of antineoplastic drug camptothecin and its derivatives

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Camptothecin, (S)-4-ethyl-4-hydroxy-1H-pyrano [3,4:6,7]-indolizino-[1,2-b]-quinoline-3,14-(4H,12H)-dione, inhibits enzyme Topoisomerase I and its derivatives are used in the pharmaceutical industry as anticancer drugs. The aim of our study is to compare the cytotoxicity of their possible reaction sites according to the ability to form complexes with copper (II) ion and the extent of electron/spin density transfer from the ligand molecule to copper in analogy with the study of antioxidants [1]. The structures of lactone form of camptothecin (Fig. 1 (a)), its commercially used derivative irinotecan (Fig. 1 (c)), its active metabolite SN38 (Fig. 1 (b)) and their complexes with copper (II) were optimized at B3LYP/6-311G* level of theory using the Gaussian09 software [2]. Electronic structures of the formed complexes were evaluated in terms of QTAIM (Quantum Theory of Atoms-in-Molecule) topological analysis of electron density [3] and NBO population analysis [4].

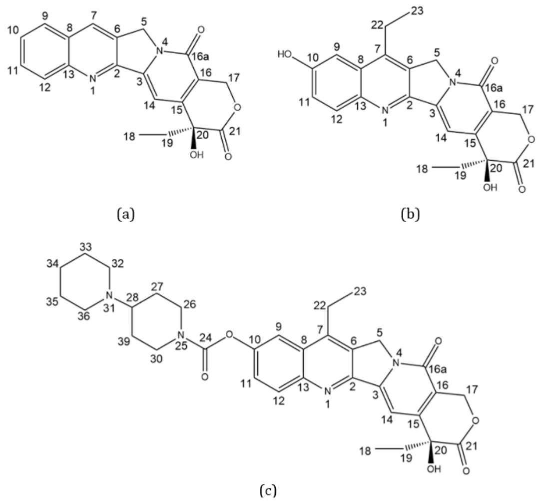

Figure 1: Atom numbering of camptothecin (a), SN38 (b) and irinotecan (c)

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Superelectrophilic Anions: Theoretical Understanding of Noble Gas Binding by $[B_{12}X_{11}]^-$

P33

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Closo-dodecaborate dianions $[B_{12}X_{12}]_2^-$ (X=H, (pseudo-)halogen) are highlystable multiply charged anions (MCAs) which are known to act as very weakly coordinating ions[1] and also exhibit properties promising for medical applications, e.g. for boron-based neutron capture therapy of tumors.[2] Collision-induced dissociation (CID) in ion traps of mass spectrometers allows for fragmentation of these ions yielding $[B_{12}X_{11}]^-$ monoanions. Experimentalists observed the formation of gas-phase adducts of these fragment ions with residual ion trap gases like H_2O and even N_2 which usually only react with strong electrophiles. We decided to explore this unexpected anion reactivity in a theoretical study: The vacant boron constitutes a positive binding site in an overall negatively charged anion and the LUMO is mainly localized at this position. This explains the strong electrophilicity, although the ion is negatively charged. The ion is even reactive enough to bind noble-gases at room temperature, e.g, Kr and Xe can be bound by $[B_{12}Cl_{11}]^-$[3] a reaction never observed for an anion previously.

This contribution presents computed properties of some representatives of $[B_{12}X_{11}]^-$ monoanions. Natural Population Analysis (NPA) predicted the highest atomic charge on the vacant boron for X=CN. Motivated by this result, the synthesis of $[B_{12}(CN)_{12}]_2^-$ was successfully performed. In CID experiments, $[B_{12}(CN)_{11}]^-$ was generated, a monoanion capable of even binding Ar(!) at room-temperature. We present a bonding analysis of the first B-Ar bond in an anion in direct comparison to B-Ar bonds formed with highly electrophilic cations known from literature. Electrostatics and dispersion forces play a significantly larger role for the Ar binding strength of the anion, compared to cations with similar Ar attachment enthalpies, as indicated by Energy Decomposition Analysis (EDA).[4]

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P34

Characterization of Ligand Non-Innocence: The Case of the Redox-Induced Electron Transfer Processes

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Complexes that possess one or more non-innocent ligands that can be isolated in several oxidation states may exhibit the so-called redox-induced electron transfer (RIET) process [1]. For instance, the dinuclear compounds exhibiting a bridging tetraoxolate ligand can experience redox reactions where the ligand is reduced and, at the same time, both transition metal centers are oxidized. The oquinone o-semiquinone catecholate redox series (from more oxidized to more reduced) also allow RIET processes in mononuclear complexes exhibiting two or more of this type of ligands. For example, the one-electron reduction of [NiII(3,6-dbsq)2] (dbsq=3,6-di-tert-butyl-1,2-benzosemiquinonate) leads to an actual oxidation of the metal center to NiIII and a simultaneous two-electron reduction of the ligands[2]. In many cases, the nature of the RIET process is not well established, as the proper characterization of the electronic structure of this type of compounds in terms of oxidation states is very challenging either experimentally nor computationally.

In this work, we first carry out benchmark calculations with different KS-DFT functionals and compare the ground state energies obtained with the experimentally reported[1]. Afterwise, we apply the inhouse developed effective oxidation states (EOS) analysis[3,4] to unravel their electronic structure. From the results obtained, we show the hability of the method for assigning oxidation states of the metal center and ligands irrespective of the spin state, identifying and characterizing possible RIET processes in the oxidation and reduction reactions studied.

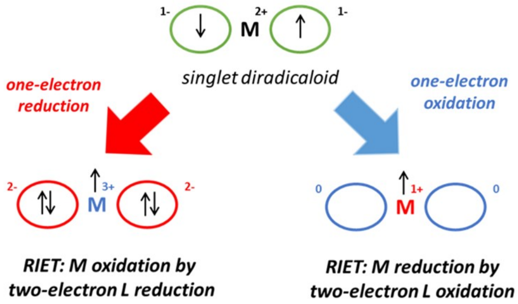

Figure 1: Representative scheme of the RIET phenomena in a monometallic transition metal complex

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Stability analysis of molecules containing transition metals at extremely high oxidation states with oxide and nitride ligands.

P35

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For many years the +VIII oxidation state has been considered as the highest energetically stable in the transition metals, as it is present in Ru(VIII) and Os(VIII) compounds both in gaseous and solid state.[1] The best known examples are tetroxides stoichiometries with tetrahedral geometry however the mixed oxide-nitride osmium anion in neutral salt is also known for over 150 years.[2] In recent years researchers investigated new compounds having the higher than (VIII) oxidation state, which can be labelled 'extreme'. In 2010 thermochemical stability of oxidation level +IX in [IrO4]+ cation was theoretically predicted by Himmel et al.[3] using electronic structure calculations. These results inspired scientist in further research four years later the abovementioned cation was reliably detected using time-of-flight photodissociation spectroscopy.[4] Besides this success also other systems has been studied i.e. Pt(X)[5], Pu(VIII)[6] or U(XII).[7] Present work focuses on the stability of iridium and platinum compounds in stoichiometries different than tetroxides trying to point where are the limits of increasing the oxidation state in late transition metals. Theoretical studies were done utilizing density functional theory (DFT) and zeroth-order regular approximation scalar relativistic Hamiltonian (ZORA) in order to find equilibrium structures with different multiplicities and the transition states between them.

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P36

Parallelised Triangulated Zero-Flux Bader Surfaces

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One of the most basic quantities that chemists are interested in is the charge on an atom in a molecule: it can give information concerning the ionicity or covalency of a chemical bond and hence gives information concerning reactivity. Zero-flux surfaces of the electron density define regions in space surrounding an atom which may be used to define charges[1] and moments. These can develop classical force fields for molecular dynamics simulations. Several groups have produced algorithms to obtain these surfaces, including triangulation-based methods[2], analytical approaches[3] and spatial decomposition methods[4]. All of these methods pursue a similar goal of fast and accurate determination of the zero-flux surfaces. We propose a new distributed memory parallelised approach, by modifying previously utilised grid-based methods[4], in order to utilise more computational power to achieve the zero-flux surfaces efficiently. In addition to this, we propose a new triangulation method for visualising the zero-flux surfaces. Examples of the zero-flux surfaces will be shown along with timings for the new method. Acknowledgements: This research is supported by an Australian Government Research Training Program (RTP) Scholarship.

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The benefits of K_β radiation

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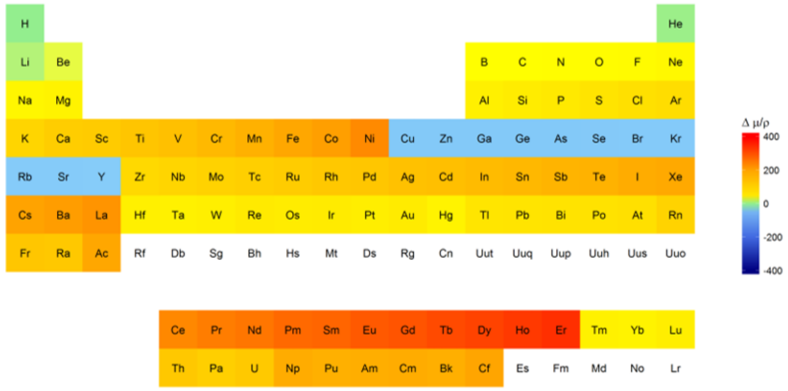
K_β is much weaker in intensity than K_α and therefore practically not used for single crystal diffraction experiments. Most X-ray labs are equipped with Mo-K_α and Cu-K_α sources, but in some cases an intermediate wavelength would be desirable. Such a compromise can be provided by Cu-K_β radiation ($\lambda = 1.39$ Å). Compared to Cu-K_α ($\lambda = 1.54$ Å) the amount of available data is increased by more than 35 per cent and the absorption significantly lowered. This can also be achieved with Mo-K_α ($\lambda = 0.71$ Å), but the quantum efficiency of the diffraction is much higher for Cu-K_β. Another general advantage of K_β radiation compared to K_α is the absence of $\alpha1/\alpha2$ splitting at higher diffraction angles. This leads to a relative improvement of the $I/\sigma(I)$ at higher resolution. Our investigations have shown that in many cases almost identical or even better quality structures could be obtained by using the Cu-K_β wavelength compared to either Mo-K_α or Cu-K_α. We even encountered some structures that could only be refined properly when Cu-K_β data was applied.[1]

Absorption Mo-Kα vs. Cu-Kβ



Differences in mass attenuation coefficients (cm^2/g).

Figure 1: Between Cu and Y Cu-K_β is less absorbing than Mo-K_α.

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P38

X-ray constrained extremely localized molecular orbitals for the study of interactions in crystals

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“Giulio Natta”

Intermolecular interactions are crucial for the formation of crystals and their properties. These properties are often rationalized in terms of the electron density distribution and its derivatives, while molecular orbitals (MOs) are less frequently analysed. Semi-experimental MOs can be obtained with the X-ray constrained WFN[1] method. In addition, MOs can be constrained to be localized on given fragments of molecules (X-ray constrained, extremely localized molecular orbitals (XC-ELMOs[2])). This localization allows for a more straightforward chemical interpretability. Furthermore, ELMOs can be stored in proper libraries[3] as electronic LEGO building blocks to reconstruct electron densities and refine crystallographic structures of large systems. In recent studies we have decided to investigate the possibility of exploiting XCELMOs to interpret crystalline interactions at an orbitalic level and not only based on the global electron density. The goal is to see which orbitals are involved in an interaction and how they change in different crystalline environments.

To accomplish this task we examined NTA-B, a compound which is of interest due its carbonyl-carbonyl interactions, which might lead to polymerization at high pressure via an addition reaction. We performed X-ray diffraction measurements up to 16 GPa, as well as geometry optimizations with Crystal17 up to 50 GPa that provided unit cell lengths and interaction distances well in agreement with the experimental results. The shortest interaction distance of two neighbouring carbonyl groups decreases from 2.84 to 2.13 Åupon going from 0 to 50 GPa; however, we have not observed any evidence for polymerization. Thus, in order to further examine the interactions, we analysed the electron densities resulting from the performed periodic calculations (mainly focusing on properties at the bond critical points) and we studied the XC-ELMOs localized on the carbonyl groups and their changes due to the interactions.

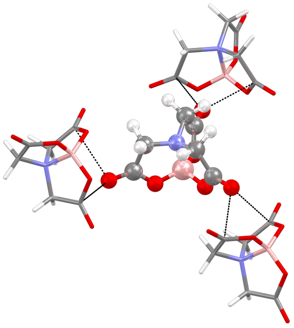

Figure 1: Carbonyl-carbonyl interactions of Boron-Nitrilotriacetate (NTA-B)

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Naphthalimide-Derived Potential Spin Crossover Devices: A Quantum Crystallography Study on Cooperativity through $\pi \cdots \pi$ Stacking Effects

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The numerous interesting properties of spin crossover (SCO) active materials, combined with the current trend to develop molecular electronics and machines has resulted in a dramatic increase in the exploration of compounds exhibiting this phenomenon. Modifying the solid-state interactions between metal complexes is essential for controlling the nature of the SCO event. Previous work has investigated the effect that hydrogen bonding and halogen bonding has on the cooperative nature of SCO behaviour, which proposed that other supramolecular interactions can also alter the nature of this cooperativity1. The focus of this work is on utilising $\pi \cdots \pi$ interactions to systematically modify the SCO transition. Naphthalimide-based functional groups(Fig 1) were identified as the target for this project because of the long-range ordering achieved through π-stacking and the interesting photophysical properties of the 1,8-naphthalimide moiety2. The electron deficient 1,8-naphthalimide systems have not only been utilised as ligand scaffolds for metal complexes, but also investigated as non-coordinating anions to incorporate this structure directing group into the lattice. While systematically varying the nature of substituents on the naphthalimide backbone, we will use quantum crystallography methods to develop an understanding of how subtle changes in electron withdrawing/donating substituents influence the nature of interactions, and accordingly how $\pi \cdots \pi$ interactions influence spin crossover properties. The calculation of the intermolecular interaction energies has resulted in an array of information that provides detailed structure-function relationships which can be used to increase control over the behaviour of SCO materials in a novel manner.

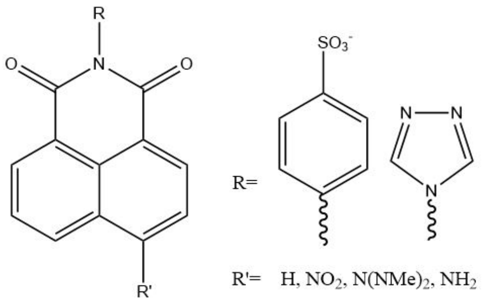

Figure 1: General structure of the Naphthalimides showing the substituents used to control the electronic nature of the species

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P40

Study of Charge-Shift Bonding in Transition-Metal Complexes

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The chemical bond is one of the most important concepts in chemistry. Recently, in addition to the ionic and covalent bonding, the charge-shift bond[1] (CSB) has been proposed in the context of the valence bond theory. As CSB is closely related to situations with strong Pauli repulsion, and transition-metals use their compact inner d-orbitals for bonding, a large role of CSB for transition-metal systems is conceivable.[2] In this work, a systematic study of the occurrence of CSB in first-row transition-metal complexes is reported, using on one side various direct energy decomposition analyses and on the other side indirect measures from real-space approaches (e.g. ELF, electron density). By systematically varying ligand types, total charge, oxidation state and metal centers, we aim at a comprehensive understanding of the role of CSB in transition-metal ligand (and metal-metal) bonding.

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Experimental and Theoretical Studies on Heteroleptic Nickel complexes of Unsaturated Hydrocarbons

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The semihydrogenation of acetylene to ethylene can be catalyzed at the surface of Hume-Rothery alloys like Fe/Al[1], Ni/Ga[2] or Ni/Zn[3] as cost-efficient substitutes for the industrially established Pd/Ag catalysts.[3] However, detailed investigations of the underlying mechanism and the exact influence of e.g. element distribution on catalytic activity and selectivity are hampered by the intrinsic difficulty of mechanistic studies of heterogeneous surface reactions. Thus, molecular models, resembling the catalytically active surface, are highly desirable. For more than a decade, we have been developing synthetic access to Hume-Rothery-like intermetallic complexes of the general formula LnTMa(ER)b (TM = transition metal; L = 2 electron donor ligand; E = Al, Ga, In, Zn).[4] The poster will discuss new synthetic routes to all zinc coordinated nickel complexes with unsaturated hydrocarbons (UHC) in the ligand sphere mimicking acetylene and ethylene bonding to the catalyst surface (Figure 1). Structure and bonding situation of such complexes will be discussed especially in the light of semihydrogenation mechanisms. The experimental data are supported by theoretical calculations on the DFT level of theory focusing on energy decomposition analysis (EDA) with the natural orbital for chemical valence extension (NOCV) as well as QTAIM to investigate the bonding situation of such compounds.

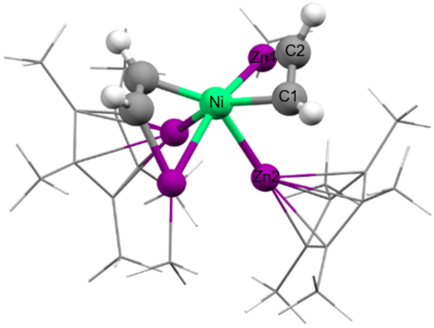

Figure 1: Calculated molecular structure of the surface model compound $[\mathrm{Ni}(\mathrm{ZnCp}\cdot)_2(\mathrm{ZnMe})_2(\mathrm{C_2H_2})_2]$ (BP86-D3/def2-TZVPP). The Cp* and Me moieties are depicted in wireframes for clarity. Color code: Ni: green, Zn: purple, C: grey, H: white.

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P42

The Complex Route to Iridoid Biosynthesis - A Mechanistic Overview

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Iridoids are a large class of bicyclic monoterpenoid phytochemicals which were first isolated from ants of the genus iridomyrmex. The common intermediate in the biosynthesis of all known iridoids is the nepetalactol.[1] Unlike other terpene biosyntheses, they are not formed by a reaction sequence involving carbocations as key intermediates. Instead, they are believed to be formed from pericyclic reactions, i. e. hetero-Diels-Alder reactions. However, the pathway which leads to the formation of iridoids is still under debate. The question remains, if it is really a pericyclic reaction or if it might be a step-wise pathway or an even more complex, off-MEP pathway.[2,3,4,5] A combined computational and experimental approach is used to examine the unresolved mechanistic questions. On the computational side, DFT-calculations to evaluate both, the PES and molecular dynamics are used to examine the different possible reaction routes (see Scheme 1). These results will be discussed on the poster.

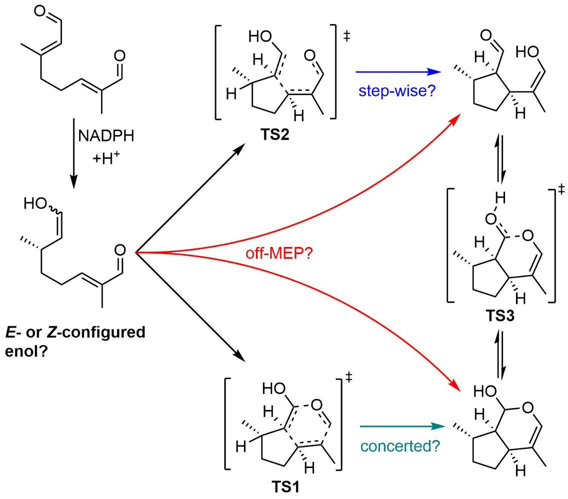

Figure 1: Scheme 1: Summary of the mechanistic aspects of the nepetalactol formation that were discussed. More detailed information will be discussed on the poster.

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Simple approach for the evaluation of the reactivity induced by oriented external electric fields

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A typical approach to increase reaction rates and control the chemo or regio selectivity is the addition of a specific catalyst in the reaction mixture. The catalyst usually interacts with the substrate and enhances its reactivity and/or modifies the selectivity of the reaction. However, there are other possibilities to control the same features on a reaction at will, such as the application of oriented external electric fields (OEEF), an approach that has been studied both experimentally[1] and theoretically.[2,3]

The simulation of the reaction energy barriers under OEEFs is computationally very demanding since requires the determination of the equilibrium geometries and vibrational frequencies of the reactants and transition states (TS) at several strengths of the external electric field. For this reason, it was suggested an approximation to compute the field dependent energy barriers in terms of the dipole moments of the reactants and TS and the strength of the electric field (Eq. 1).[4] Although this approximation is computationally very efficient, unfortunately its accuracy is sometimes not good enough to predict the OEFF induced reactivity. We have proposed[5] improving this approach including in the expansion the linear polarizabilities of the reactants and TS (Eq. 2).

We have studied the electric field induced reactivity of several systems such as the 1,3-dipolar reaction between diazomethane and 1-methoxyethylene, the Diels-Alder reaction between cyclopentadiene and maleic anhydride, and [3+2] cycloadditions between azomethine ylides. In some cases, the approximation based only on the dipole moments leads to reaction barriers with deviations larger than 5 kcal/mol respect to exact values. On the contrary, the errors in the barriers obtained with our approach are in the range of 0.1-1 kcal/mol. Therefore, our approach is far more reliable and still computationally very cheap.

$$\Delta E^{\ddagger}(F) = -(\mu_{TS} - \mu_S)F \quad Eq(1)$$

$$\Delta E^{\ddagger}(F) = -(\mu_{TS} - \mu_S)F - \frac{1}{2}(\alpha_{TS} - \alpha_S)F^2 \quad Eq(2)$$

Eq 1. Dipolar approach and Eq 2. Our approach for the evaluation of OEEF.

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P44

Quantification of pi-bond strength: Are similar results obtained through various approaches?

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pi-bonds are formally defined by the lateral overlap of orbitals on neighbouring atoms maintaining a nodal plane characterised by zero electron density in the plane perpendicular to the overlap, containing the nuclei. These bonds may be covalent, as in the simple case of ethylene $CH_2{=}CH_2$, or dative, as in the Dewar-Chatt-Duncanson model where the pi-retrodonation from a metal center to a ligand forms a partial pi-bond. However, there is no clear physical basis for determining a straightforward and unique method to quantify pi-bond.[1] From a chemical point a view, the presence of a pi-bond between two atoms connected by a pi-bond induces a shortening of the bond, a stronger binding energy, and the presence of a significant energy barrier to rotate around this bond. It is not currently clear whether these different features are equivalent to define the strength of a pi-bond. In this work, we have investigated the pi-bond formed between an N-heterocyclic carbenes (NHC) and the $BH_2{}^+$ borenium moiety. The NHC-borenium complexes are known to activate H_2 and to catalyse hydrogenation reactions,[2] and their activity has been shown to be related to their Lewis acidity.[3] Assuming that the strength of the $NHC{-}BH_2{}^+$ pi-bond modulate the Lewis acidity at the borenium moiety,[4] we have selected a set of 37 NHC for which the strength of the $NHCBH_2{}^+$ pi-bonds has been computed. To that end, several empirical indicators of the pi-bond, including bond length, energy barrier of rotation along the bonding axis and IR C-B stretching frequency, have been computed using DFT calculations. Furthermore, several energetic and electronic features of pi-bonds have been computed using NBO, EDA-NOCV and QTAIM approaches. A thorough comparison of these data allows correlations to be established only for some of the computed properties, thus making it possible to gain a unified and quantitative measurement of this fuzzy chemical concept.

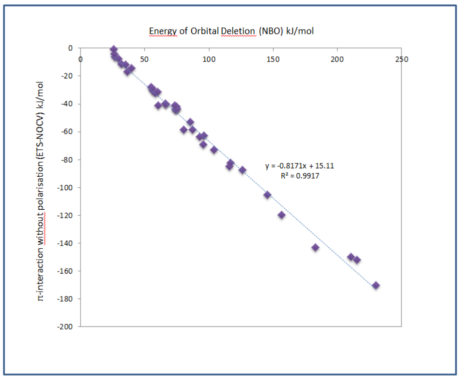

Figure 1: Correlation between Energy of Orbital Deletion computed using NBO Analysis and pi interaction energy without polarisation computed using ETS-NOCV

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Stabilization of sulfur-substituted lithium compounds

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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 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 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.

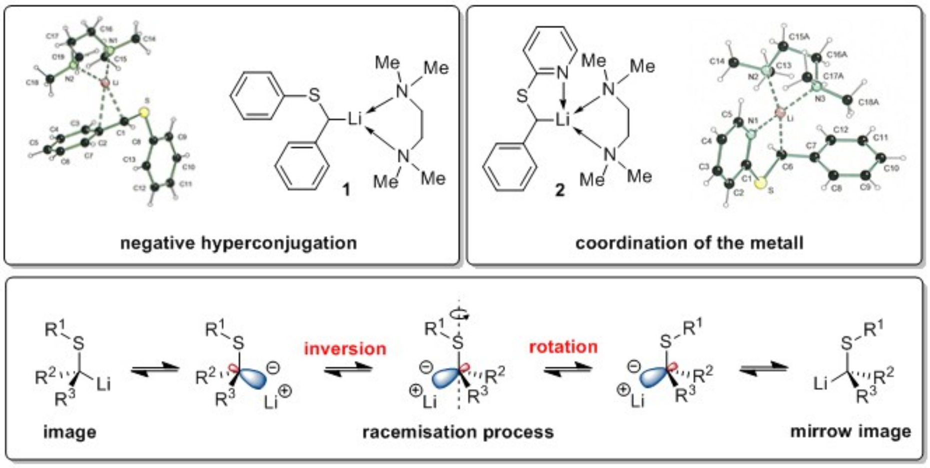

Figure 1. Crystal structures and racemisation process of sulfur-substituted lithium compounds

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P46

Recent progresses in theoretical investigation on halogen bonding

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Halogen bond (XB) is a non-covalent interaction [1] that occurs between an electrophilic region, associated with a halogen atom (X) in a molecule, and a nucleophilic region (B) in another, or the same, molecule according to the scheme R-X$\cdots$B. The ElectroStatic Potential (ESP) mapped on an isosurface of electron density shows a positive spot in the region outward the halogen atom along the R-X bond direction (the so-called sigma hole) and a negative belt around the halogen perpendicular to R-X. The presence of the sigma hole, able to interact with the nucleophilic region of B, imposes a linear geometry for the interaction [2]. It was previously reported that in protein-ligand complexes XB and hydrogen bond (HB) are geometrically perpendicular and energetically independent on each other [3]. In other words, in R-X$\cdots$B$\cdots$H-R interacting systems the presence of XB does not perturb the geometry and energy of HB and vice versa. We have however demonstrated that this is not true when B is the pi-system of benzene, using XCN as XB donors and the water molecule as HB donor. When R-X and R-H interact on either sides of the benzene ring, we observe in fact an increase of the binding energy of both XB and HB interactions, suggesting that they cannot be considered independent on each other. Another aspect here discussed concerns the problem of describing the anisotropy of the ESP around the halogen atom by means of Molecular Mechanics (MM) force fields. Traditional approaches, based on atom centred charges, do not allow to reproduce such anisotropy and then to describe XB. We have proposed a strategy [4,5] to overcome this limitation, based on the introduction of pseudo-atom(s) properly placed around the halogen atom, which allows to reproduce the sigma hole and the full anisotropy of the ESP around the halogen itself, both for the heavier (I and Br) halogens [4] and for chlorine [5].

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Metal-organic Frameworks (MOFs) as prospective hybrid materials in optical applications

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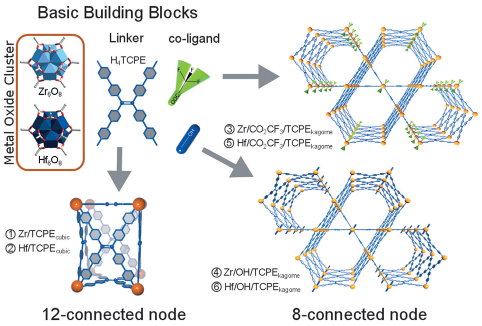

Figure 1. Basic building blocks and structures of the reported zirconium and hafnium MOFs with the H4TCPE (tetrakis[4-(4-carboxyphenyl)phenyl]ethylene) linker molecule (1-6). [6]

Optics, as a branch of physics, deals with the spreading of light and its interaction with matter. It can be divided into two sub-fields: linear optics and nonlinear optics. Linear optics focus on processes, where the intensity of the output light shows a linear dependency on the incoming light intensity, whereas in nonlinear optical (NLO) systems this property is violated.[1] These effects have been studied in several material classes including a variety of different organic dye molecules as well as inorganic particles.[2-3] However, often these material are limited towards their applicability due to unfavourable inherent properties such as toxicity and restricted tunability of wavelength.[4] Inorganic-organic solid-state hybrid materials (coordination polymers (CP), metal-organic frameworks) have the great potential to overcome those problems. One prominent example are their luminescence properties, since the incorporation of chromophore linker molecules into the solid material increases the emission properties by reduction of non-radiative energy decay. Additionally to this significant advantage of MOFs and CPs an uncontrolled aggregation of chromophores in a highly concentrated solutions leading to fluorescence quenching [5] is prevented while a high chromophore density is enabled. Our group is focussing on MOFs and their photophysical properties as well as processes of energy transfer inside the materials. Our approach is to synthesize organic dye molecules as chromophores, incorporate them in solid-state hybrid materials and investigate their properties to deepen the understanding towards a structure-photophysical-property relationship. Recently, we reported different optical active zirconium and hafnium MOFs (Fig. 1), by incorporating the H4TCPE linker molecule, showing high two-photon cross section values up to 3600 GM.[6] This renders MOFs a highly interesting material class to investigate towards applications in photonic research.

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Bonding analysis on heavier-ylidenes

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Since their first synthesis, isolation and characterization in 1991 by Arduengo, the N-heterocyclic carbene (NHC) compounds have attracted wide interested in the organometallic and inorganic chemistry community.[1] Their unique stability and capability to stabilized otherwise unstable compounds have triggered investigations aiming at tailoring their electronic properties by structural modifications. In this context, for instance, Bertrand and co-workers have successfully reported the synthesis of the cyclic(alkyl)amino carbene (cAAC) demonstrating their superior stabilization propertied due to their stronger σ-donor and π-acceptor properties.[2] The quest for a broader variety of properties has led to extending such structural variations on heavier analogues of ylidenes. This has prompted us to explore the origins of the stabilization and electronic properties on the heavier ylidenes. We have investigated the energetics, structural data and electronic properties of the series of ylidenes (Figure 1). In order to gain insight into nature of the main chemical bonds, we have performed a detailed bonding analysis in the light of Effective Oxidation States (EOS)[3] and Energy Decomposition Analysis (EDA) in combination with Natural Orbitals for Chemical Valence (NOCV).[4]

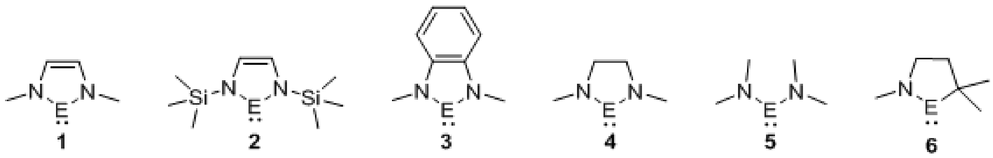

Figure 1. Studies series of ylidenes where E= C, Si, Ge, Sn, Pb.

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The weakly coordinating anion $[Al(OTeF_5)_4]^-$: Stabilization of elusive cations and Brønsted superacids

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The pentafluoroorthotellurate (F_5TeO^-) group is a versatile ligand for the stabilization of inorganic compounds in high oxidation states. The properties of the F_5TeO^-group high electronegativity comparable to that of fluorine, charge delocalization, robustness against electrophiles, and high sterical demand lead to a great variety of unique pentafluoro-orthotellurates.[1-4] We report the synthesis and characterization of the novel weakly coordinating anion[5] $[Al(OTeF_5)_4]^-$ as counterion for alkali metal and reactive p-block cations as well as about a conjugated Brønsted superacid.

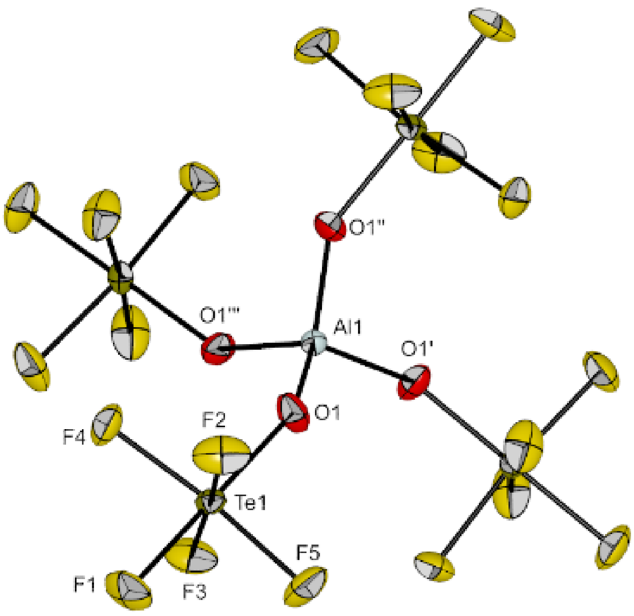

Figure 1. Molecular structure of the weakly coordinating anion [Al(OTeF5)4] obtained from X-ray crystal structure analysis of $[PPh_4][Al(OTeF_5)_4]$

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P50

From Linear to Circular Polycyclic Compounds: Aromaticity study on Singlet and Triplet States

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The aromaticity term is associated with cyclic molecular systems with a certain spatial and electronic structure that causes electron delocalization, providing enhanced stability. The quintessential example of aromatic molecules is benzene and its derivatives. However, there are plenty of other interesting examples, with a large variety of aromaticity types and shapes. Some particular examples are; Chichibabins oligo-p-phenylenes, their cyclic version cyclo-p-phenylenes (CPPs), and different types of porphyrins. Some derivatives of the latter three examples can be stable in radicalary and/or cationic forms, which have many potential applications for electronic devices. [1-3] Here, we are particularly interested in the study of its highly tunable electronic character depending on the elongation of the π-system, the spin and the exocyclic substituents, as well as the different classes of aromaticity that they present depending on its linear or circular shape (Figure 1). To do so, the systems were treated at DFT level of theory and posteriori analyzed by means of several aromaticity descriptors including NICS, FLU, AVmin, AV1245 and EDDB, between others.[4] Our results allow to determine the role of the aromaticity on the stability of the systems and characterize the different aromatic pathways present in the molecules.

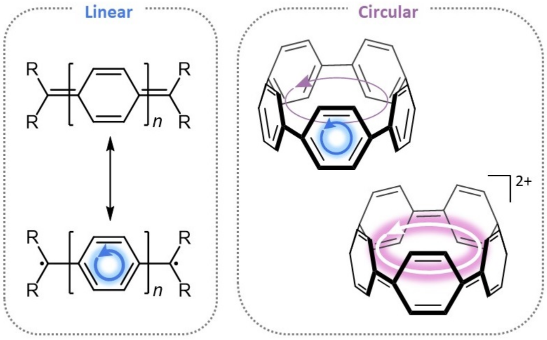

Figure 1. Schematic representation of linear and circular forms of polyphenylene and the proposed aromatic circuits.

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Experimental & Theoretical Charge Density Study of Bonding Interactions in $FeSb_2$

P51

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A decade ago $FeSb_2$ 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 $FeSb_2$ 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 $FeSb_2$.

Therefore, an X-ray charge density study has been conducted based on measurements at $\sim$ 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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P52

The role of the electrostatic interactions in complexes of IFIT proteins with RNA

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The aim of my project is to characterize electrostatic interactions in selected complexes of IFIT1 and IFIT5 proteins with RNA. IFITs (Interferon-induced proteins with tetratricopeptide repeats) are effectors of innate immune system, which are expressed in cells infected by viruses. By binding foreign RNA they prevent synthesis of viral proteins in human host cell. IFIT1, IFIT2 and IFIT5 bind different forms of RNA (with triphosphate group or cap at 5 end of RNA), however literature data are not consistent about selectivity of IFITs protein and their preferred RNA forms. Electrostatic energy usually has the most significant contribution to interaction energy and can be calculated for large complexes, thus it is a perfect tool for estimating interaction energy in biomacromolecules. One of the more advanced methods to calculate this energy is University at Buffalo Pseudoatom DataBank (UBDB) together with Exact Potential Multipole Method (EPMM). UBDB enables reconstruction of charge density for macromolecules in quantitative manner. By UBDB+EPMM approach, which takes also charge penetration effects into account, it is possible to compute electrostatic energies with similar accuracy as with quantum chemistry methods.

Calculations of energy will be based on the structures of IFIT5 and IFIT1 proteins deposited in PDB. I want to verify the hypothesis of the lack of influence of RNA sequence on interaction energy in IFIT-RNA complexes investigating IFIT5-pppRNA complexes. Moreover I will examine how modifications at 5' end of RNA alter interaction strength. Calculated interaction energies will be compared with dissociation constants of complexes from literature. Describing the nature of IFIT proteins interaction can help to expand our knowledge about mechanism of selective binding RNA and how human immune system recognizes and destroys viruses.

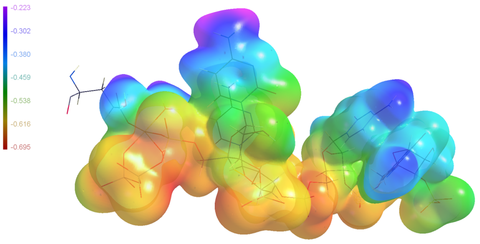

Figure 1. Electrostatic potential of oligoRNA pppCCCC with Mg (H2O)3 (e Bohr-1) mapped on the isosurface (0.002 e Bohr-3) of electron density reconstructed with the UBDB databank.

Project was financed from the grant PRELUDIUM11 of National Science Centre, Poland nr 2016/21/N/ST4/03722.

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Uniquely malleable electronic structure of chloranilic acid

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Chloranilic acid (I) is a quinoid compound with motley chemical behaviour: it is a good ligand, proton donor and acceptor, and capable of forming remarkably strong π-interactions. Stacks of chloranilate rings, face-to-face or offset, systematically arise from those π-interactions in the crystal phase.[1] We have obtained crystals of chloranilic acid (I), of its monoanion (II) and its dianion (III) with alkali metals as counter-ions. Simultaneously, we prepared two complexes in which chloranilate moiety acts as a bridging (IV) and terminal (V) ligand. Subsequently, we examined charge density distributions in these compounds to establish what gives rise to their disparate geometries and observable properties.[2] We used topological analysis of experimental and theoretical charge density to characterise atom and bond properties in the investigated compounds. We also compared the findings to those of similar compounds with nitranilate anions.[3] Electron density at bond critical points and calculated mapping of electrostatic potential reveal delocalization effects present in compounds (II-IV), a p-quinone structure of the chloranilic acid (I) and an o-quinone structure of the complex (V). This is consistent with previous evidence from IR spectroscopy.[4]

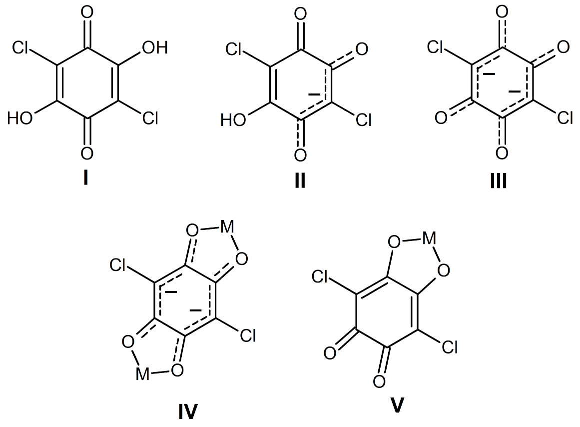

Figure 1. Malleability of chloranilate electron structure

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P54

Radiation damage free ghost diffraction with atomic resolution

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The X-ray free electron lasers can enable diffractive structural determination of protein nanocrystals and single molecules that are too small and radiation-sensitive for conventional X-ray diffraction. However the electronic form factor may be modified during the ultrashort X-ray pulse due to photoionization and electron cascade caused by the intense X-ray pulse. For general X-ray imaging techniques, the minimization of the effects of radiation damage is of major concern to ensure reliable reconstruction of molecular structure. Here we show that radiation damage free diffraction can be achieved with atomic spatial resolution by using X-ray parametric down-conversion and ghost diffraction with entangled photons of X-ray and optical frequencies. We show that the formation of the diffraction patterns satisfies a condition analogous to the Bragg equation, with a resolution that can be as fine as the crystal lattice length scale of several Ångstrom. Since the samples are illuminated by low energy optical photons, they can be free of radiation damage.

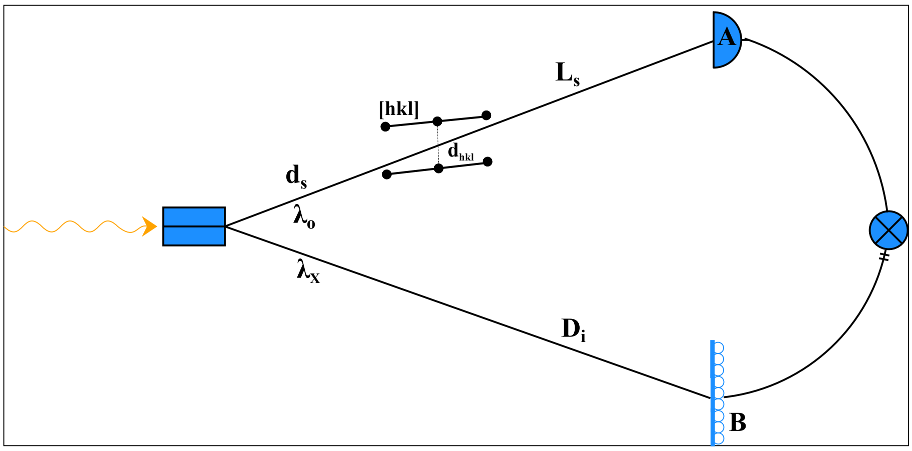

Figure 1. Proposed layout for two-color two-photon ghost diffraction using entangled X-ray and optical photon pairs

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[2] Europhys. Lett. (EPL) 120, 16003 (2017)

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

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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.

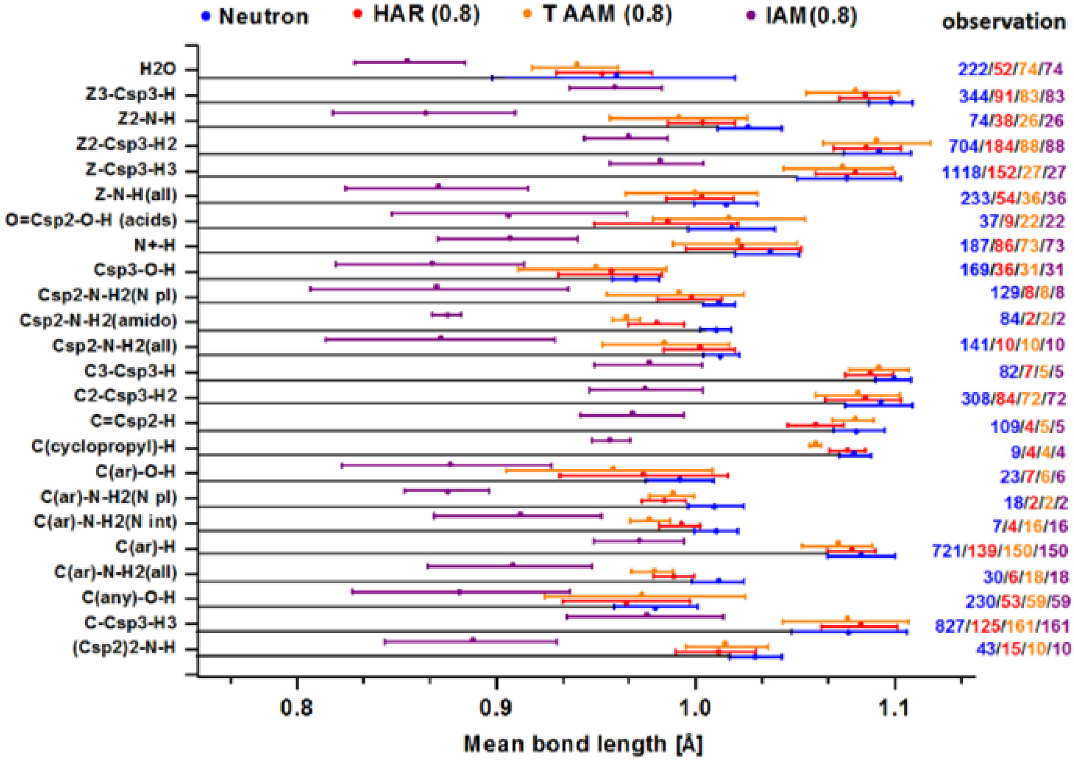

Figure 1. Comparison of the X-H bond distances from X-ray and neutron data refinement at 0.80 resolution for the selected 81 structures.

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 dmin ≤ 0.83 Å. 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 were refined using TAAM via DiSCaMB integrated with Olex2 and the X-H bond lengths thus obtained are 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.

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