

FA3-MS20-P01

Prediction of Unusual Reactivity of Siloxanes from Electronic Properties. Simon Grabowsky^a, Maxie F. Hesse^b, Wolfgang Morgenroth^c, Carsten Paulmann^d, Jens Beckmann^b, Peter Luger^a. ^a*Freie Universität Berlin, Anorganische Chemie.* ^b*Universität Bremen, Anorganische Chemie.* ^c*Universität Frankfurt, Geowissenschaften.* ^d*Universität Hamburg, Mineralogie.*
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Material properties of siloxanes are governed by the inherently low basicity of the siloxane linkage Si-O-Si and thus its inability to form hydrogen bonds with polar molecules like water. Due to the importance of the linkage in minerals (e.g. quartz, feldspars) and polymers (e.g. silicones), it is a point of major interest to find ways to tune the properties of the siloxane linkage to develop new classes of materials. The idea is to influence the chemical properties of the siloxane linkage – basicity serves as the test case in this study – by variation of the Si-O-Si bond angle.[1] The vast amount of siloxane compounds exhibit Si-O-Si angles between 130° and 180°. Tetrahedral angles do not occur in nature, but only in a few exceptional synthetical cases.

Various quantum-chemical calculations were carried out on disiloxane H₃SiOSiH₃. The Si-O-Si angle was varied from small angles to linearity in a many-step potential-energy surface scan with small angle increments to observe the development of chemical properties dependent on the bond angle. Electron density and the electron localizability indicator (ELI, [2]) were obtained at each angle. It resulted that disiloxane is indeed not able to bind hydrogen-bonding donors at large Si-O-Si angles; only for Si-O-Si angles smaller than 165° hydrogen bonding is generally feasible; only for angles smaller than 130° the hydrogen-bond energy becomes competitive; at angles smaller than 100°, siloxanes are even better hydrogen-bond acceptors than ethers. Discontinuous changes of the shapes of the oxygen lone pairs are crucial to explain this behaviour, which can be visualised by the Laplacian of the electron density and the ELI. Catastrophe theory describes these cusps and allows to classify different structural stability domains of disiloxane with different chemical properties like basicity.[3]

To examine this finding experimentally, four siloxane compounds were synthesised and crystallised. Two of them comprise exceptionally strained siloxane linkages, which was achieved by forcing the linkage into a five-membered ring system. The other two comprise relaxed siloxane linkages, which can be found in minerals or polymers. High-resolution X-ray measurements at low temperatures were performed on synchrotron beamlines F1 and D3 of HASYLAB at DESY in Hamburg. Silanol-siloxane hydrogen bonds with the siloxane linkage as acceptor could indeed be found in the crystal structures of the compounds with small Si-O-Si angles. Electronic properties obtained by means of electron density and ELI varied significantly between compounds with small and with large Si-O-Si angles, so that the predictions from the potential-energy surface scans could be confirmed for compounds with potential for rational material development.

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Fast property comparison of fluoroquinolones with the revised Invariom database. Julian J. Holstein^a, Christian B. Hübschle^a, Birger Dittrich^a. ^a*Institut für Anorganische Chemie, Georg-August-Universität, Göttingen, Germany.*
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Fundamental research on antibacterial agents is urgently needed, since resistance in bacteria is mounting [1] and new antibiotics are scarce [2]. Fluoroquinolones are a well developed synthetic class of anti-infective agents [3], with several positive pharmaceutical attributes like broad-spectrum activity, good bioavailability and a low incidence of side effects. They also have a rigid core-structure that makes them well suited for structural studies, and a number of molecules from the fluoroquinolone family have been investigated here. Our initial focus was the determination of accurate molecular coordinates from high-resolution, but also normal resolution X-ray diffraction data, in case the former are not easily obtained. Accurate structures were then derived from least-squares refinement with non-spherical scattering factors of the invariom model [4]. A revised version of the invariom database is applied to a larger number of compounds for the first time. It is based on the Hansen-Coppens multipole formalism [5]. A comparison of molecular conformations, electron density and their electrostatic potential was performed. Qualitative illustrations in terms of transparent 3D isosurfaces are complemented by an quantitative analysis [6] as introduced by Politzer.

While our efforts already show that high-quality structural information can indeed be obtained almost routinely for a series of compounds of biological relevance, current efforts are directed to a better understanding of molecular properties and function.

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Estimation of intermolecular interactions of the nucleic acid bases. Katarzyna N. Jarzemska, Paulina M. Dominiak. *Chemistry Department, University of Warsaw Pasteura 1, 02-093, Warszawa.*
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The UBDB databank consists of all atom types found in peptides, proteins and some other biologically relevant molecules [1]. It had been already shown that the databank corresponds very well to the electron density in a number of amino acids when compared to conventional *ab initio* methods at the B3LYP/6-31G** level, and also, reproduces quite well the electrostatic interaction energies (~1 kcal per mole).

Recently, the atom definition algorithm implemented in the lsdB programme has been modified so, as to provide more precise atom's descriptions, and the databank itself has been extended by a set of over 50 new atom types. The aim was to

calculate the aspherical atoms' parameters for atoms present in RNA and DNA molecules, and to enable the modelling of some other biological complexes of interest (e.g. minor groove binders). Reconstruction of the electron density enables us to perform interaction energy calculations for such systems.

Newly obtained pseudoatom models were first tested on a set of over 200 nucleic base pairs, and small charged molecular complexes. Electrostatic interaction energies were calculated for the densities reconstructed using UBDB (EPMM method) [2], and then compared against quantum calculations performed for the same systems (eg. adenine dimer, guanine-cytosine pair) at the two levels of theory *i.e.* first order electrostatic term HF/aug-cc-pVDZ and B3LYP/6-31G**. Correlation between the electrostatic interaction energy values obtained using those methods is high, while the linear coefficient is close to one. UBDB+EPMM satisfactorily reconstructs the electrostatic interaction energy, and what is particularly important, it closely reproduces the energetical trends.

The total interaction energy was estimated for the sample structures (containing DNA and RNA bases and their modifications) using the UBDB databank, and other atom-atom potential methods. Quantum mechanical interaction energy calculations (force field) were also performed. We compared all the results to get a clear idea about the accuracy and limits of all those approaches and generally to validate all available methods in this field. Good estimation of total interaction energy is very important in the potential applications of our method in the drug design and molecular biology.

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Hirshfeld surfaces from experimental charge density data. Radosław Kamiński, Anna A. Hoser, Krzysztof Woźniak. *Department of Chemistry, University of Warsaw, Warszawa, Poland.*

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Crystal engineering methods have recently attracted much attention due to their potential applications in predicting and designing new functional materials. Hirshfeld surfaces [1] have become a very popular tool to understand the packing of molecules in the solid state as well as intermolecular interactions between them. However, typical surfaces are defined using spherical atomic densities, which is not always the best option; especially when dealing with very accurate experimental charge density data. Thus, the whole effort to gain electron density information from the solid state is not fully utilized when applying such surfaces in the analysis. Therefore, here we propose a new approach to obtain Hirshfeld surfaces utilizing the charge density data obtained from multipole refinement with the Hansen-Coppens formalism. [2] Our methodology is tested on simple molecular examples such as, for example, α -oxalic acid dihydrate showing hidden potential of these inter-molecular surfaces.

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Magnetoelastic coupling in the triangular lattice antiferromagnet CuCrS₂ investigated by neutron and X-ray diffraction, neutron polarimetry and inelastic neutron scattering. Julia C. E. Rasch^{a,b}, Martin Boehm^a, Clemens Ritter^a, Hannu Mutka^a, Jürg Schefer^b, Lukas Keller^b, Galina M. Abramova^c, Antonio Cervellino^d and Jörg F. Löffler^e. ^a*Institut Laue-Langevin, 6 Rue Jules Horowitz, BP 156, FR-38042 Grenoble Cedex 9, France.* ^b*Laboratory for Neutron Scattering, ETH Zurich and Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.* ^c*L.V. Kirensky Institute of Physics, SB RAS, Krasnoyarsk RU-660036, Russia.* ^d*Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.* ^e*Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, CH-8093 Zurich, Switzerland*
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CuCrS₂ is a triangular lattice Heisenberg antiferromagnet with a rhombohedral crystal structure. We report on neutron and synchrotron powder diffraction results which reveal a monoclinic lattice distortion at the magnetic transition and verify a magnetoelastic coupling [1]. CuCrS₂ is therefore an interesting material to study the influence of magnetism on the relief of geometrical frustration. Polarimetry has been used to determine the magnetic structure to be a spin density wave and to exclude a helical arrangement. Because of the magnetoelastic coupling, the system is assumed to be able to select a magnetic ground state and to overcome frustration. Additionally a magnetic resonance mode has been found at $\hbar\omega=12\text{meV}$ which evidences a dimerization of Cr ions in the triangular planes [2].

[1] Julia C. E. Rasch et al, *Phys. Rev.* 80 (2009) 104431, 1-6. [2] Julia C. E. Rasch et al, submitted to PRL.

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On the significance of low and zero intensity observations. Julian Henn, Kathrin Meindl. *Institute of Inorganic Chemistry, University of Göttingen, Germany.*
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Counting statistics determine the minimum error present in an X-ray measurement. Thus, weak and zero intensity observations are naturally insignificant. However, a weak intensity may appear as significant by accident due to large variations in the variance of an intensity measured with low redundancy N . We investigate the significance of weak and zero intensity observations for the optimistic limiting case of a Poisson distribution for the individual reflections [1]. In real measurements additional sources of error are present the contribution of which even reduces the significance of weak and zero intensity observations. The redundancies required for