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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