MS22 Molecular structure and chemical properties: chemistry meets charge density

Chairs: Dr. Vladimir Stilinovic, Dr. Jacob Overgaard

MS22-O1

Benchmarking lithium amide versus amine bonding by charge density and energy decomposition analysis arguments

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First, lithium amides are versatile C-H metallation reagents of vast industrial demand because of their high basicity combined with weak nucleophilicity, [1] applied worldwide annually in kilotons. Second, bonding is the most basic concept in chemistry, but there are no dashes known from the Lewis diagram in nature. Experimental charge density from high resolution diffraction data and topological analyses quantifies bonding beyond plane interatomic distances. Covalent, electrostatic and donating bonding are the three most widespread concepts. The computational energy decomposition analysis adds their energy contributions. With these two interlocked methods we revisited industrial important amine-donated lithium amides, quantified covalent Li–N, electrostatic Li^+N^- and donating Li←N bonding and paved the way to modify their reactivity. [2]

Fig. 1 Partitioning of the interaction energy into the Pauli, dispersion, electrostatic and orbital terms gives a 71-72 % ionic and 25-26 % covalent character of the Li–N, different to the old dichotomy of 95 to 5 %. In this light, there is much more potential to steer reactivity with various substituents and donor solvents than anticipated so far. [3]
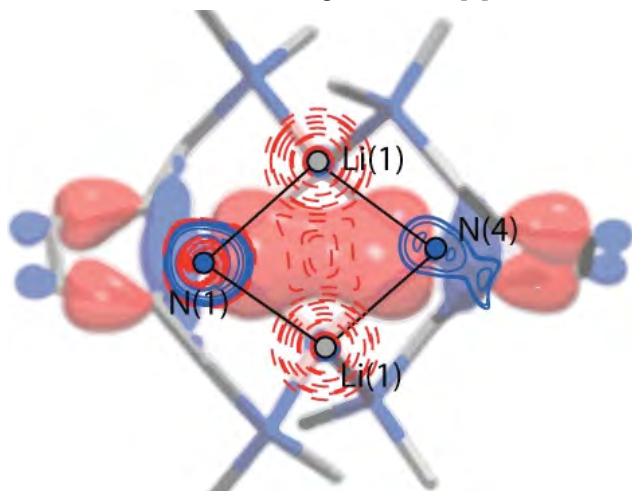
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MS22-O2

Complementary bonding analyses based on quantum crystallography

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Extracting information about chemical bonding from a molecular wavefunction or an experimental electron density is an ambiguous task since the notion of a chemical bond is itself a fuzzy concept that is not measurable and can therefore not be defined rigidly. There are recent heated debates on fundamental terms such as donor-acceptor interactions,[1] hypervalency,[2] or bond paths [3] in the literature. Even the meaning of ionicity and covalency is under question.[4] However, no chemist would deny that the chemical bond is a useful concept.

We do not claim that we can solve the debates, or redefine chemical bonding. However, there are hardly any studies that attempt to compare the results from a large variety of bonding descriptors on a single set of compounds without focusing on a specific tool or favoring one. Moreover, there are no studies that can show a comparison of results from experimental and theoretical investigations using the same orbital, real-space and energy bonding descriptors. Therefore, we have embarked on a systematic comparison of modern bonding descriptors from those three realms (specifically: quantum theory of atoms in molecules, source function, electron localizability (ELI), natural bond orbitals, natural resonance theory, valence bond calculations, different types of energy decomposition analyses, bond orders etc.), and we derive them from high-level theoretical calculations as well as experimental refinements of X-ray diffraction data within the new field of quantum crystallography.

We will show case studies for oxides of second- and third-period elements, for oxyanions such as nitrate, sulfate, phosphate, perchlorate that are of fundamental importance for chemistry, and for pentacoordinated silicon compounds. The results shed new light on hypervalency, charge-shift bonding, and ionicity vs. covalency concepts.

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