

wavefunction of an ideal system and that, quite often more limited, but referred to a real system, obtained from an experimental ρ derived from X-ray diffraction data.

The potential uses of the SF are, however, yet not fully explored. In a preliminary work, we addressed the question of whether the SF is or is not capable to reveal electron conjugation [3]. Question arose because of a recent claim [4] according to which “ π -electron delocalization in the benzene ring is not manifest in the SF when the reference point (rp) - the point at which the atomic sources for its density are calculated - is taken at the C-C bond critical point (bcp)”. Reasoning behind this statement is the null contribution from π molecular orbitals (MOs) to ρ in their nodal plane. However, since σ - and π -distributions are not independent, but self-consistently interrelated, we conjectured that some, albeit small, effect of electron conjugation could also be manifest when the rp lies in the π -nodal plane, even though π -orbitals do not obviously yield *direct* contributions to ρ in that plane. Results on a series of increasingly π -conjugated systems demonstrate that *this is actually the case*. By looking at the C-C bcp electron density for the shortest bond(s) in cyclohexene, cyclohexadiene, benzene, i.e. those bonds with largest double-bond character, one observes that both the SF and the SF% contributions of the C atoms other than those directly involved in such a bond increase with decreasing double bond character and electron localization of the bond. The enhanced S% value then becomes largely more evident when analysed using rps for which the effect of π -electron conjugation takes place directly through π -electron distribution rather than, indirectly, through σ - π electron interdependency.

In this work, the analysis is extended to more complex systems, formed by more than one ring, with fully conjugated or partially interrupted sequence of formal double-bonds and with planar or non planar geometry. In the case of benzene, the analysis is also performed on a ρ derived through multipole refinement of a set of X-ray diffraction data taken on a benzene molecular crystal. In the inspected cases and regardless of the theoretical or experimental origin of ρ , the SF reveals capable to detect electron conjugation. Such an ability is independent from a σ and π separation of ρ , since the SF tool was applied to the *total* ρ . This observation is important in view of the possibility to recover electron conjugation effects *using both ρ 's derived experimentally* (hence without σ and π separation being allowed) and ρ 's where *the departure from symmetry inhibits a proper separation* of σ and π contributions. Using a MO approach, the σ and π contributions to the SF values can also be revealed and quantified.

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Descriptors of charge density for estimating the energy of coordinate bonds

Alexandra O. Borissova, Mikhail Yu. Antipin, Konstantin A. Lyssenko, *X-ray Structural Centre, Nesmeyanov Institute of Organoelement Compounds RAS, Moscow (Russia)*. E-mail: xelat@ineos.ac.ru

Various quantum descriptors have been employed in establishing the QSAR/QSPR relationship in chemistry and biochemistry, but the main objective of this approach is to relate the electronic properties derived from calculations for isolated molecules with their macroscopic properties. The useful bridge between these two steps is the investigation of experimental charge density distribution function ($\rho(r)$) via high-resolution X-ray diffraction analysis and extracting the

necessary quantum descriptors of charge density from this data to relate them with more sound physical quantities.

The quantum theory of *Atoms in Molecules* [1] together with Espinosa's correlation scheme [2] provides the unique opportunity of estimating the energy of weak closed-shell interactions from first principles on the basis of one of the descriptors of molecular structure, namely, the value of potential energy density ($v(r)$) in the corresponding bond critical point. Recently the application of this approach was extended to the case of strong hydrogen bonds, in other words, the interactions of intermediate type [3]. The topological analysis of various coordination bonds based on the experimental $\rho(r)$ showed the similarity of strong hydrogen bonds and semipolar bonds of a moderate strength from the quantum descriptors' point of view [4].

We tested the applicability of this approach to estimate the dissociation of AuCl-PPh₃ complex [5]. The Au-P bond energy estimated via Espinosa correlation (57.9 kcal/mol) was close to the dissociation energy of the complex according to MP2 calculation (53.2 kcal/mol). This finding as well as the recent data for lanthanide complexes [4] showed this approach can be used at least for the semi-quantitative description of the coordination bonds.

To generalize the usage of quantum descriptors for the estimation of the metal-to-ligand binding energies, we performed the systematic high-resolution XRD analysis of a wide range of coordination and organometallic complexes and examined the relative strength of different metal-ligand bonds. Results will be presented for ruthenocene [6], cymantrene [7], and various coordination complexes of titanium, copper, zinc, palladium, and cadmium [8]. They cover a wide range of interactions - from the weakest metal...hydrogen ones to strong metal-carbon bonds. We also investigated the influence of intermolecular interactions on the bonding within first coordination sphere of metal atoms.

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The atomic energy as the descriptor for the stereoelectronic interactions

Ivan S. Bushmarinov, Konstantin A. Lyssenko, Mikhail Yu. Antipin, *X-ray Structural Centre, A. N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, Moscow, (Russia)* E-mail: ib@ineos.ac.ru

The term 'stereoelectronic effect' comes from the molecular mechanics approach and defines a conformational preference not explainable in terms of steric effects. One of the most fundamental of such effects is the generalized anomeric effect which dictates that in the R-X-C-Y systems, where X is bearing a lone pair (lp), and Y is more electronegative than carbon atom, the gauche conformation is generally the most stable [1]. It is explained in terms of lp-X-C-Y stereoelectronic interaction (SEI): the charge transfer from X's lone pairs to the σ^*_{C-Y} antibonding orbital. Until recently the study of energetic characteristics of SEI was limited to second-order perturbation analysis

of natural bond orbitals (NBO). This method can only be applied to the wavefunction obtained by either HF or Kohn-Sham DFT methods.

However, it has been shown that R.F.W. Bader's quantum theory of atoms in molecules (QTAIM) can be also used for such analysis. The computational works by R. Mosquera [3] have shown that the SEIs lead to changes in integrated QTAIM charges and energies of participating atoms. We have rationalized these data and developed a universal approach to analysis of SEIs by QTAIM methods: we have shown that the lp-X-C-Y interaction leads to decrease of charge and energy for X and Y atoms and to increase of both for carbon atom [2]. As our method is based on QTAIM, it can be applied to both experimental and calculated charge density.

We have shown the applicability of our approach for interpretation of SEI in organic compounds of different classes including saturated thioorganic heterocycles containing N—C—S fragment, glucose anhydrides (O—C—O), organic cyanides, azides and triazoles (N—C—FG, where FG is a multi-atom group) and tight ionic pairs $N=C^+ \dots I^-$ (as an extreme case of SEI). We have managed to separate the effects of SEI and lp repulsion on the conformational preferences of the thioheterocycles, systematically investigated by high-resolution XRD experiments and a number of quantum-chemistry calculations. Furthermore, the results obtained for N—C—FG allow for a deep insight into the nature of SEI, showing that the complex groups participate in such interactions as a whole, rather than by their terminal atom, as the results of NBO analysis suggest. For the $N=C^+ \dots I^-$ system we have studied the strength of residual C...I binding and demonstrated the inconsistency of the NBO data [4]. Overall, our approach has been shown to complement traditional NBO analysis in all cases and for some compounds it has produced additional information about the presence and nature of intramolecular interactions.

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Electron density topology and interaction energy in hydrogen bonded systems

I. Mata,^a E. Molins,^a E. Espinosa,^b I. Alkorta,^c ^a*Institut de Ciència de Materials de Barcelona, CSIC, Bellaterra (Spain)*. ^b*Institut Jean Barriol, Nancy-Université, Vandoeuvre-lès-Nancy (France)*. ^c*Instituto de Química Médica, CSIC, Madrid (Spain)*. E-mail: imata@icmab.es

The existence of empirical dependencies between electron density properties at the hydrogen bond critical point (HBCP) and bonding distance in H...O hydrogen bonds was demonstrated from a large compilation of HB topological data in experimental charge density studies [1]. These dependencies agree with those derived from theoretical calculations on a large set of hydrogen bonded complexes in gas phase [2]. Moreover, calculations show that H...A interactions can be classified into families according to the acceptor A, each family being characterized by a set of these dependencies with the bonding distance.

An in depth theoretical study of one of these families (A = F) is being undertaken in order to understand the dependency of the electron density properties with the interaction energy E_i , such as the

phenomenological relationships observed between E_i and the potential energy density at HBCP, which was established from a combination of theoretical and experimental data [3]. Hydrogen bonded dimers under an external electric field that emulates a polarizing environment (for example a crystal environment) are being used as case examples [4].

In the picture of the HB arising from this study, performed in the framework of the Quantum Theory of Atoms in Molecules (QTAIM) [5], interaction energy and equilibrium distance are given by the balance between a stabilizing contribution, mostly related to the mutual polarization of donor and acceptor, and a destabilizing contribution associated to the early steps of the transformation of the HB into a chemical bond. The environment of the interaction, represented by the substituents and the external electric field, tunes the interaction energy as well as the properties at HBCP, giving rise to the aforementioned dependencies between these quantities [6]. The scattering of values around the average dependencies can be explained by the complexity of the environment effects. As this scattering is smaller, the property is better suited for the estimation of the HB energy from the electron density.

From this analysis, the curvature along the HB at the HBCP is better estimator of the HB energy than the potential energy density. The exponential dependency of this curvature with the HB energy spans from very weak to very strong interactions and presents small scattering of values in the theoretical case. In the experimental case, this property presents smaller experimental error than the laplacian, which is in principle an excellent estimator for medium and strong HB.

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TOPAZ – neutrons going smaller

Henrik F. Clausen,^{a,b} Christina Hoffmann,^b Xiaoping Wang,^b Matthew Frost,^b Bryan Chakoumakos,^c Mark A. Spackman,^d Bo B. Iversen^a ^a*Center for Materials Crystallography, Aarhus University*, ^b*TOPAZ, Spallation Neutron Source, Oak Ridge National Laboratory*, ^c*HB-3A, High Flux Isotope Reactor, Oak Ridge National Laboratory*, ^d*Department of Biomedical, Biomolecular and Chemical Sciences, University of Western Australia*. E-mail: hfano@chem.au.dk

Supramolecular chemistry is the foundation for the design and development of materials with potential applications reaching from catalysis to gas storage. Understanding intermolecular interaction is crucial for these systems, and hence the precise determination of atomic positions, especially hydrogen, is important. The model compounds for the present studies are hydroquinone host-guest systems, $3C_6H_4(OH)_2 \cdot xS$, with S being the enclathrated solvent.[1]

Single crystal neutron experiments have until recently required a large sample (several cubic millimeters), which for some materials is unattainable. The immense power of the Spallation Neutron Source is utilized at the TOPAZ instrument to study single crystalline samples of sub-millimeter size, and thereby accessing a regime that so far has been unexplored. The goal is to be able to study the exact same crystal using a neutron source as used on the home X-ray source.

The first results from the TOPAZ instrument are promising, as