FA4-MS11-O4

Ab Initio Prediction of H-bond Energies and/or Geometries. <u>Paola Gilli</u>[a], Valerio Bertolasi[a], Gastone Gilli[a]. *[a]Department of Chemistry and Centre for Structural Diffractometry, University of Ferrara, 44100 Ferrara, Italy.*
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D−H⋯:A H-bonded interactions (D and :A = H-bond donor and acceptor) display a wide interval of binding energies, E_{HB}, ranging from less than one to more than 30 kcal mol^{-1} (45 kcal mol^{-1} if [F⋯H⋯F]$^-$ bonds are considered) because of two independent factors: (*i*) H-bonds are the stronger the more electronegative the donor (D) and acceptor (:A) atoms are [1]; (*ii*) for a same D-A couple [or *H-bond electronegativity class, EC(D,A)*] H-bonds are the stronger the more similar the proton affinities of D and A are, a fact easily expressible in terms of the *PA/pK$_a$ equalization principle* [2-4] for which really strong H-bonds can be observed only when the differences $\Delta PA = PA(D^-) - PA(:A)$ or $\Delta pK_a = pK_a(D-H) - pK_a(A-H^+)$ tend to zero (PA being the gas-phase proton affinity and pK_a the co-logarithm of the corresponding acid-base dissociation constant in water). These properties are at variance with all other types of chemical bond and derive from the *dual nature of the H-bond*, which is not really 'a bond' but rather 'two bonds' formed by a same central proton with the two lone pairs located on the so-called donor and acceptor atoms.

These considerations emphasize the role played by *PA/pK$_a$ equalization* in strengthening the H-bond, a hypothesis often invoked but never fully verified in the past which is now reconsidered in this Communication by a new instrument, *the pK$_a$ slide rule*. This is a bar-chart reporting, in separate scales, the pK_a's of the D−H proton donors and :A proton acceptors most frequently involved in D−H⋯:A bond formation (103 entries over the $-14 \leq pK_a \leq 53$ range). Allowing the two scales to shift so to bring into coincidence the donor and acceptor molecules, the ruler permits graphical evaluation of ΔpK_a and then empirical appreciation of D−H⋯:A bond strengths according to the pK_a equalization principle.

Systematic screening of two classical databases (NIST gas-phase enthalpies and CSD geometries) was carried out for all the most important X−H⋯X H-bonds having $\Delta pK_a = 0$, leading to the assessment of the maximum energies, $E_{HB,MAX}$, and the shortest D⋯A distances, $d_{D⋯A,min}$, for the most important electronegativity classes. Comparison of data has led to formulate the general equation

(1) $E_{HB} = E_{HB,MAX} \exp[-k(d_{D⋯A} - d_{D⋯A,min})]$, which permits easy prediction of energies given the geometries, and viceversa. The combined use of the pK_a slide rule and eq (1) will be illustrated in a number of practical applications.

[1] Desiraju G.R., Steiner Th., *The Weak Hydrogen Bond*; Oxford University Press: Oxford, **1999**. [2] Gilli P., Pretto L., Gilli G., *J. Mol. Struct.*, **2007**, 844-845, 328-339. [3] Gilli P., Pretto L., Bertolasi V., Gilli G., *Acc. Chem. Res.*, **2009**, 42, 33-44. [4] Gilli G., Gilli P., *The Nature of the Hydrogen Bond. Outline of a Comprehensive Hydrogen Bond Theory*; Oxford University Press: Oxford, **2009**.

Keywords: h-bond energies; PA/pKa-equalization; pKa slide rule

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Electron Diffraction, X-ray Powder Diffraction, Lattice Energy Minimisation, and Pair Distribution Function Analysis to Determine the Crystal Structures of Pigment Yellow 213, $C_{23}H_{21}O_9N_5$.
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Pigment Yellow 213, a commercial azo pigment used for car coatings, exists in a greenish-yellow α-phase, and a brown β-phase. The X-ray powder diagram of the α-phase could be indexed in multiple ways, and it was not possible to determine which is the correct one, even by means of LeBail fits with GSAS. Therefore the lattice parameters of the triclinic unit cell were determined by electron diffraction. Lattice energy minimisations were used to predict possible crystal structures, but the calculations failed, since the molecule adopts an unusual conformation which was never observed before, and which was not regarded in the lattice energy minimisations. Finally the crystal structure was solved from laboratory X-ray powder data using real-space methods with TOPAS. A subsequent Rietveld refinement (TOPAS) on synchrotron data converged with a smooth difference curve.

For the first time, pair distribution analyses (PDF) were applied to organic pigments. The PDF analysis of the α-phase, based on synchrotron powder data, confirmed the determined crystal structure. The β-phase is a nanocrystalline powder which does not show any reliable Bragg-peak in the X-ray diffractogram. The PDF analysis of the β-phase reveal that (1) the β-phase exhibits a layer structure with a layer distance of about 3.3Å like the α-phase, (2) the local structures of the β-phase is similar to that of the α-phase, and (3) the correlation length (i.e. domain size) of the β-phase is about 4 nm only. Thus the PDF method is able extract some information on the crystal structure of this organic compound from the X-ray powder diagram, although the crystallite size is so low and the powder diagram consists of some humps only.

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