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The Electron-Pair Saturation Rule. A New Way of Looking at Crystal Packing. Paola Gilli, Valerio Bertolasi, Gastone Gilli. *Department of Chemistry and Centre for Structural Diffractometry, University of Ferrara, Italy.*
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Packing forces can be divided in two large groups. The first is physical and includes: *(i) van der Waals (vdW)* forces as a balance of repulsion (exchange) and attraction (dispersive) interactions; and *(ii) electrostatic multipolar* forces as a sum of monopolar and dipolar interactions. The second is chemical and arises from: *(iii)* groups which are either Brønsted acids (proton donors, D–H) or Brønsted bases (proton acceptors, :A) and may interact by forming D–H⋯:A H-bonds; and *(iv)* groups which are either Lewis bases (electron donors, :D) or Lewis acids (electron acceptors, A) and may interact by forming D⤙A electron donor -acceptor (EDA) or charge-transfer (CT) interactions. This classification is quite useful in H-bond studies where directly leads to the pK_a *equalization principle* [1,2] for which really strong H-bonds occur only when the difference $\Delta pK_a = pK_a(\text{D–H}) – pK_a(\text{A–H}^+)$ tends to zero, but has proved to be inadequate for packing studies where the EDA/H-bond separation substantially hinders any unified treatment. The present contribution tackles this problem by the following strategy:
1. All possible EDA interactions have been rearranged following the seminal Mulliken classification [3];
2. The dichotomy between proton exchange and charge transfer is removed by reinterpreting the X/C─H⋯:Y H-bond as a donor-acceptor X/C–H←:Y adduct linked by a σ*←n EDA interaction, analogous to that occurring in X/C–Hal←:Y halogen bonds; in this way all contacts (except vdW) become EDA interactions where the electron is the unified exchange particle;
3. These methods were applied to analyse 239 short contacts in the X-ray structures of picric acid and 14 of its adducts with nitrogen bases, finally leading to assess the novel electron-pair saturation rule for which 'all electron donors of a closed-shell molecule, either non-bonding pairs of lone pairs or π-bonding pairs of multiple bonds, become spontaneously engaged in EDA interactions with the electron acceptors present, as far as these are available; when the acceptors are insufficient to saturate all donors, the latter are saturated in order of decreasing EDA interaction strength';
4. Final results allow to reclassify attractive forces in two groups: *(i) physical* interactions due to *atomic* charges and dispersive forces and widely independent of the molecular constitution; *(ii) chemical* interactions (including EDA interactions and X–H⋯:Y and C–H⋯:Y H-bonds) which can be intended as holistic properties of whole molecules reacting among themselves by incipient (molecular interaction) or full (dative bond) nucleophilic addition to fulfil the saturation rule, that is to remove from the external molecular surface the maximum number of *points of residual reactivity* associated with bonding or non-bonding unsaturated electron pairs. It is

shown that this way of intending molecular interactions provides a particularly easy way to look at the crystal packing.

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Hydrogen bonds and dynamics of crystalline amino acids: a synergetic effect of combining X-ray diffraction and single-crystal polarized Raman spectroscopy. Elena V. Boldyreva[a,b], Boris Kolesov[a,c].
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The properties of hydrogen bonds in crystals attract much attention, since they determine the crystal structures, their stability with respect to changes in temperature and pressure, non-linear optical properties, etc. Crystalline amino acids are also considered as biomimetics, and the knowledge of the dynamics of their crystal structures is helpful, to understand dynamics of biopolymers. Precise diffraction data can give valuable information on the position of atoms in the crystal structure and on the distribution of the electron density. At the same time, in case of static or dynamic disorder the diffraction techniques can give only averaged information, and are often not very efficient. It may be difficult, if at all possible to evaluate the parameters characterizing the barriers of rotation of hydrogen-bonded molecular fragments. A comparison of the relative strength of hydrogen bonds, if based on diffraction data, relies exclusively on the geometric parameters, what may be misleading. The exact position of H-atoms in a hydrogen bond may be difficult to find from X-ray diffraction data. At the same time, polarized Raman spectra measured from single crystals in several orientations at multiple temperatures and/or pressures may give an insight into fine details of the geometry and dynamics of hydrogen bonds and their role in phase transitions and solid-state reactivity. In the present contribution we shall illustrate this on several examples, including phase transitions in L-serine, L- and DL-cysteine, pressure-induced proton transfer in the crystals of oxalic acid dihydrate and several oxalates of selected amino acids, as well as the unique properties of selected hydrogen bonds in L-alanine on variations of temperature and pressure.

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