Inter-anion O–H$^-$···O$^-$ hydrogen bond like interactions: the breakdown of the strength–length analogy

Dario Braga,[a] Fabrizia Grepioni[a] and Juan J. Novoa[b]

[a] *Department of Chemistry G. Ciamician, University of Bologna, 40126 Bologna, Italy.*
E-mail: dbraga@ciam.unibo.it and grepioni@ciam.unibo.it
[b] *Departament de Química Física, Facultat de Química, Universitat de Barcelona, 08028 Barcelona, Spain.*
E-mail: novoa@zas.qf.ub.es

It is demonstrated that inter-anion O–H$^-$···O$^-$ interactions, commonly regarded as strong hydrogen bonds, are not associated with energetically stable anion–anion interactions; inter-anion O–H$^-$···O$^-$ act as a tugboat interaction that control anion aggregation and minimise anion–anion repulsions.

Strength and directionality render the hydrogen bond[1] (HB) the masterkey interaction in supramolecular chemistry[2] and in crystal engineering.[3] Commonly the HB is defined as a stable interaction between an A–H donor and a B acceptor, being A and B electronegative atoms or electron rich groups.[1,4,5] Strong HB are recognised in the solid state by the presence of H···B and A···B separations shorter than van der Waals contact distances and by A–H···B angles that tend to linearity. In these cases the length–strength analogy is believed to hold, *i.e.* the shorter the acceptor–donor distance the stronger the bond. It is customary to distinguish between neutral HB, when both A–H and B belong to neutral fragments, and ionic HB when ions are involved as donors and/or acceptors.[1,4] The case in which both donor and acceptor belong to negatively charged systems, *i.e.* A–H$^-$···B$^-$, falls in this latter category.

In the following we demonstrate, in the prototypical case of inter-ionic O–H$^-$···O$^-$ interactions commonly found in salts of polyprotic acids [such as $KHCO_3$ and KHC_2O_4 (*vide infra*)], that ionic HB are not energetically stable because they are associated with inter-anion electrostatic repulsions.

Experimentally, O–H$^-$···O$^-$ interactions possess the same geometrical properties as neutral O–H···O bonds. The distribution of inter-molecular/ionic O···O distances for neutral O–H···O and O–H$^-$···O$^-$ interactions, as obtained from a search of systems containing carboxylic–carboxylate groups within the Cambridge Structural Database[6] (CSD), are compared in Fig. 1. Inter-anion O–H$^-$···O$^-$ interactions constitute a very well defined subset and are distinct from neutral O–H···O bonds. O$^-$···O$^-$ separations are significantly shorter, both as mean values and as lowest deciles, than O···O distances. Such a decrease in length is traditionally taken as indicative of a substantial increase in HB strength. This observation is in apparent contradiction with another seemingly simple argument: when the charge is delocalised the electrostatic interaction between small anions is repulsive. We face the intriguing question: how possibly the interaction between anions, which are supposed to repel each other electrostatically, can lead to shorter O···O separations than in the corresponding neutral aggregates?

In order to tackle this problem we have used the HF and B3LYP methods with the 6-31 + G (2d,2p) basis set[8] to compute at the *ab initio* level the first-neighbour inter-anion energies[7] for several crystals taken from the CSD sample.[9a–d] Both methods are well suited to deal with the type of ionic interactions discussed herein.[9a,e]

We have chosen to discuss the representative case of potassium hydrogen oxalate, KHC_2O_4.[10] An analysis of the charge distribution on the $[HC_2O_4]^-$ anion shows that the negative charge is delocalised over the whole anion, with a slightly more negative charge on the deprotonated oxygen atom.[11] Fig. 2 allows to rationalise the ion packing in crystalline KHC_2O_4. The $[HC_2O_4)^-$ anions form chains separated by O···O distances of 2.522 Å. The crystal can be described as a stacking sequence of corrugated layers formed by K^+ cations and by $[HC_2O_4]^-$ chains, respectively (Fig. 2b).

The presence of short O···O separations along the $[HC_2O_4]^-$ chains is the first point to address. The interaction energy computed for two consecutive $[HC_2O_4]^-$ units in the experimental orientation is repulsive [+39 and +46 k cal mol^{-1} (1 cal = 4.184 J) at the HF and B3LYP levels, respectively]. The molecular electrostatic (MEP) map[12] of the isolated anion (Fig. 3) shows that a +1 charge always experiences an attractive interaction except at very short distance from the nuclei. The most negative regions in the $[HC_2O_4]^-$ MEP map are on the oxygens of the deprotonated group, whereas the least negative ones are on the OH region of the protonated group. The absence of positive regions in the MEP map indicates that, irrespective of the relative orientation, two $[HC_2O_4]^-$ anions repel each other electrostatically. The stability of the anionic chain arises from the presence of the K^+ cations. This can be demonstrated by calculating[8] the interaction energy within the subunit $K_2(HC_2O_4)_2$ which is stable against its dissociation into two K^+ and two $[HC_2O_4]^-$ ions (−232 and −334 k cal mol^{-1} at the HF and B3LYP levels, respectively). This indicates that K^+···$[HC_2O_4]^-$ attractive interactions largely predominate over repulsive K^+···K^+ and $[HC_2O_4]^-$···$[HC_2O_4]^-$ terms. In accord with the observed packing, the geometry of the subunit does not

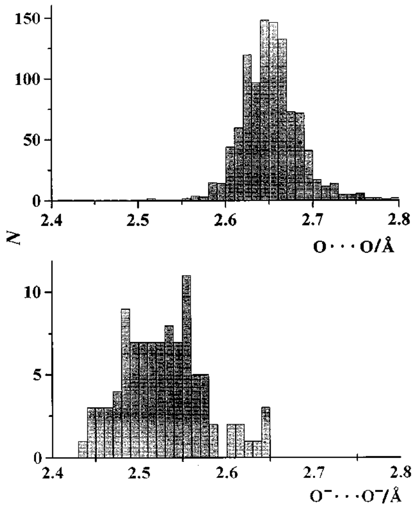

Fig. 1 Histograms of the two populations of O···O separations for neutral O–H···O (top) and inter-anion O–H$^-$···O$^-$ (bottom). Mean values for the O···O separations are 2.652(1) and 2.528(5) and lowest deciles are 2.615 and 2.462 Å, respectively. Intermolecular search on systems containing carboxylic/carboxylate groups based on a cut-off distance of 2.8 Å; duplicate hits manually removed.

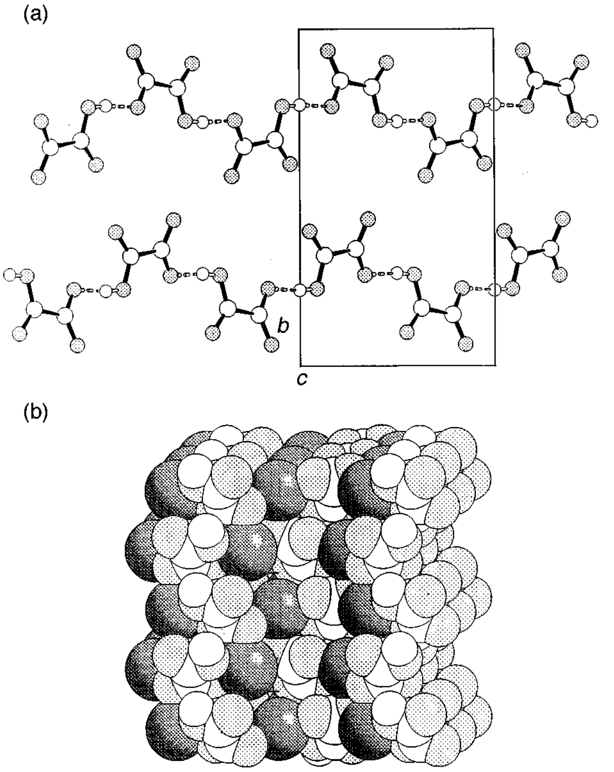

Fig. 2 The experimental packing in crystalline KHC_2O_4. (a) Chains of $[HC_2O_4]^-$ anions. (b) Space filling representation of the ion organisation.

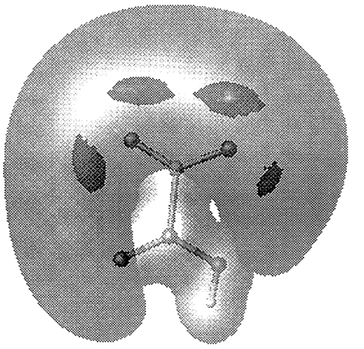

Fig. 3 Molecular electrostatic (MEP) map of an isolated $[HC_2O_4]^-$ anion computed at the HF/6-31 + G (2d,2p) level. Dark regions correspond to -170 kcal mol^{-1}, light grey to -100 kcal mol^{-1}, and light regions around the nuclei to +10 kcal mol^{-1}.

change significantly when fully optimised. To understand why hydrogen bond-like short distances and geometry are maintained on packing $[HC_2O_4]^-$ anions we computed the interaction energy by varying systematically the relative orientation of two $[HC_2O_4]^-$ anions at a fixed distance of 7 Å between the centres of mass. The two most stable (*i.e.* least repulsive) orientations correspond to the chain present in crystalline KHC_2O_4 and to the dimer found in other salts, respectively. Thus the inter-anion HB corresponds to the orientations that favour overlap of the least repulsive MEP regions on the anions. It is important to emphasise that, since $[HC_2O_4]^-\cdots[HC_2O_4]^-$ repulsions are much smaller than $K^+\cdots[HC_2O_4]^-$ attractions, the inter-anion O···O equilibrium distance along the chain is attained at a shorter O···O separation than in neutral HBs. This is a manifest break-down of the widely accepted length–strength relationship in hydrogen bonded solids.

If a bond between two atoms/molecules/ions is taken as anything that requires energy to be broken (whether large or small amount of energy does not matter) then the $O–H^-\cdots O^-$ interaction cannot be considered a bond because the ionic chains (or dimers) would 'fall apart' if the cations were removed. Therefore, the $O–H^-\cdots O^-$ interaction should be regarded as a *pseudo*-HB because it minimises inter-anion repulsions, but it is not stabilising on an absolute scale.

What is it, then? It is a tugboat interaction, that does not link ions (as an intermolecular chemical bond would do) but rather organises the ions in space, hence conferring directionality to anion–anion electrostatic interactions. The OH group on the anion becomes a probe capable, in the process of crystal nucleation and construction, of exploring the potential energy hypersurface of another anion to find the site of higher nucleophilicity even within the 'thick fog' of a negative field. This understanding has enormous implications in crystal engineering studies, mainly when ionic building blocks are involved,[13] as in organic conductors and superconductors,[14] and in the devise of new synthetic strategies to obtain robust materials.[15] Ionic solids are much more stable than most molecular solids, including those formed of hydrogen bond connected molecules. The inter-anion HB allows the utilisation of molecular synthons within strong ionic fields.

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