

Are all short O–H···O contacts hydrogen bonds? A quantitative look at the nature of O–H···O intermolecular hydrogen bonds

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The hydrogen-bonded nature of short O–H···O contacts has been investigated by comparing the components of the intermolecular interaction energy in the O–H···O contacts present in the H₂O···H₂O, H₂O···(OH[−]) and (OH[−])···(OH[−]) model dimers, and then in the more chemically significant H₂C₂O₄···H₂C₂O₄, H₂C₂O₄···(HC₂O₄[−]) and (HC₂O₄[−])···(HC₂O₄[−]) dimers, oriented as in the crystal of KHC₂O₄. The energy components were computed by means of intermolecular perturbation theory (IMPT). The inter-anion contacts are found to be repulsive due to the dominant repulsive character of the electrostatic term, the strongest terms in all dimers analyzed in this work. The same term is attractive in the neutral O–H···O and even stronger in the charge assisted O–H···O[−] contacts, whose hydrogen-bonded character is well known.

The hydrogen bond is considered as the strongest of all weak non-covalent interactions present in molecular crystals, able to control the packing in neutral molecular crystals, hence the way molecules self-recognize and aggregate in the solid state.¹ It is thus common practice, when trying to rationalize the packing of a given molecular crystal, to focus first on the interactions established between hydrogen bond donor (X–H) and acceptor (Y) groups.² The normal procedure is to search for all X–H···Y contacts satisfying geometrical conditions depending on the ‘strength’ of the interactions, *e.g.*, X···Y < X_{vdw} + Y_{vdw} and X–H···Y > 90°–100° in the case of X/Y = O/N, or H···Y < H_{vdw} + Y_{vdw} and X–H···Y > 90°–100° in the case of X = C and Y = O/N. If these criteria are used to construct search queries in CSD investigations,³ a statistical analysis of the preferred geometry of a selected contact can be made, from which information can be obtained on the energetic character of the interaction, as the observed structures tend to concentrate in the low energy regions of the potential energy surface for the selected interaction,⁴ that is, the most likely contacts are those around the energetic minima, other orientations also being possible but with decreasing probability. A corollarium of this assumption is the so-called *length–strength relationship* (which states that the shorter the contact, the stronger the interaction associated with it).

The previous assumption on the distribution of contacts is valid *only* if the X–H···Y interactions are of the same type, *i.e.*, are located on the *same* effective potential energy surface. However, in this communication we will demonstrate that, given the same O–H···O geometry, the nature of the contacts changes with the charge and relative orientation of the fragments. We will prove this by investigating the energetic components of the interaction energy, as obtained using rigorous *ab-initio* methods. Therefore, if the O–H···O, O–H···O[−] and

O–H[−]···O[−] interactions lie on different potential energy surfaces, a statistical analysis mixing these three classes may yield physically meaningless average results. This difference has not been considered in many of the statistical analyses carried out up to now on molecular crystals, which included neutral and charged ionic crystals, without consideration of the charge present in their fragments. Furthermore, the study is of interest to evaluate if there is a change in the nature of the O–H···O, O–H···O[−] and O–H[−]···O[−] short contacts. Up to now, there is a general trend to consider all three contacts as classes of hydrogen bonds (neutral in the first case, and charged in the next two cases). Our quantitative analysis on the energy components does not support the hydrogen-bonded nature of the O–H···O[−] short contacts, despite the fact that they could be considered as hydrogen bonds by just looking at their topology and geometry.

We will first show the different nature of the O–H···O interaction in the H₂O···H₂O, H₂O···(OH[−]) and (OH[−])···(OH[−]) model dimers in which the O–H···O geometry is forced to be the same (the three dimers are the result of detaching one and two protons from the neutral water dimer, see Fig. 1). Then, we will also see how the same ideas hold for the H₂C₂O₄···H₂C₂O₄, H₂C₂O₄···(HC₂O₄[−]) and (HC₂O₄[−])···(HC₂O₄[−]) dimers, taken as representative examples of observed situations in experimental crystals. We have already shown⁵ that O–H···O interactions between neutral molecules and between small anions in crystals of dicarboxylic acids and of monodeprotonated dicarboxylates respectively, play fundamentally different roles. In the case of anions, the O–H[−]···O[−] interactions do not correspond to stable intermolecular bonds but rather serve to minimize inter-anion repulsions. This type of analysis has been applied also to the C–H···O[−] and π -stacking interactions in ionic salts, invariably showing the importance of taking into explicit account the overall fragment charges in the analysis of non-covalent intermolecular interactions.⁶

The changes in the nature of the O–H···O interaction in the dimer models shown in Fig. 1 at a fixed geometry of the contact can be followed by carrying out an intermolecular perturbation theory (IMPT) *ab-initio* analysis of the interaction energy.⁷ IMPT computations⁸ give a quantitative and rigorous breakdown of the total energy of each dimer into physically meaningful components: electrostatic, exchange repulsion, polarization, charge transfer, and dispersion.⁹ The IMPT method is free of the unwanted basis set superposition errors present in other methods and due to the use of truncated basis sets. Table 1 shows the results obtained for the energy decomposition of the H₂O···H₂O, H₂O···(OH[−]) and (OH[−])···(OH[−]) model dimers, calculated using the 6-

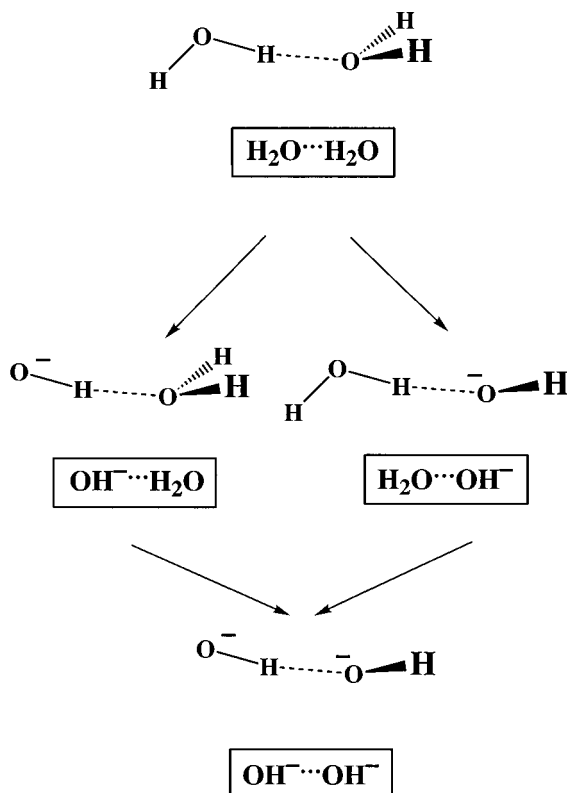


Fig. 1 $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$, $\text{H}_2\text{O}\cdots(\text{OH}^-)$ and $(\text{OH}^-)\cdots(\text{OH}^-)$ model dimers. The charged dimers have been obtained from the experimental geometry of the neutral water dimer by subtracting one or two protons, while keeping the dimer geometry frozen.

31+G(2d,p) basis set. To test the basis set influence on the IMPT analysis, we repeated the analysis with other basis sets, the best being the aug-cc-pVTZ basis,¹⁰ which is known to give a very accurate description of the properties of hydrogen-bonded complexes.¹¹ The results are displayed graphically in Fig. 2. The basis set influence on the size of the energy components is small in all cases and the same qualitative conclusions are reached.

The results in Table 1 can be rationalized as follows: the exchange-repulsion term is always repulsive, while the sum of the polarization, charge transfer and dispersion terms is always attractive and not very different in value from the exchange repulsion. Thus, the existence of an overall attractive or repulsive interaction depends essentially on the sign of the electrostatic interaction. Consequently, it is important to rationalize the behavior of the electrostatic term. Taking as a reference the neutral water dimer, $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$, the relatively small and attractive electrostatic term can be attributed to the local dipole–dipole component of the electrostatic energy of the O–H groups, oriented with the positive end of one dipole pointing towards the negative end of the other. When a negative charge is present in one of the fragments, such as in the case of the two orientational isomers shown in Fig. 1 for the loss of a proton from one of the water molecules of a

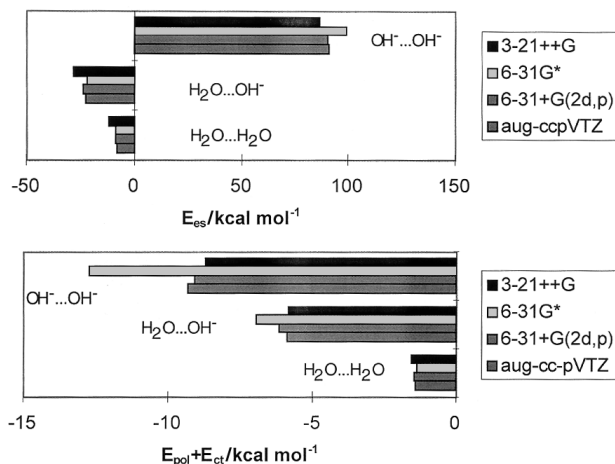


Fig. 2 Bar diagrams indicating the magnitude and sign of the electrostatic component (upper panel) and the sum of the polarization and charge transfer components (lower panel) as computed from an IMPT analysis using the indicated basis sets. Within each panel, the first set of four bars corresponds to the $(\text{OH}^-)\cdots(\text{OH}^-)$ dimer, the next set to the $\text{H}_2\text{O}\cdots(\text{OH}^-)$ dimer, and the last set to the $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$ dimer.

$\text{H}_2\text{O}\cdots\text{H}_2\text{O}$ neutral water dimer, i.e., $\text{H}_2\text{O}\cdots(\text{OH}^-)$ or $(\text{OH}^-)\cdots\text{OH}_2$, the dominant contribution to the electrostatic term is the charge–dipole one, stronger than the dipole–dipole contribution. These interactions are normally considered within the class of charge-assisted hydrogen bonds, because they are stronger than neutral hydrogen bonds, although one should differentiate between two cases. When the two fragments are properly oriented, as in the $\text{H}_2\text{O}\cdots(\text{OH}^-)$ dimer, where the OH bond dipoles of water point their positive ends towards the OH^- anion, the interaction becomes more stable than in the neutral dimer, as expected. However, the interaction becomes repulsive when the O–H[−] dipole is oriented towards the negative end of the two OH bond dipoles, that is, it is neither charge-assisted nor a bond; thus, *not every charge-assisted OH[−]⋯O contact is energetically stable*. Finally, when both fragments are charged, e.g., $(\text{OH}^-)\cdots(\text{OH}^-)$, the dominant electrostatic contribution comes from the charge–charge term, repulsive in this case given the identical charge on both fragments. Consequently, there is a change in *sign and magnitude* of the electrostatic component in the $(\text{OH}^-)\cdots\text{OH}_2$ and $(\text{OH}^-)\cdots(\text{OH}^-)$ dimers, which becomes repulsive, and the overall interaction energy is also repulsive. Therefore, as we will discuss below, these contacts are no longer hydrogen bonds (they are not energetically stable, one of the key conditions for the existence of a bond¹²). Clearly, the most favorable situation of all the O–H[−]⋯O contacts considered here can be expected to occur when the X–H[−]⋯Y interaction is fully ‘charge-assisted’, i.e., when the X–H donor belongs to a cation and the Y acceptor to an anion, X–H⁺⋯Y[−], with the various contributions all summing up to *reinforce* the interaction.¹³ As a matter of fact, charge-assisted hydrogen bonds are being widely employed in crystal engineering experiments.¹⁴

Table 1 Values of the electrostatic (E_{es}), exchange repulsion (E_{er}), polarization (E_{pol}), charge transfer (E_{ct}), and dispersion (E_{disp}) components of the total energy (E_{total}), computed by the IMPT method for the model dimers of Figs. 1 and 3

Dimer	E_{es}	E_{er}	E_{pol}	E_{ct}	E_{disp}	E_{total}
$\text{H}_2\text{O}\cdots\text{H}_2\text{O}$	−8.9	6.9	−0.7	−0.7	−1.7	−5.2
$\text{H}_2\text{O}\cdots\text{OH}^-$	−23.9	11.1	−4.1	−2.1	−2.6	−21.6
$\text{OH}^-\cdots\text{H}_2\text{O}$	2.4	10.0	−1.1	−0.9	−2.3	8.1
$\text{OH}^-\cdots\text{OH}^-$	90.5	12.6	−5.9	−3.2	−3.6	90.4
$\text{H}_2\text{C}_2\text{O}_4\cdots\text{H}_2\text{C}_2\text{O}_4$	−26.1	36.0	−4.6	−5.5	−13.3	−14.5
$\text{H}_2\text{C}_2\text{O}_4\cdots\text{HC}_2\text{O}_4^-$	−41.9	36.2	−9.0	−6.8	−15.1	−36.6
$\text{HC}_2\text{O}_4^-\cdots\text{HC}_2\text{O}_4^-$	16.7	40.4	−8.8	−6.6	−15.8	25.9

When the IMPT analysis is performed on the $\text{H}_2\text{C}_2\text{O}_4 \cdots \text{H}_2\text{C}_2\text{O}_4$, $\text{H}_2\text{C}_2\text{O}_4 \cdots (\text{HC}_2\text{O}_4^-)$ and $(\text{HC}_2\text{O}_4^-) \cdots (\text{HC}_2\text{O}_4^-)$ dimers we reach the same conclusions, as revealed by a look at the data collected in Table 1. They were obtained using the 3-21++G basis set, with the dimers oriented as indicated in Fig. 3 (notice that the geometrical orientation of the $\text{OH} \cdots \text{O}$ contact was deliberately forced to be the same). While the interaction is energetically stable for the neutral and $\text{H}_2\text{C}_2\text{O}_4 \cdots (\text{HC}_2\text{O}_4^-)$ dimers, it becomes repulsive for the $(\text{HC}_2\text{O}_4^-) \cdots (\text{HC}_2\text{O}_4^-)$ dimer. Once again, the energy is dominated by the electrostatic component in the three dimers, with much smaller changes in the other components. The electrostatic component in the $\text{H}_2\text{C}_2\text{O}_4 \cdots (\text{HC}_2\text{O}_4^-)$ dimer is more stable than in the neutral $\text{H}_2\text{C}_2\text{O}_4 \cdots \text{H}_2\text{C}_2\text{O}_4$ dimer, reflecting the favorable influence of the properly oriented charge-dipole term present in the electrostatic component. The electrostatic component in the $(\text{HC}_2\text{O}_4^-) \cdots (\text{HC}_2\text{O}_4^-)$ dimer is repulsive. Therefore, the driving force for the existence of short $\text{O}-\text{H} \cdots \text{O}$ contacts within the $(\text{HC}_2\text{O}_4^-) \cdots (\text{HC}_2\text{O}_4^-)$ dimer, present in the KHC_2O_4 crystal and other ionic crystals, cannot be the presence of repulsive interactions between these dimers. Instead, as mentioned in our previous study, it is the presence of $(\text{K}^+) \cdots (\text{HC}_2\text{O}_4^-)$ interactions generated by the potassium cations located between the HC_2O_4^- anions that makes the crystal energetically stable, because they are stronger than the $(\text{HC}_2\text{O}_4^-) \cdots (\text{HC}_2\text{O}_4^-)$ repulsion.

Hydrogen bonds are often defined in textbooks and scientific papers *solely* on the basis of the distance and angularity of the $\text{X}-\text{H} \cdots \text{Y}$ contact. However, according to Pauling,¹² in order to be bonded atom pairs ought to form an energetically stable association, (*i.e.*, something that *requires energy in order*

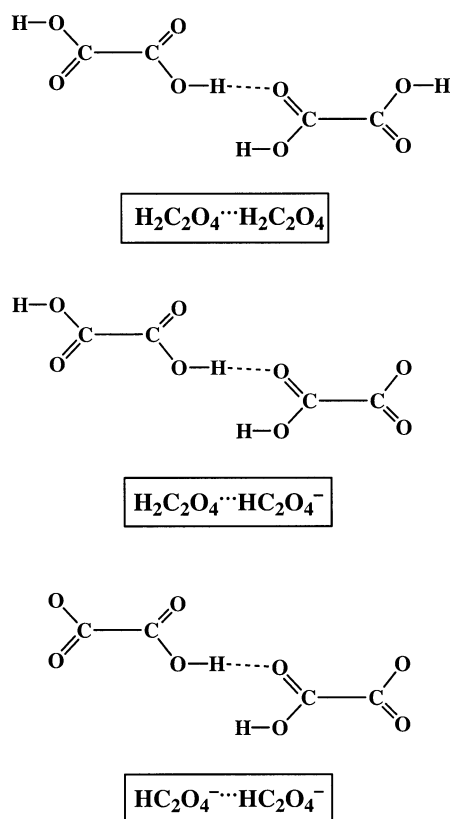


Fig. 3 Geometrical arrangement of the $\text{H}_2\text{C}_2\text{O}_4 \cdots \text{H}_2\text{C}_2\text{O}_4$, $\text{H}_2\text{C}_2\text{O}_4 \cdots (\text{HC}_2\text{O}_4^-)$ and $(\text{HC}_2\text{O}_4^-) \cdots (\text{HC}_2\text{O}_4^-)$ dimers, from top to bottom. The first two are obtained from that for the KHC_2O_4 crystal by adding one or two protons, while keeping the dimer geometry frozen (see ref. 5 for details). The parameters of the $\text{O}-\text{H} \cdots \text{O}$ contact are the following: $r(\text{H} \cdots \text{O}) = 1.482 \text{ \AA}$, $\text{O} \cdots \text{H}-\text{O} = 178.4^\circ$.

to be broken). The analysis of the two sets of dimers shows that, even in the presence of the same geometrical arrangement, this is not always the case. The dominating, strongly repulsive, electrostatic term in the anion-anion dimers makes the formation of a stable (hydrogen) bond impossible, that is, the anion-anion interaction in the two cases considered here has an energetic component consistent with an ionic interaction. The repulsive nature of the interaction is also found in the $\text{OH}^- \cdots (\text{H}_2\text{O})$ dimer due to its inadequate orientation. Therefore, we have at the same distance and orientation a different energetic character, in contrast to what direct use of the length-strength relationship would indicate: one *must* discriminate between ‘interaction’ and ‘bond’ for the same geometrical arrangement of a given pair of donor and acceptor groups, and take into consideration the charge present on each fragment of the interacting molecules.

Our results can be generalized as follows: whether a $\text{X}-\text{H} \cdots \text{Y}$ interaction for a given geometrical arrangement will be a bond or not depends on the charge and relative orientation of the donor and acceptor fragments. In other words, the utilization of purely geometric criteria in the analysis of selected groups of interactions may be misleading because short intermolecular distances may result as a *consequence* of other non-local dominant interactions, such as those between ions in crystalline salts.

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References

- (a) G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, Berlin, 1991; (b) P. A. Kollman and L. C. Allen, *Chem. Rev.*, 1972, **72**, 283; (c) S. Scheiner, *Rev. Comput. Chem.*, 1991, **2**, 165.
- See, for example (a) L. Brammer, D. Zhao, F. T. Ladipo and J. Braddock-Wilking, *Acta Crystallogr., Sect. B*, 1995, **51**, 632; (b) C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 397; D. Braga, F. Grepioni and G. R. Desiraju, *J. Organomet. Chem.*, 1997, **548**, 33; D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.
- F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 31.
- H.-B. Bürgi and J. C. Dunitz, in *Structure Correlation*, ed. H.-B. Bürgi and J. C. Dunitz, VCH, Weinheim, 1994, vol. 1, ch. 5.
- D. Braga, F. Grepioni and J. J. Novoa, *Chem. Commun.*, 1998, 1959.
- (a) D. Braga, F. Grepioni, E. Tagliavini, J. J. Novoa and F. Mota, *New J. Chem.*, 1998, **22**, 755; (b) D. Braga, C. Bazzi, F. Grepioni and J. J. Novoa, *New J. Chem.*, 1999, **23**, 577.
- I. C. Hayes and A. J. Stone, *J. Mol. Phys.*, 1984, **53**, 83; A. J. Stone, *The Theory of Intermolecular Forces*, Clarendon Press, Oxford, 1996, ch. 6.
- Computed using the Cadpac 6.1 code included as part of the Unichem 4.1 suite of programs.
- H. Humeyama and K. Morokuma, *J. Am. Chem. Soc.*, 1977, **99**, 1316.
- R. A. Kendall, T. H. Dunning, Jr and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796.
- (a) S. S. Xantheas, *J. Am. Chem. Soc.*, 1995, **117**, 10373; (b) S. S. Xantheas and T. H. Dunning Jr., *J. Chem. Phys.*, 1993, **99**, 8744; (c) J. J. Novoa, M. Planas and C. Rovira, *Chem. Phys. Lett.*, 1996, **251**, 33; (d) J. J. Novoa and M. Planas, *Chem. Phys. Lett.*, 1998, **285**, 186.

- 12 L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals. An Introduction to Modern Chemistry*, Cornell University Press, Ithaca, 3rd edn., 1960, p. 60.
- 13 D. Braga and F. Grepioni, *New J. Chem.*, 1998, **22**, 1159.
- 14 See, for example: (a) D. Braga and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, 1999, 1; (b) M. W. Hosseini and A. De Cian, *Chem. Commun.*, 1998, 727; (c) C. B. Aakeröy and M. Nieuwenhuyzen, *J. Mol. Struct.*, 1996, **374**, 223; (d) V. A. Russell, C. C. Evans, W. Li and M. D. Ward, *Science*, 1997, **276**, 575.

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