On the charge delocalisation in partially deprotonated polycarboxylic acid anions and zwitterions forming $^{(-)}$O–H···O$^{(-)}$ interactions in the solid state

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A database analysis of the structural effects of inter-anion hydrogen bonding interactions between mono-deprotonated polycarboxylic acid and zwitterionic molecules has been carried out. It has been shown that the deprotonated –COO groups, irrespective of the charged or neutral nature of the species, are strongly polarised in the solid state, behaving as –COO$^{(-)}$ groups. In contrast, the protonated groups, whether in anions or zwitterions, behave exactly as in neutral molecules. The same behaviour is shown by the smallest dicarboxylic acid anion, the hydrogen oxalate anion. Charge localisation onto the deprotonated carboxylate groups is seen as a means of exploiting the stabilising contribution of dipole–dipole interactions in conjunction with charge-assisted O–H···O interactions. The few cases of symmetric or nearly symmetric O–H···O interactions are discussed.

The hydrogen bond (HB) is from all points of view the key interaction in biological systems,[1] as well as in crystal engineering[2] and supramolecular chemistry.[3] Since the HB has a fundamentally electrostatic nature, the use of ionic building blocks has important consequences on solid state superstructures.[4]

It is customary to distinguish between neutral HB, X–H···Y, when both X–H donors and Y acceptors belong to neutral fragments, and *ionic HB* in which ions are involved, either as donors or acceptors or both. Ionic hydrogen bonds have been studied spectroscopically[5] and theoretically.[6] Resonance-assisted O–H···O HBs exist in π-conjugated systems, for example in crystalline β-diketone enols.[7] *Charge-assistance* is the possibility of enhancing the polarity of the groups involved in the HB by utilising cationic donors and anionic acceptors instead of neutral molecules.[8] Since charge-assistance may strengthen the HB interaction, it is widely employed in crystal engineering.[9,10]

However, while charge assistance in the presence of cationic donors and anionic acceptors, such as N–H$^{(+)}$···O$^{(-)}$ or C–H$^{(+)}$···O$^{(-)}$, is easy to understand since the ionic charges are 'in the right place' with respect to the HB donor–acceptor system, the situation is more problematic when the ions carry charges of the same sign, as in the case of $^{(-)}$O–H···O$^{(-)}$ interactions.[11] It has been shown, by means of *ab initio* calculations in the case of the hydrogen oxalate anion, that the dominant inter-anion Coulombic repulsion renders the $^{(-)}$O–H···O$^{(-)}$ HB unstable with respect to dissociation in the absence of counterions.[12a] More recently[12b] it has been shown that the most stable arrangement of small hydrogen acid anions, such as HCO_3^-, $HC_2O_4^-$, $HC_4O_4^-$, $HC_5O_5^-$, in both vacuum and condensed phases is the ring dimer formed with two $^{(-)}$O–H···O$^{(-)}$ interactions, while the anionic chain observed in many hydrogen acid salts, including hydrogen oxalates, is unstable with respect to dissociation in the absence of counterions. Under this latter condition, the $^{(-)}$O–H···O$^{(-)}$ interaction is better described as a stabilising interaction that reduces inter-anion repulsions. Whether the $^{(-)}$O–H···O$^{(-)}$ interaction can be considered a *bona fide* HB rather than a bond is not without controversy: the existence of a small covalent component in the interaction has been claimed in support of a more traditional view of the $^{(-)}$O–H···O$^{(-)}$ interaction as a conventional hydrogen bond.[13]

In this paper we approach the problem from a different perspective. We focus our attention on the *structural effect* of proton removal on the groups participating in $^{(-)}$O–H···O$^{(-)}$ interactions between mono-deprotonated polycarboxylic acid anions and between zwitterions containing both protonated [COOH] and deprotonated [COO$^-$] groups. The reasons for this choice are manifold. Since *partially deprotonated polycarboxylic acids* can form both $[COOH]_A$···$[COOH]_A$ and $[COOH]_A$···$[COO^-]_A$ inter-anionic HB interactions, one may wonder whether there is a recognisable difference in O···O separations between the two HB interactions, and between these and the $[COOH]_N$···$[COOH]_N$ HBs formed between neutral molecules. Furthermore, an analysis of the C–O distances within donor and acceptor groups should provide some information on the extent of charge localisation on the deprotonated $[COO^-]_A$ group with respect to the $[COOH]_A$ group upon formation of inter-ionic HB interactions. The analysis of zwitterionic molecules will broaden the perspective since these molecules may also display interactions of the type $[COOH]_{ZW}$···$[COO^-]_{ZW}$ in the solid state, thus allowing a discussion of the structural effects in crystals containing *formally* neutral molecules.

While neutral carboxylic acids and anions have been extensively studied theoretically,[6] structurally[14] and spectroscopically,[5] similar comprehensive studies of zwitterionic polycarboxylic acids are, to the best of the authors' knowledge, not available. In order to tackle these problems we have

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searched the CSD[15] for neutral and partially deprotonated polycarboxylic acids. The investigation of the occurrence and metrics of a given intermolecular or inter-ionic interaction in the solid state allows one to define the limits of its reproducibility, and hence of its transferability among different solid state structures.[16,17]

Results and discussion

The numerical results of the CSD searches for the $[COOH]_N \cdots [COOH]_N$, $[COOH]_A \cdots [COOH]_A$ and $[COOH]_A \cdots [COO^-]_A$ intermolecular interactions are summarised in Table 1 and compared with those obtained for the $[COOH]_A \cdots [COO^-]_A$ sample confined to the hydrogen oxalate anion (see below). Before proceeding it should be pointed out that the samples, though not very large (compared with the nearly 200 000 crystal structures available in the CSD!), represent the behaviour of a small but very well defined class of interactions.

The results of the searches are grouped in chemically related subsets and will be described with reference to the four columns reported in Table 1, while the fragments utilised in the CSD search are shown in the table heading. The following considerations are possible.

Columns I and II: O···O distances between protonated groups belonging to anions, $[COOH]_A \cdots [COOH]_A$, are strictly comparable, both in mean values and in lowest deciles, with those between neutral molecules $[COOH]_N \cdots [COOH]_N$. In both neutral molecules and ions the C–O and C–O(H) distances can be grouped into two distinct sets of long and short ones (C1–O1 > C1–O2 and C2–O4 > C2–O3). Hence, there is no appreciable 'structural consequence' of the fact that the protonated COOH group belongs to an anion or to a neutral molecule.

Column III: O···O distances between protonated and deprotonated groups, $[COOH]_A \cdots [COO^-]_A$, are shorter than those between protonated groups belonging to anions, $[COOH]_A \cdots [COOH]_A$, and consequently, also than those between neutral molecules, $[COOH]_N \cdots [COOH]_N$ (column I and II, respectively].[12] The distributions of O···O distances for the two cases $[COOH]_A \cdots [COOH]_A$ and $[COOH]_A \cdots [COO^-]_A$ are compared in Fig. 1. It should be pointed out that the difference in mean values between the two sets [2.644_8 *vs.* 2.532_3 Å] is strictly comparable to the difference observed in the more general analysis of O···O separations between neutral carboxylic acids and hydrogen carboxylic acid anions [2.652_1 *vs.* 2.538_5 Å].[12]

C–O distances within $[COOH]_A$ groups show the same trend as those in $[COOH]_N$ (C1–O1 > C1–O2), indicating that the COOH donor does not feel the different nature of the acceptor site. C–O distances within $[COO^-]_A$ groups show a much smaller difference in length (C2–O3 ≃ C2–O4), with mean values almost intermediate between those in the protonated groups. Even without extracting the very few cases of symmetric $[COO\cdots H\cdots COO]_A$ interactions (but see below) the comparison suggests that, at least in the solid state, proton removal from the COOH group leaves the extra electron essentially localised on the deprotonated $[COO^-]$ system.

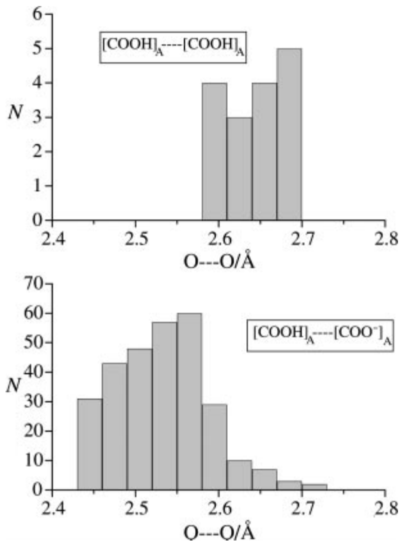
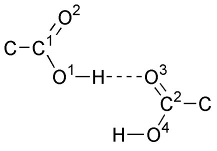
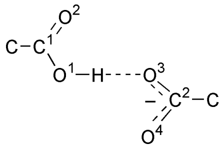


Fig. 1 Inter-anion HB interactions: comparison of the histograms of O···O distances in crystals of partially deprotonated carboxylates. Top: $[COOH]_A \cdots [COOH]_A$ interactions between fully protonated groups. Bottom: $[COOH]_A \cdots [COO^-]_A$ interactions between protonated and deprotonated carboxylates.

Column IV: In order to verify the effect of anion size on the extent of delocalisation we have run the same analysis on the smallest possible dicarboxylic acid anion, namely the hydrogen oxalate $HC_2O_4^-$. The data in column IV show that both donor $[COOH]_A$ and acceptor $[COO^-]_A$ sites of the $HC_2O_4^-$ anion behave almost exactly as those in the larger sample of all polycarboxylic acid anions (columns II and III). Fig. 2 shows a comparison of the distance distribution histograms for the four independent C–O distances (C1–O1 > C1–O2; C2–O3 ≃ C2–O4). Therefore, even in the case of the small $HC_2O_4^-$ anion, the protonated $[COOH]_A$ groups are geometrically similar to neutral $[COOH]_N$ groups and the extra electron remains 'confined' onto the deprotonated $[COO^-]_A$ groups. That the two C–O distances within $[COO^-]_A$ groups

Table 1 Comparison of average parameters (Å) for neutral and partially deprotonated polycarboxylic acids. Values in italics represent the lowest decile

Fragment used for the intermolecular search (O1···O3 < 2.8 Å)

Interaction	I $[COOH]_N \cdots [COOH]_N$ N = Neutral system	II $[COOH]_A \cdots [COOH]_A$ A = Anionic system	III $[COOH]_A \cdots [COO^-]_A$ A = Anionic system	IV $[COOH]_A \cdots [COO^-]_A$ A = $HC_2O_4^-$
				
O1···O3	2.665_3	2.644_8	2.532_3	2.545_6
	2.613	*2.585*	*2.458*	*2.458*
C1–O1	1.298_1	1.308_5	1.301_1	1.299_1
C1–O2	1.224_1	1.215_4	1.211_1	1.208_1
C2–O3	1.225_1	1.224_3	1.261_1	1.256_2
C2–O4	1.297_1	1.300_5	1.238_1	1.234_2

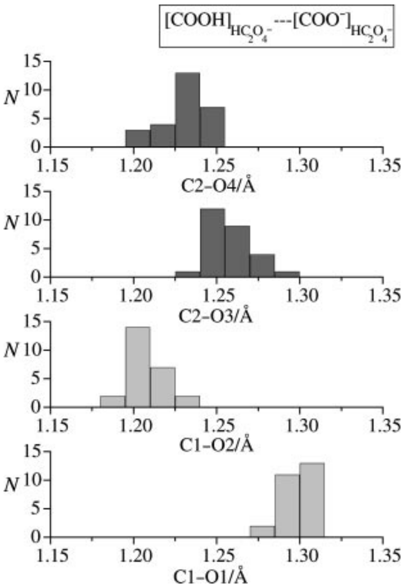


Fig. 2 Inter-anion HB interactions involving exclusively the hydrogen oxalate anion: comparison of the histograms of the four groups of C–O distances (see scheme in Table 1).

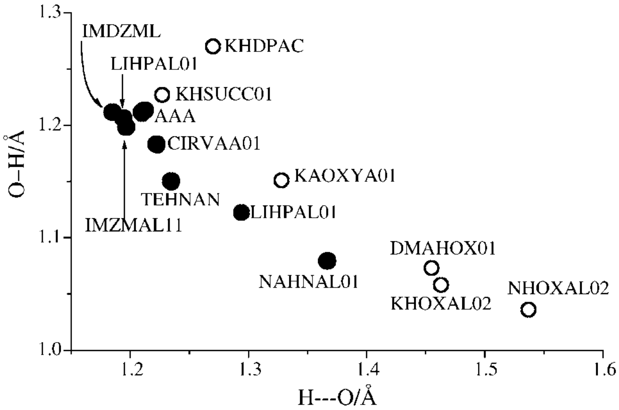


Fig. 3 Scattergram of O–H and H···O distances for structures of hydrogen polycarboxylic acid anions determined by neutron diffraction. Filled circles (●) represent the *intra*molecular interactions, while empty circles (○) represent *inter*molecular interactions. CSD refcodes are reported, except for compound AAA, which is available in ref. 19.

have similar values had been observed before.[18] It has also been shown that the difference between the two distances correlates with the O···O separations: the shorter the separation, the greater is the difference between the C–O distances, with the one corresponding to the acceptor atom usually longer than that involving the other oxygen atom.[18]

In summary, COOH groups possess the same average metrics, irrespective of the neutral or ionic nature of the system they belong to, and irrespective of the protonated or deprotonated nature of the acceptor site. On the other hand, the deprotonated [COO$^-$] groups appear to *keep* the negative charge after proton removal, irrespective of the size of the acid anion. At this stage one may wonder if the same 'conservative' behaviour is shown by protonated and deprotonated groups on passing from ionic to neutral crystals. The only possibility of studying the [COO$^-$] group geometry in a neutral environment is provided by crystals of zwitterionic molecules (see below). Before addressing this question, however, we need to examine the few cases of nearly symmetric [COO···H···COO]$_A$ interactions.

As a matter of fact, one of the recurrent issues in discussions on strong O–H···O bonds is that of the hydrogen atom position along the bond.[1a] This aspect is also relevant for the above discussion on the average geometry of the –COOH and [COO$^-$] groups. The CSD contains both X-ray and neutron diffraction data. When the position of the hydrogen atom is important, as it is in this case, X-ray structures cannot be trusted completely and one has to resolve to focus only on neutron structures.

There are only a few hydrogen polycarboxylic acid anions whose structures have been determined by neutron diffraction and their refcodes[19] are shown in Fig. 3, where O–H(donor) and H···O(acceptor) distances are plotted. It is interesting to note that the very few cases of symmetrical or *quasi* symmetrical O–H···O bonds (*i.e.*, those for which the difference between the two distances, Δ, is smaller than 0.1 Å) correspond either to intramolecular interactions, or to intermolecular O–H–O interactions involving oxygen atoms related by a crystallographic element of symmetry (usually an inversion centre, but also a two-fold axis, *etc.*). Although there are few cases in which the difference between the O–H and H···O distances is fairly small, there is no case of symmetrical interaction with atoms in general positions. This point is relevant because the presence of a crystallographically imposed symmetry on the O–H–O system does not allow one to discriminate between an artefact of the space-averaging characteristic of diffraction and a true location of the H-atom mid-way along the bond.

Carboxylic zwitterions, that is those that contain the deprotonated –COO$^{(-)}$ group, represent an interesting family of compounds because the molecules are formally neutral. Crystals of zwitterionic molecules are particularly relevant for the present discussion because they are *formally molecular* in nature: they do not contain ions carrying charges of opposite sign. The number of zwitterionic molecules is quite large (493 zwitterions containing –COO$^{(-)}$ and NH$_3^{(+)}$) but those that fulfil the precondition of this work, namely the simultaneous presence of a protonated –COOH and a deprotonated –COO$^{(-)}$ group, are much more limited in number (46). The sample is, however, still amenable to some statistical considerations, mainly in light of the observations made above.

Fig. 4 shows the distribution of distances for the [COOH]$_{ZW}$···[COO$^-$]$_{ZW}$ interactions. It is easy to appreciate that *although formally neutral* the zwitterionic molecules behave, in HB formation, *exactly as their anionic partners.* The O···O separations [2.568$_8$, *2.455* Å] are comparable in length to those observed for inter-anionic systems. This is an indication that proton removal (or proton transfer) "leaves" the extra charge essentially localised on the –COO group. The distribution of C–O distances within the –COOH and –COO$^{(-)}$ groups, analogous to that shown in Fig. 2 for hydrogen oxalate salts, is shown in Fig. 5. The distributions are characterised by precisely the same trends as observed in

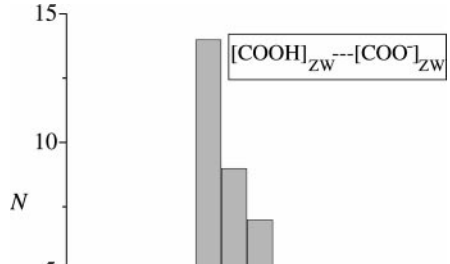


Fig. 4 Inter-zwitterion HB interactions: histogram of O···O distances in crystals of zwitterions containing both –COO$^-$ and –COOH groups.

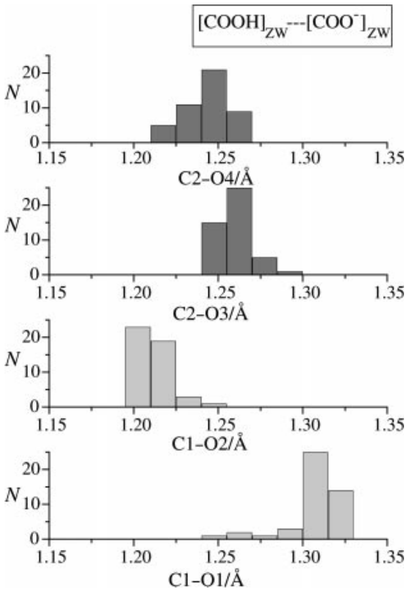


Fig. 5 HB interactions involving zwitterions: comparison of the histograms of the four groups of C–O distances (see scheme in Table 1).

the general sample and in the sample of distances for hydrogen oxalate anions. In terms of average values the distances are C1–O1 1.307$_2$, Cl–O2 1.211$_2$, C2–O3 1.260$_2$ and C2–O4 1.242$_2$ Å.

In order to put the above analysis in a more straightforward chemical context, we have selected two representative classes of polycarboxylic acids, namely amino acids and organometallic dicarboxylic acids. Even though the CSD does not contain any example of the *same* amino acid in neutral, zwitterion, and hydrochloride forms, it is still possible to find closely related compounds in the family of derivatives of glutamic acid. Fig. 6 compares O···O interactions in derivatives of glutamic acid: (*a*) neutral amino acid (CILDOQ 2.790 Å), (*b*) zwitterionic form (CXGLUA10 2.455 Å) and (*c*) hydrochloride form (AMBZGU10 2.711 Å). The interaction involving the formally neutral system conforms to the general behaviour shown above, that is the O···O separation falls in the set of short distances.

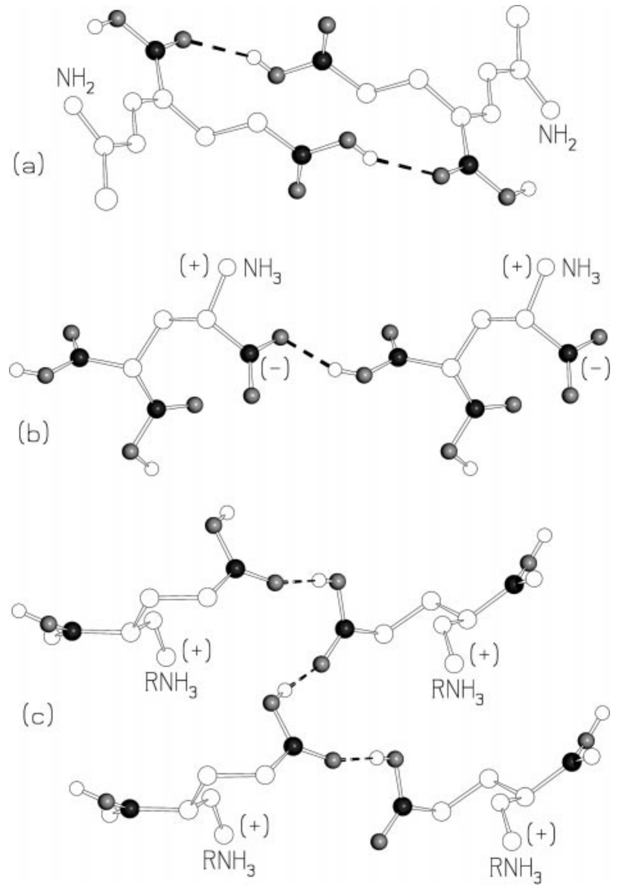


Fig. 6 A comparison of O···O interactions in three derivatives of glutamic acid: (*a*) the *neutral* amino acid CILDOQ (2.790 Å); (*b*) the *neutral zwitterionic* form CXGLUA10 (2.455 Å), and (*c*) the *ionic hydrochloride* form AMBZGU10 (2.711 Å); Cl^- anions are not shown for clarity. Shaded atoms represent the COO/COOH groups; H atoms, except those of the COOH groups, are omitted for clarity.

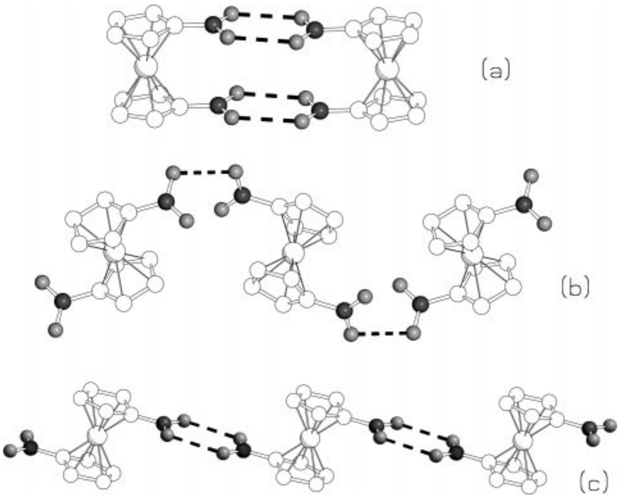


Fig. 7 A comparison of O···O interactions in some organometallic dicarboxylic acids: (*a*) the *neutral* dimer in $[(C_5H_4COOH)_2Fe^{II}]$ (2.606 Å), (*b*) the *neutral zwitterion* in $[(C_5H_4COO)(C_5H_4COOH)Co^{III}]$ (2.456 Å), and (*c*) the *cationic* chain in $[(C_5H_4COOH)_2Co^{III}]^+[PF_6^-]$ (2.600 Å); $[PF_6^-]$ anions are not shown for clarity. Shaded atoms represent the COO/COOH groups; H atoms, except those of the COOH groups, are omitted for clarity.

Organometallic molecules provide an analogous set of observations on chemically different systems. Fig. 7 compares O···O interactions in (*a*) the *neutral dimer* $[(C_5H_4COOH)_2Fe^{II}]$ (2.606 Å), (*b*) the chain formed by the neutral *zwitterion* $[(C_5H_4COO)(C_5H_4COOH)Co^{II}]$ (2.456 Å) and (*c*) the *cationic* chain in $[(C_5H_4COOH)_2Co^{III}]^+$ $[PF_6]^-$ (2.600 Å).[20] Even such a small sample allows us to see that the acids in their fully protonated forms, whether neutral or cationic, show long O···O separations in both catemer or ring motifs, while the zwitterionic molecules, whether organic or organometallic, show short O···O separations, thus behaving as deprotonated ionic species. In other words, the difference in O···O separations between [COOH]···[COOH] and $[COOH]\cdots[COO^-]$ interactions *does not depend on the neutral or ionic nature of the amino acid or of the complex, but on the acceptor group.*

Conclusions

These observations can be rationalised by considering the balance of interactions responsible for crystal cohesion. It has been pointed out that the terms attraction/repulsion should be used to refer to forces acting between atoms and molecules, while the terms stabilisation/destabilisation should be used to refer to energies.[21] It is consequential that stabilising interactions can be efficacious even in the presence of repulsive forces. Polycarboxylate anions are polarisable anions. Even though there is a significant covalent contribution in strong HB,[1a,6,7] it appears that the preservation of a marked electron localisation on the deprotonated group allows full advantage of the stabilising contribution provided by the HB interaction to be taken, even when the building blocks are small and carry the same charge (*i.e.*, subjected to repulsive forces). It goes without saying that, in the absence of counterions, *i.e.*, in a vacuum, this contribution would not be sufficient to keep the anions together.[12] In the crystalline state, however, crystal cohesion is guaranteed by the presence of an equal number of cations and anions, so that +/− attractions overcompensate for the +/+ and −/− repulsions. In conclusion, inter-anionic HB interactions in the solid state provide directionality and additional stabilisation in the presence of Coulombic forces. Similar reasoning may apply to ionic solutions (but the effect of solvation needs to be taken into account[5b,c]) and may also be relevant to the understanding of the behaviour of biomolecules containing polycarboxylic functions. In spite of many relevant studies,[22] a theoretical assessment of the effect of ionic charges on non-covalent interactions still represents a challenging task.

Experimental

Data were retrieved from the October 1999 version of the CSD for all crystal structures with an exact match between chemical and crystallographic connectivity on fragments (shown in Table 1) designed with the QUEST software and a cut-off distance on intermolecular O···O separations of 2.8 Å. All entries were manually screened. The program VISTA was used to construct the histograms. Five separate searches were carried out: (*i*) neutral polycarboxylic acids (no. obs. 564), (*ii*) polycarboxylic acid anions, (no. obs. $[\mathrm{COOH}]_A\cdots[\mathrm{COOH}]_A$ and $[\mathrm{COOH}]_A\cdots[\mathrm{COO}^-]_A$, 18 and 291, respectively); (*iii*) hydrogen oxalate anions (no. obs. 43); (*iv*) zwitterions derived from polycarboxylic acids and containing a $\mathrm{NH_3}^+$ group (no. obs. $[\mathrm{COOH}]_{zw}\cdots[\mathrm{COO}^-]_{zw}$, 46); (*v*) neutron data (no. obs. $[\mathrm{COOH}]_A\cdots[\mathrm{COO}^-]_A$, 12). The presence of the H-atom in the HB was required for a *bona fide* identification of the interactions, even though this reduced the already small population of the $[\mathrm{COOH}]_A\cdots[\mathrm{COOH}]_A$ interactions. Except for the case of search (*v*), no distinction between X-ray and neutron structures was performed. For selected examples the references to the original structural papers may be obtained from the CSD refcodes.

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References

1 (*a*) G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer–Verlag, Berlin, 1991; (*b*) G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999.

2 See, for a general entry: (*a*) *Crystal Engineering: from Molecules and Crystals to Materials*, ed. D. Braga, F. Grepioni and A. G. Orpen, Kluwer Academic Publishers, Dordrecht, 1999; (*b*) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.

3 (*a*) J. M. Lehn, *Angrew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; (*b*) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen and D. M. Gordon, *Acc. Chem. Res.*, 1995, **28**, 37.

4 (*a*) D. Braga and F. Grepioni, *Chem. Commun.*, 1996, 571; (*b*) A. D. Burrows, C.-W. Chan, M. M. Chowdry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, 329; (*c*) S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357.

5 See, for example: (*a*) J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91; (*b*) M. Meot-Ner (Mautner), *J. Am. Chem. Soc.*, 1984, **106**, 1257; (*c*) M. Meot-Ner (Mautner) and L. W. Sieck, *J. Am. Chem. Soc.*, 1986, **108**, 7525; (*d*) J. C. Spekman, *Struct. Bonding* (*Berlin*), 1972, **12**, 141.

6 See, for example: (*a*) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, 1977, **99**, 1316; (*b*) M. S. Gordon and J. H. Jensen, *Acc. Chem. Res.*, 1996, **29**, 536; (*c*) O. N. Ventura, J. B. Rama, L. Turi and J. J. Dannenberg, *J. Phys. Chem.*, 1995, **99**, 131; (*d*) C. Lee, G. Fitzgerald, M. Planas and J. J. Novoa, *J. Phys. Chem.*, 1996, **100**, 7398.

7 V. Bertolasi, P. Gilli, V. Ferretti and G. Gilli, *Chem. Eur. J.*, 1996, **2**, 925 and references therein.

8 D. Braga and F. Grepioni, *New J. Chem.*, 1998, **22**, 1159.

9 D. Braga and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, 1999, 1.

10 (*a*) M. W. Hosseini and A. De Cian, *Chem. Commun.*, 1998, 727; (*b*) L. Brammer, D. Zhao, F. T. Ladipo and J. Braddock–Wilking, *Acta Crystallogr., Sect. B*, 1995, **51**, 632; (*c*) C. B. Aakeröy, *Acta Crystallogr., Sect. B*, 1997, **53**, 569.

11 D. Braga, F. Grepioni, E. Tagliavini, J. J. Novoa and F. Mota, *New J. Chem.*, 1998, **22**, 755.

12 (*a*) D. Braga, F. Grepioni and J. J. Novoa, *Chem. Commun.*, 1998, 1959; (*b*) D. Braga, L. Maini, F. Grepioni, F. Mota, C. Rovira and J. J. Novoa, *Chem. Eur. J.*, 2000, in press.

13 T. Steiner, *Chem. Commun.*, 1999, 2299.

14 Z. Berkovitch–Yellin and L. Leiserowitz, *J. Am. Chem. Soc.*, 1982, **104**, 4064.

15 F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.

16 D. Braga, F. Grepioni, P. Sabatino and G. R. Desiraju, *Organometallics*, 1994, **13**, 3532.

17 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.

18 J. D. Thomas, *Acta Crystallogr., Sect. B*, 1977, **33**, 2867.

19 The refcode is not available for the structure reported in: D. Madsen, C. Flensburg and S. Larsen, *J. Phys. Chem.*, 1998, **102**, 2177.

20 D. Braga, L. Maini, M. Polito and F. Grepioni, *Organometallics*, 1999, **18**, 2577.

21 J. D. Dunitz and A. Gavezzotti, *Acc. Chem. Res.*, 1999, **32**, 677.

22 See, for example: (*a*) C. R. A. Catlow, J. D. Gale and R. W. Grimes, *J. Solid State Chem.*, 1993, **106**, 13; (*b*) L. Ojamae, K. Hermansson, C. Pisani, M. Causà and C. Roetti, *Acta Crystallogr., Sect. B*, 1994, **50**, 268; (*c*) J. E. McGrady and D. M. P. Mingos, *J. Chem. Soc., Perkin Trans. 2*, 1995, 355.