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Hydrogen bond strength and bond geometry in cyclic dimers of crystalline carboxylic acids

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In a study of 101 crystal structures of carboxylic acids we have observed a clear trend in the difference between the formally single and formally double C—O bond distances, as observed by X-ray diffraction, with a clear-cut distinction between aromatic acids, where the two distances are similar, and non-aromatic acids, where the two distances distinctly differ by 0.06–0.12 Å. A tentative energy classification – within the limits of the many assumptions – and a correlation with the O···O separation over the hydrogen bond indicate that the stability of the carboxylic acid dimer increases as the difference between the two apparent C—O distances becomes smaller, owing to an increasing Coulombic contribution to the dimerization energy. No simple hypothesis is adequate for a complete explanation of the origin, of the details and of the variations of this phenomenon. As often happens in crystal chemistry problems, one is presumably confronted with a balance of several subtle intra- and intermolecular factors.

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1. Introduction

The C=O···H—O hydrogen bond is considerably strong, its estimated energy ranging between 130 kJ mol^{-1} for ionic or resonance-assisted intramolecular bonds (Gilli & Gilli, 2000) and *ca* 30 kJ mol^{-1} for the relatively weaker intermolecular bond in crystals (Gavezzotti, 2007). The formation of an intermolecular cyclic dimer including two of these strong binding entities would seem an obvious choice for crystallizing molecules of carboxylic acids, but a considerable percentage of organic crystals show the alternative catemer motif (Leiserowitz, 1976) in which each molecule binds two other molecules in a chain motif. When the cyclic dimer is adopted in the solid state, the eight-membered system shows a propensity to disorder, whose nature, static or dynamic, has been the subject of extensive analysis, by combined temperature-dependent neutron diffraction and NMR (Fischer *et al.*, 1986; Meier & Ernst, 1986; Wilson *et al.*, 1996; Nygren *et al.*, 2005; Wilson *et al.*, 2006), and by computation (Middlemiss *et al.*, 2007). More perspective on the problem is available in a recent neutron diffraction and theoretical study of the aspirin crystal (Wilson, 2005). We report in this communication some attempts at establishing a link between molecular electronic structure and the occurrence of such disorder by an analysis of the energies and geometries of carboxylic acid crystals. The results show some clear-cut trends but also – as usual in organic crystal chemistry – a puzzling combination of antagonistic intra- and intermolecular factors.

2. Methods

Space-group information, cell parameters and atomic coordinates of non-H atoms of 101 carboxylic acids forming cyclic dimers were retrieved from the Cambridge Structural Database (Allen, 2002). They were chosen to be small molecules for computational feasibility, with an *R* factor not exceeding 0.05 in most cases. Of these 45 are aromatic, *i.e.* with the —COOH group directly bound to an aromatic ring (including a few polymorphs and multiple determinations, 33 different compounds); 12 are unsaturated, *i.e.* with the acid group

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bound to an sp^2 or sp C atom; 44 are aliphatic or saturated, *i.e.* with the acid group bound to an sp^3 carbon. The positions of H atoms bound to carbon were generated according to standard geometrical rules (Gavezzotti, 2008). The location of the atoms in the carboxyl group often poses a problem, because of disorder. Judging from the difference between the formally double and single carbon–oxygen bond distances, ΔR_{CO}, in organic acids one may observe a wide spectrum of possibilities, from complete separation of single and double bonds with $\Delta R_{CO} \simeq 0.1$ Å to an almost complete identity with $\Delta R_{CO} \simeq 0$. Nevertheless, none of the entries selected for the present work mentions a necessity of refining double positions for the O atoms, while an inspection of displacement parameters shows neither exceptionally large U_{eq} values for these atoms nor displacement ellipsoids elongated along the direction of the carbon–oxygen bond. On the contrary, many reports do include split positions for the H atom with temperature-dependent occupancy factors (see *e.g.* Wilson *et al.*, 1996). For our analyses and calculations we have adopted the following unified criteria:

(i) O-atom positions were retained as reported in the cif files of the Cambridge Structural Database;

(ii) for those entries where the position of the carboxyl hydrogen is reported (either as single occupancy or as the major occupancy site when two sites are reported) the C—O—H bond angle was retained but the O—H distance was normalized at 1.0 Å;

(iii) for the few entries which do not report any position for the H atom, the hydrogen coordinates were generated with an O—H distance of 1.0 Å and a C—O—H angle of 110°, in the plane of the COO group.

We are aware that these are questionable assumptions which will be discussed later in this paper in the light of the results. The table in the supplementary material contains the full list of entries with all the data used in the present communication.[1]

The interaction energy in the cyclic dimers was estimated by the *PIXEL* method (Gavezzotti, 2003; see Gavezzotti, 2008, for the most recent version of the package, and deposited material, for more detail). A point-by-point calculation of the charge density at the MP2/6-31G** level is carried out on the molecule in the exact geometry, as extracted from the X-ray study (except for the renormalized H-atom positions), by the *GAUSSIAN* package (Frisch *et al.*, 2003), with a step of 0.08 Å. The density is then contracted to 4 × 4 × 4 super-pixels. Coulombic and first-order polarization energies are calculated by the ordinary formulae from electrostatics. The static polarization term is supposed to take care of the fact that the calculation neglects any deformation on approaching molecules. The dispersion energy is evaluated by a London-type expression using locally distributed polarizabilities. The repulsion term is taken as proportional to the overlap between charge densities, also calculated by numerical integration. The Coulombic term is non-empirical, since no parameters enter its evaluation. Polarization, dispersion and repulsion terms depend on a few empirical parameters. The total energy between the pair of molecules in the cyclic hydrogen-bonded dimer, as if it were in the gas phase, is then calculated as the sum of the Coulombic, polarization, dispersion and repulsion terms.

3. Results and discussion

Fig. S1 (deposited) shows that the difference between the formally single (longer) and formally double (shorter) apparent bond lengths, ΔR_{CO}, decreases with increasing temperature for aromatic acid crystals, confirming, as expected, that a temperature-dependent phenomenon is occurring. The static geometrical model implicit in our assumption of molecular geometry (see preceding section) portrays the COO group at a time-averaged (as is proper of an X-ray experiment) point along the reaction coordinate that brings the system from a carboxyl group to a carboxylate anion, with a H atom between the two O atoms. Within the limits of this model, Fig. 1 shows the plot of the PIXEL dimerization energy as a function of ΔR_{CO}. There is a clear trend to more stabilizing energies as ΔR_{CO} decreases, *i.e.* the more the geometry of the COO group resembles the carboxylate anion geometry. That this is due to an increased Coulombic contribution is shown in Fig. S2 (deposited), where the plot of the Coulombic contribution as a function of ΔR_{CO} closely resembles the plot in Fig. 1. The dispersion term is nearly constant (between −17 and −21 kJ mol^{-1}), irrespective of the nature of the system to which the COOH group is attached; in our model dispersion is too short-range to selectively influence the formation of a cyclic carboxylic acid dimer. Smaller ΔR_{CO} and increasing stabilization go with shorter O···O separation, as shown in Fig. 2. Indeed, the patterns in Figs. 1, 2 and S2 (deposited) agree in indicating a stronger hydrogen bond with a larger reduction of the difference between the two apparent C—O bond distances. We deduce that our static model gives a reasonable representation.

Figs. 1, 2 and S2 (deposited) also show clear-cut separations between the cluster of aromatic acids and the rest of the sample: with few exceptions, only those acids in which the carboxyl group is directly bound to an aromatic system can have $\Delta R_{CO} < 0.06$. Several hypotheses to account for this phenomenon can be proposed, and they will be discussed in turn.

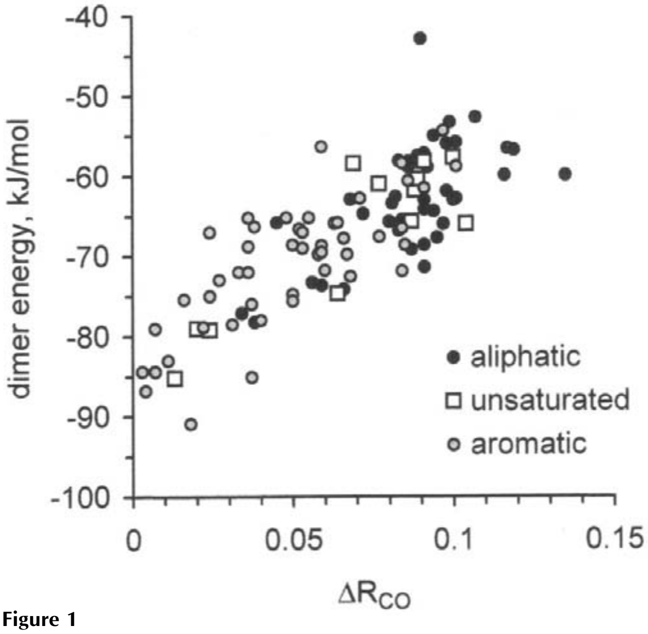

Figure 1
PIXEL total energy for the carboxylic acid cyclic dimers extracted from their crystal, as a function of ΔR_{CO}, the difference between the formally single and formally double carbon–oxygen bond lengths in the COOH group (Å as units). The three squares (unsaturated) in the aromatic acid domain, lower left part of the graph, are for tetrolic, cinnamic and crotonic acids.

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[1] Supplementary data for this paper, including a description of the PIXEL set-up, a table with all the crystallographic and energy data, Figs. S1, S2 and S3, are available from the IUCr electronic archives (Reference: BS5060). Services for accessing these data are described at the back of the journal. For reproducibility of the calculations described here, the *PIXEL* computer software and input and output files are available from the author upon request. A full documentation for the computer programs used with worked examples is available at the author's website, http://users.unimi.it/gavezzot.

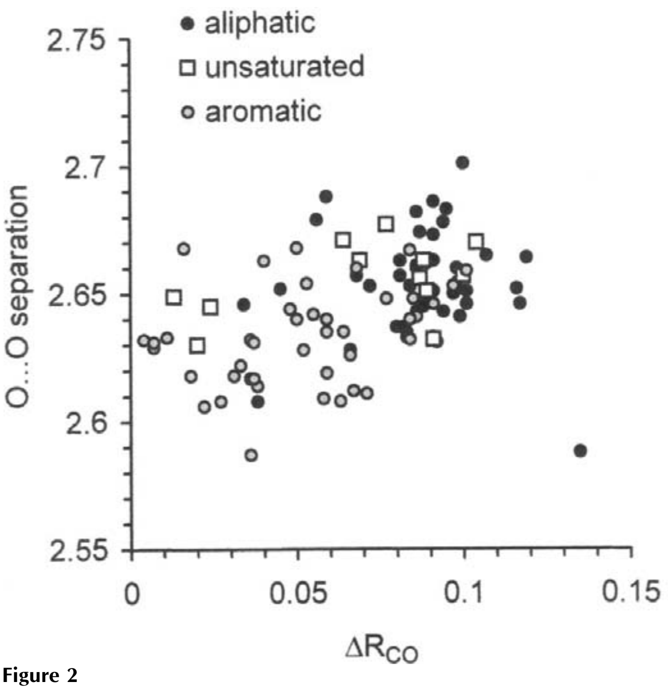

Figure 2
Same dimers as in Fig. 1: the oxygen–oxygen separation over the hydrogen bond. The outlier at the lower right corner of the graph (refcode BETCEI) has no obvious explanation.

(i) *Conjugation*: In this hypothesis, the COOH group resonates with the aromatic system *via* electronic conjugation. This is against the evidence for a dynamic effect, and is also denied by a plot of $\Delta R_{\rm CO}$ against the dihedral angle between the aromatic plane and the plane of the COO group, that shows total scatter (Fig. S3, deposited); *i.e.* the trend towards the carboxylate geometry is also present with high values of this angle and consequent disruption of conjugation.

(ii) *Induction by substituents*: The fact that most aromatic acids but no aliphatic acids show two nearly identical C—O distances coexists with the fact that the pK_a of benzoic acid is about three times as large as that of acetic acid; one is tempted to relate the solid-state effect to the relative stability of the carboxylate anion. However, $\Delta R_{\rm CO}$ values do not correlate with the presence of electron-withdrawing or -attracting substituents on aromatic rings, and, for example, chloroacetic acids (pK_a 100–1000 times that of acetic acid) have nearly the same $\Delta R_{\rm CO}$ as their unsubstituted counterparts. The fact that tetrolic acid ($\rm CH_3C{\equiv}CCOOH$) and cinnamic acid, although not aromatic, are intruders in the aromatic acid cluster (Fig. 1) seems however to confirm that a certain availability of polarizable electrons is necessary for $\Delta R_{\rm CO}$ to decrease.

(iii) *Ortho effects*: Nearly all aromatic acids that have a high $\Delta R_{\rm CO}$ have a bulky substituent *ortho* to the carboxyl group. Particularly striking is the case of 2-naphthoic acid ($\Delta R_{\rm CO} = 0.018$) *versus* 1-naphthoic acid ($\Delta R_{\rm CO} = 0.097$). In terms of acidity, this is the opposite of the *ortho* effect in solution (the pK_a of *ortho*-substituted benzoic acids are 3–10 times those of their *para* counterparts).

(iv) *Solid-state environment*: In crystals the relative stability on interchanging the C=O and C—O bonds must also depend on the local, short-range intermolecular environment of each of the two O atoms. It is tempting to postulate that these environments have more chances of being similar in the planar geometry of the aromatic ring than in the more twisted structures that result from bonds between sp^3 C atoms. This hypothesis is supported by the solid-state *ortho* effect mentioned above, but is also very difficult to prove or disprove by simple static energy calculations, let alone by geometrical inspection. If this hypothesis were well-founded, the dynamic barriers observed by temperature-dependent NMR would refer to the intermolecular energy differences at the O atoms rather than, or at least as well as, to the migration of the proton along the O···O direction.

4. Conclusions

A clear distinction between aromatic and non-aromatic acids appears as regards the difference between the two C—O distances, as observed by X-ray diffraction in carboxylic acid crystals, for those compounds that form cyclic dimers. Crystals where a catemer is formed instead, on a preliminary survey, do not show proton disorder: the case would however deserve a separate study – although the formation of chain motifs is a rare occurrence for carboxylic acids. Our tentative energy classification indicates – within the limits of the many assumptions – that the stability of the carboxylic acid dimer increases as the difference between the two apparent C—O distances becomes smaller. The presence of an aromatic system or of a reservoir of polarizable electrons attached to the carboxyl group seems a necessary condition. Otherwise, no single hypothesis seems adequate for a cogent explanation of the many facets of this phenomenon. As usual in crystal chemistry problems, when looking at structural detail one is presumably confronted with a delicate balance of several intra- and intermolecular factors. Such a final sentence is becoming a classic in critically oriented papers on the relationship between molecular and crystal structure.

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