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Breakdown of the hydrogen bond strength–length analogy: a revision

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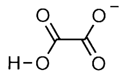
A recent study which addressed the nature of the association between hydrogenoxalate anions in the solid state came to the conclusion that short OH···O contacts between these species did not constitute an attractive interaction, but one which simply minimized inter-anion repulsion; in the light of new crystallographic evidence and a solution study, some issues raised in this work need to be re-evaluated.

It was recently put forward that an interaction which had the physical appearance of a short, charge-assisted hydrogen bond was, in fact, not a hydrogen bond. The case of the hydrogenoxalate anion **1** was examined in detail by Braga *et al.*[1] using



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computational methods, where the conclusion was reached that charge delocalization over the whole species meant that no attractive force of interaction could be present between these anions, despite the fact that they organize into chains in the solid state connected through close, interanionic OH···O contacts. This then led to the reassignment of these contacts as the 'least repulsive' orientation of the two species, rather than a bond. This, finally, was cited as a breakdown of the widely accepted length–strength inverse analogy of hydrogen bonding, since, despite its shortness, the H-bond was not strong, indeed not even a bond but a repulsive interaction held in place by a stronger cation–anion network.

One problem with the above assertions is contextual. To be sure, in a vacuum and in the absence of counterions, the isolated OH···O interaction is not sufficient to keep the interanionic complex associated.[2] Under such circumstances, as was claimed, the relationship could not be characterized as 'bonding', since energy would be required to maintain it, rather than dissociate it. This view, however, does not take into account that the association of any two species consists of a combination of interaction energies, the totality of which must result in a net force of attraction. In salts of **1**, four primary interactions are present: (+)–(−), (+)–(+), (−)–(−) and OH···O. These interactions can be modeled and evaluated individually, but the report in question isolated two of the interactions and compared them to each other, *i.e.* (−)–(−) to OH···O, found the former dominant, and came to the conclusion the latter was therefore not enthalpically favorable.[1]

Perhaps the most significant feature of this work was however the remarkable and counterintuitive finding that the absence of positive regions in the molecular electrostatic potential map calculated for **1** indicated that, 'irrespective of the relative orientation, two $HC_2O_4^-$ anions repel each other electrostatically.'[1] This suggested that, under *no* circumstances could the OH···O interaction in question ever be considered 'bonding'.

We first confronted this issue by doing a study of the behavior of soluble salts of **1** in chloroform solution by ^1H NMR spectroscopy. We chose as counter ion the large, non-coordinating tetrapropylammonium cation. Systematic variation of the concentration [Pr_4N^+**1**$^-$] produced a classic H-bonding isotherm for the acidic proton in the NMR (Fig. 1), to which a curve could be fit modeled either on linear oligomers or on a combination of cyclic H-bonded dimers plus linear oligomers to give association constants K_a = 294 or 226, respectively.[3] Parallel control studies of acetic acid and the tetrapropylammonium acetate–acetic acid (1:1) complex under the same experimental conditions gave association constants for these species of 89 and 861, respectively, the latter value reflecting the charge-assisted nature of the bond.[4] No noteworthy change in chemical shift for the protons of the counterion was observed in any case. If acetic acid and its acetate complex can be taken as reasonable models for the hydrogen bonding between hydrogenoxalates, the **1**···**1** association can not be accounted for by cyclic dimers alone, but requires a substantial contribution from charge-assisted linear interactions. Clearly, however, the repulsion term (−)–(−) leads to less effective hydrogen bonding in **1**···**1** than for AcO^-···HOAc, although its influence is greatly diminished relative to vacuum by the dynamic charge-screening effects of the solvent and counterions.

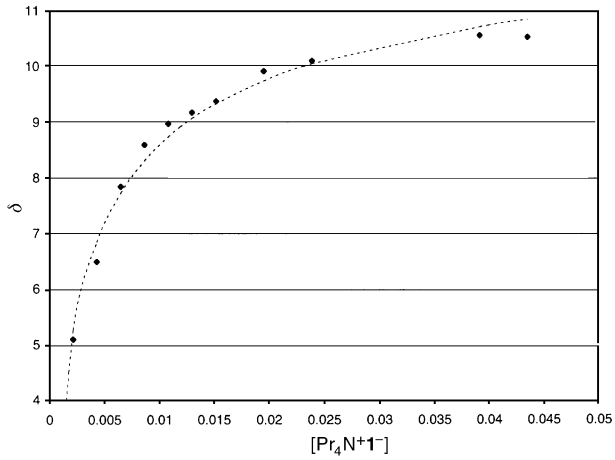

Fig. 1 Plot of the variation in chemical shift of the acidic proton in [Pr_4N^+**1**$^-$] with increasing concentration; (●) experimental, (----) best fit curve.

Our second approach to examining the nature of the OH···O interactions in **1** was crystallographic. If it is indeed the case that this interaction is actually repulsive, despite the very short O···O contact distance of 2.52 Å in potassium hydrogenoxalate (the example used in ref. 1), then distancing the cationic centers from hydrogenoxalate chain would be likely to disrupt this 'explosive' motif. In any case, the tremendous electrostatic compression which would be experienced by two *repulsive* functions (O^- and OH) being forced into such close proximity should be relaxed as less effective cations lose influence over the anions. We chose to test this concept by preparing the tetramethyl- and tetraethyl-ammonium hydrogenoxalate salts and determining their X-ray crystal structures.† Although the tetrapropylammonium salt is also a solid, X-ray quality crystals could not be obtained, and the higher alkylammonium hydrogenoxalates are oils. As shown in Fig. 2, the hydrogen bonded chain is preserved in the Me_4N^+ and Et_4N^+ salts, thus no

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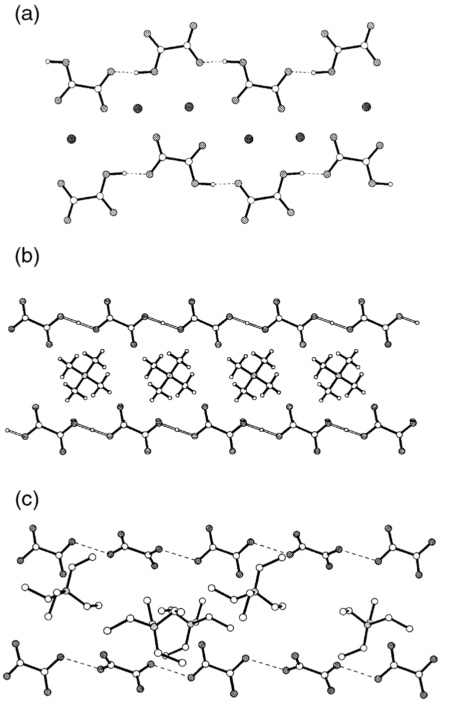

Fig. 2 (*a*) X-Ray crystal structure of [K$^+$**1**$^-$] (ref. 5). (*b*) X-Ray crystal structure of [Me$_4$N$^+$**1**$^-$]. The hydrogen bond appears to be symmetric with the hydrogen atom located equidistant between two oxygen atoms. Note, however, that it is not always possible to distinguish between an ordered H atom on a symmetry element from two disordered H atoms close to that symmetry element. Although the electron density contour maps gave no sign of disorder, the assignment of this hydrogen as an ordered atom in the center of the H-bond is not conclusive. (*c*) X-Ray crystal structure of [Et$_4$N$^+$**1**$^-$].

disruption of the motif occurs. Furthermore, the O···O distances in both the Me$_4$N$^+$ (2.476 Å) and Et$_4$N$^+$ (2.485 Å) derivatives are actually shorter than for the K$^+$ salt (2.518 Å),[5] even though the separation between the charged center of these cations and the H-bonded chain is considerably greater than for the K$^+$ ion.

In conclusion, if no hydrogen bonding were possible between hydrogenoxalate anions, as suggested,[1] we would expect no **1**···**1** interaction in solution; we would anticipate the lengthening of the OH···O contact and the eventual disruption of the chain motif in the solid as more weakly coordinating counterions are used; and in any case, very short O···O distances, typically diagnostic of strong or very strong hydrogen bonds,[6] would not be expected. In fact, all of the experimental observations suggest the contrary, *i.e.* a case is clearly made for hydrogen bonding between hydrogenoxalates in solution, and the O···O distances actually decrease in the solid state on association with more diffuse cations.

Indeed, one must consider the overall picture of **1**···**1** and its counterions in terms of a balance of interactions, two 'associative' [(+)–(−), and OH···O] and two dissociative [(+)–(+), (−)–(−)], with the net effect, both in solution and the solid state, being the assembly of hydrogenoxalate anions into aggregates of some description, depending on the medium. The assertion that a breakdown in the H-bonding length–strength analogy has been observed (based on the hypothesis that interanionic OH···O contacts are not hydrogen bonds) must herewith be revised: although no direct measurement of the quality of these interactions has been made, the experimental evidence supports their characterization as hydrogen bonds, and there is at present no argument to suggest that the length–strength analogy should not apply in this or related cases.

We also note that in the course of this study, Steiner[7] produced statistical evidence that the O–H and H···O distances in $^-$[O–H]···O$^-$ hydrogen bonds were consistent with those in undisputed hydrogen bonded systems, as well as citing the key example of dimethylammonium hydrogenoxalate, whose counterions do not bridge the hydrogenoxalates and thus can not be responsible for the assembly of the '*pseudo*-hydrogen bonded' chain, as implied by Braga *et al.* for [K$^+$**1**].[1] We feel our spectroscopic and crystallographic studies are complementary with the results of Steiner, and that the weight of experimental evidence now strongly implies that the computational model of the electron density in **1** used by Braga *et al.* is not an ideal representation, since it does not predict the observed association.

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Notes and references

† *Crystal data:* for [Me$_4$N$^+$**1**$^-$]: C$_4$H$_{12}$N$^+$C$_2$HO$_4$$^-$, M = 163.17, monoclinic, a = 8.386(2), b = 5.700(2), c = 9.456(2) Å, β = 103.81(3)°, U = 438.9(2) Å^3, T = 220(2) K, space group $P2/n$ (alt. $P2/c$, no. 13), Z = 2, D_c = 1.235 g cm^{-3}, μ(Mo-Kα) = 0.103 mm^{-1}, 867 unique reflections (R_{int} 0.019) measured and used in all calculations. Final R_1 [752 $F \geqslant 4\sigma(F)$] = 0.0420 and wR (all F^2) was 0.120. Data collection at temperatures below 220 K was impossible due to the presence of a phase change.

For [Et$_4$N$^+$**1**$^-$]: C$_8$H$_{20}$N$^+$C$_2$HO$_4$$^-$, M = 219.28, monoclinic, a = 14.291(6), b = 10.933(7), c = 15.38(2) Å, β = 90.99(11)°, U = 2403(4) Å^3, T = 220(2) K, space group $P2_1/c$ (no. 14), Z = 8, D_c = 1.212 cm^{-3}, μ(Mo-Kα) = 0.092 mm^{-1}, 3133 unique reflections measured and used in all calculations. Final R_1 [1959 $F \geqslant 4\sigma(F)$] = 0.152 and wR(all F^2) was 0.422. The structure contains extensive disorder affecting all four methylene groups in one of the cations. One of the oxalate anions is less seriously affected, with disorder in both oxygen atoms of one CO$_2$$^-$ terminus. There is a major [0.854(10)] component to the methylene disorder but the anion disorder is 50:50 within estimated standard uncertainties.

CCDC 182/1718. See http://www.rsc.org/suppdata/cc/b0/b002361m/ for crystallograpic files in .cif format.

1 D. Braga, F. Grepioni and J. J. Novoa, *Chem. Commun.*, 1998, 1959; see also: D. Braga, F. Grepioni, E. Tagliavini, J. J. Novoa and F. Mota, *New. J. Chem.*, 1998, 755.

2 The measured hydrogen bond enthalpy in KHC$_2$O$_4$ is 51.4 kJ mol^{-1} (M. S. Rozenberg, *Spectrochim. Acta, Part A*, 1996, **52**, 1559), whereas the simple point charge model $q_a q_b/4\pi\varepsilon\varepsilon_0 r$ gives a value of 270 kJ mol^{-1} for the interanionic repulsion in vacuum.

3 A least-squares fitting procedure was used to obtain K_a from the expression for the calculated chemical shift values. An expression for hydrogenoxalate where equilibria between a cyclic dimer, linear dimer, linear trimer and linear tetramer are taken into account is:

$$\delta_{calc} = \delta_{dimer}\frac{2K_d[O\times H]^2}{[O\times H]_i} + \delta_{end}\frac{\Sigma_n K_a{}^{n-1}[O\times H]^n}{[O\times H]_i} + \delta_{complex}\frac{\Sigma_n(n-1)K_a{}^{n-1}[O\times H]^n}{[O\times H]_i}$$

where K_d is the association constant for the cyclic dimer and is given the value 89 as determined for acetic acid in deuterochloroform under strictly anhydrous conditions, and δ_{dimer} is the associated chemical shift for this dimer. K_a is the association constant for the equilibria between monomeric **1** and the **1**···**1** linear dimer and each n-mer up to n = 4. The values of δ_{end} and $\delta_{complex}$ represent the chemical shifts of the non-associated protons at the end of the chain and the hydrogen bonded protons present in these oligomers, respectively. The value [OxH]$_i$ is the total concentration of hydrogenoxalate and [OxH] is the concentration of non-hydrogen bonded hydrogenoxalate present at equilibrium. The equilibria present in the (Pr$_4$N$^+$AcO$^-$)(AcOH) system can be modeled on a similar expression.

4 The K_a value for acetic acid dimerization in chloroform is consistent with those in the same concentration range as determined by IR spectroscopy: G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, 1954, **76**, 5248.

5 F. H. Moore and L. F. Power, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 873.

6 P. Gilli, V. Bertolasi, V. Ferretti and G. Gilli, *J. Am. Chem. Soc.*, 1994, **116**, 909.

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