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Cooperative assistance in a very short O–H··O hydrogen bond. Low-temperature X-ray crystal structures of 2,3,5,6-pyrazinetetracarboxylic and related acids

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In contrast to the well documented role of charge- and resonance-assistance in very short hydrogen bonds, a very short $O–H_{acid}\cdots O_{water}$ hydrogen bond [O···O 2.4791(13) Å] in the title acid is ascribed to the cumulative stabilisation from σ- and π-bond cooperativity.

Very short (very strong) O–H···O hydrogen bonds are formed with unusually activated donors and acceptors, as between an acid and its conjugate base ($O–H\cdots O^-$) or in the hydrates of strong acids ($O^+–H\cdots O$). With H···O distances in the range 1.2–1.5 Å (O···O 2.2–2.5 Å), very short H-bonds have a significant covalent component (O–H ≈ H···O) and bond energies in the range 15–40 kcal mol^{-1}. The substantial covalent character of very short H-bonds, a result of three-centre–four-electron contribution, $O^{\bullet}–^{\bullet}H\cdots^{\bullet\bullet}O \leftrightarrow O^{\bullet\bullet}\cdots H^{\bullet}–^{\bullet}O$, is responsible for their distinctive properties: the near linear geometry (θ = 170–180°), the lengthening of O–H distance (up to 0.2 Å) and the very large IR bathochromic shifts (up to 2000 cm^{-1} in ν_s).[1] Typical examples are the intramolecular hydrogen bonds in monobasic salts of dicarboxylic acids.[2] Very strong hydrogen bonds are relevant in the context of proton transfer phenomena in chemical and biological systems and they have been studied with spectroscopic, crystallographic and computational methods.[1a] The overall picture that emerges from such studies is that very short H-bonds have a quasi-covalent character. This is in contrast to strong hydrogen bonds (H···O 1.5–2.2 Å, O···O 2.5–3.2 Å, energy 4–15 kcal mol^{-1}) that are largely electrostatic in nature.[1b]

In addition to charge-assisted hydrogen bonding (CAHB: $O–H\cdots O^-$, $O^+–H\cdots O$) in carboxylic acids, very short hydrogen bonds have been observed in the neutral β-diketone enol fragment, ···O=C–C=C–OH···, wherein resonance-assistance through π-bonds (RAHB) results in unusual bond shortening.[3] We show here that a composite array with σ- and π-bond cooperativity, $O–H\cdots O{=}C–O–H_{acid}\cdots O_{water}–H\cdots O$, can shorten an *inter*molecular $O–H_{acid}\cdots O_{water}$ hydrogen bond into the regime of the very short H-bond (O···O < 2.50 Å). This kind of H-bond array has been referred to as 'polarisation enhanced hydrogen bonding' by Jeffrey.[1a] Our example of a very short hydrogen bond is: (i) intermolecular, (ii) not of the charge-assisted type,[4] (iii) not of the acid–conjugate-base type[5] and (iv) does not contain highly activated donor/acceptor groups.[6]

Recrystallisation of 2,3,5,6-pyrazinetetracarboxylic acid **1**† from 20% aqueous HCl afforded diffraction quality crystals of the dihydrate. Low-temperature (123 K) single crystal X-ray analysis of $\mathbf{1}\cdot 2H_2O$ ($P\bar{1}$, Z = 1)‡ showed it to contain a very short $O–H_{acid}\cdots O_{water}$ H-bond [d = 1.50 Å, D = 2.4791(13) Å, θ = 170.3°]§ that is part of cooperative array **I** [Figs. 1 and 2(a)]. In this very short H-bond, both the carboxylic acid O–H donor ability and the water O atom acceptor basicity are simultaneously enhanced through polarisation, as shown in Fig. 2(b). Such a strong polarising effect involving water was noted recently in the complex, $Ph_3P{=}O$–1,4-diethynylbenzene–H_2O (4 : 1 : 2).[7] The other O–H···O/N bonds in the crystal are in the short to medium range (Table 1).

In order to probe such a polarisation-induced H-bond shortening in related acids, the crystal structures of pyrazine-2,3-dicarboxylic acid **2** and 5,6-dimethylpyrazine-2,3-dicar-

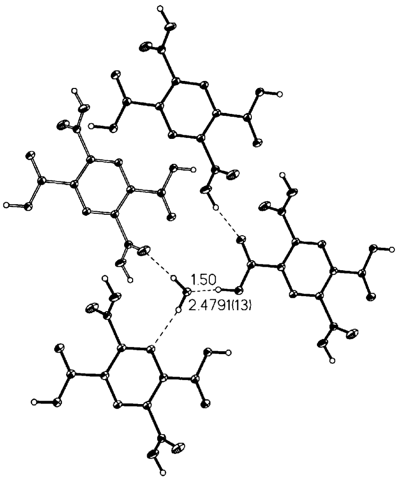
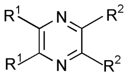


Fig. 1 Crystal structure of tetra-acid **1** showing the cooperative O–H···O synthon **I**. The water molecule acts as a H-bond donor to the CO_2H group of the next layer (shaded differently). Metrics of the very short O–H···O bond are indicated. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.



1: $R^1 = R^2 = CO_2H$
2: R^1 = H, $R^2 = CO_2H$
3: R^1 = Me, $R^2 = CO_2H$

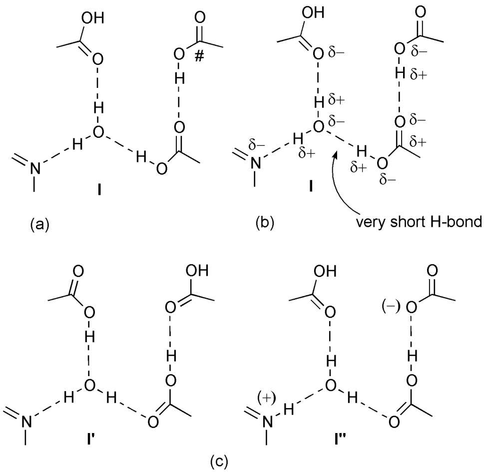


Fig. 2 (a) Cooperative synthon **I** in tetra-acid **1**. The acid group marked # is replaced with H_2O in diacids **2** and **3**. (b) Donor and acceptor groups enhanced by polarisation in **I**. (c) Tautomer synthons **I′** and **I″** (not observed).

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Table 1 Geometry of O–H···O/N hydrogen bonds and C–O bond lengths

Acid	Hydrogen bond geometry									
	O–H···O				O–H···N				Bond length	
	O–H/Å	*D*/Å	d^a/Å	θ/°	O–H/Å	*D*/Å	d^a/Å	θ/°	C–O/Å	C=O/Å
$\mathbf{1}^b$	0.96(3)	2.4791(13)	1.50	170.3	0.85(3)	2.9393(16)	2.01	156.1	1.3113(17)	1.2022(15)
	0.91(2)	2.7010(12)	1.74	162.6					1.2957(16)	1.2174(14)
	0.89(2)	2.7811(12)	1.80	171.9						
$\mathbf{2}^c$	1.05	2.562	1.58	170.9	0.73	2.840	1.87	166.4	1.304	1.208
	0.86	2.922	2.04	147.4						
$\mathbf{3}^b$	0.968(18)	2.5269(12)	1.55	167.2	0.87(2)	2.8963(13)	1.97	155.1	1.3143(13)	1.2122(13)
	0.872(18)	2.8747(12)	1.92	162.4						

[a] *d* Values are neutron-normalised (O–H 0.983 Å). [b] This work. [c] Ref. 8.

boxylic acid **3** were analysed. Diacid **2** is reported as a dihydrate (*C*2/*c*).[8] Diacid **3** was also determined to be a dihydrate by low-temperature X-ray diffraction (*Pbcn*).‡ Both these crystal structures contain synthon **I** with O···O distances in the short (strong) regime [$\mathbf{2}\cdot 2H_2O$ 2.562, $\mathbf{3}\cdot 2H_2O$ 2.5269(12) Å]. The very short O–H···O bond in **1** compared to the short bond in **2** and **3** may be rationalised through differences in their extended arrays: the CO_2H donor in **1** [marked with # in Fig. 2(a)] is replaced by H_2O in **2** and **3**. The relative shortness of the O–H···O bond in **3** compared to **2** could be because the donor O–H_{acid} is more polarised by the stronger O–H_{water}···O = C–O–H bond in **3** [2.922 *vs.* 2.8747(12) Å].

Another reason for the very short O–H_{acid}···O_{water} bond in tetra-acid **1** compared to the short H-bond in diacids **2** and **3** is the presence of twice as many electron-withdrawing groups in the former structure. Thus, molecular (4 CO_2H groups on a *N*-heterocycle) and supramolecular (extended cooperative array **I**) features act in concert, resulting in the very short O–H···O bond in **1**. An analysis of the Cambridge Structural Database (April 2000 update) substantiates our observation. While CO_2H···OH_2 H-bonding is present in many carboxylic acids (*ca.* 150 contacts in the range O···O 2.40–2.80 Å),¶ the very short H-bond region (< 2.50 Å) contains mostly the oxalic acid dihydrates (11/13). In these crystal structures, activation of the donor O–H in the 1,2-dicarboxylic acid moiety results in very short O–H_{acid}··O-$_{water}$ bonds, a point not mentioned in the original publications.[9]

A novel feature of this work is the influence on H-bond shortening of cooperative stabilisation, a phenomenon hitherto not discussed in the extensive literature[1–6] on very short hydrogen bonds. Once again, akin to polarisation by water,[7] precedent for H-bond shortening through cooperative assistance comes from the weak C–H···O category, namely 2-ethynyladamantan-2-ol.[10] The presence of two types of CO_2H groups in the same crystal, one that engages in a very short H-bond and the other with a normal H-bond, permits an assessment of O–H bond lengthening (Table 1). Thus, the very short O–H···O bond in **1** displays the expected characteristics: near linear geometry (θ = 170.3°), O–H lengthening (0.1 Å) and O–H ν_s in agreement with the reported correlation (1398 cm^{-1}).‖

In order that our σ- and π-bond cooperativity argument through synthon **I** is tenable, the presence of tautomers **I′** and **I″** in tetra-acid **1** [Fig. 2(c)] must be rigorously excluded, because such motifs would contribute towards resonance stabilisation (**I** ↔ **I′**↔ **I″**), and in effect negate the present hypothesis. Carboxylic acid groups may be characterised as C=O and C–O or as a delocalised carboxylate by their single and double bond lengths.[11] A difference of > 0.1 Å implies a static CO_2H group while a smaller difference (< 0.02 Å) means a resonating or disordered carboxylate. The > 0.1 Å difference between C–O and C=O bond distances in **1–3** (Table 1) confirms that synthon **I** is present in their crystal structures, and not a resonance-stabilised motif.

In summary, we have shown that polarisation through a finite σ- and π-bond cooperative array can shorten an O–H···O bond into the very strong regime. This study adds to our knowledge of the traditional H-bond shortening phenomena, namely through charge- and resonance-assistance.

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Notes and references

† *Synthesis*: tetra-acid **1**: oxidation of phenazine with $KMnO_4$ (R. J. Light and C. R. Hauser, *J. Org. Chem.*, 1961, **26**, 1296). Diacid **3**: by the oxidation of 2,3-dimethylquinoxaline under identical conditions.

‡ *Crystal data*: tetra-acid **1**: 2,3,5,6-pyrazinetetracarboxylic acid dihydrate ($C_8H_4N_2O_8\cdot 2H_2O$, *M* = 292.16); triclinic, space group $P\bar{1}$, a = 5.4409(3), b = 6.4041(3), c = 8.6995(3) Å, α = 98.572(3), β = 107.374(3), γ = 105.519(3)°, V = 269.97(2) Å^3, Z = 1, D_c = 1.797 Mg m^{-3}, Nonius Kappa CCD area detector, T = 123 K, μ = 0.171 mm^{-1}, λ(Mo-Kα) = 0.71073 Å, ω scan mode, 1219 unique reflections, 1125 with $F_o > 4\sigma(F_o)$, no absorption corrections. Structure solution and refinement with standard methods (SHELX97); H-atoms refined isotropically. Final R = 0.030 (obs.), 0.032 (all); $wR(F^2)$ = 0.080 (obs.), 0.082 (all).

Diacid **3**: 5,6-dimethylpyrazine-2,3-dicarboxylic acid dihydrate ($C_8H_8N_2O_4\cdot 2H_2O$, *M* = 232.19); orthorhombic, space group *Pbcn*; a = 12.6454(3), b = 9.0812(3), c = 8.8800(3) Å, V = 1019.74(5) Å^3, Z = 4, D_c = 1.512 Mg m^{-3}, Nonius Kappa CCD area detector, T = 123 K, μ = 0.131 mm^{-1}, λ(Mo-Kα) = 0.71073 Å, ω scan mode, 1161 unique reflections, 1059 with $F_o > 4\sigma(F_o)$, no absorption corrections. Structure solution and refinement with standard methods (SHELX97); H-atoms refined isotropically. Final R = 0.031 (obs.), 0.034 (all); $wR(F^2)$ = 0.084 (obs.), 0.086 (all). CCDC 182/1850. See http://www.rsc.org/suppdata/cc/b0/b007346f/ for crystallographic files in .cif format.

§ *d* Values in this study are neutron-normalised (O-H 0.983 Å).

¶ Screens −28, 35, −55, 57, 85, 88, 153 were applied. Organometallic crystal structures were excluded.

‖ See ref. 1(*a*), p. 222.

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