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Unexpectedly Strong Hydrogen Bonding in Some Tetrahydro-4,7-phenanthroline-1,10-dione-3,8-dicarboxylic Acids

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Summary Tetrahydro-1,10-dioxo-4,7-phenanthroline-3,8-dicarboxylic esters exist in the oxo-hydroxy form with a strong intramolecular O–H · · · O hydrogen bond; an even stronger intermolecular bond is present in the corresponding carboxylic acids which gives rise to D-type bands in the i.r. spectrum.

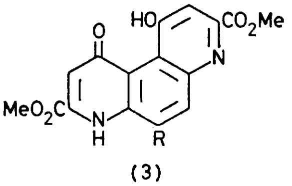
'D-TYPE' bands[1] in the i.r. spectrum are associated with extremely strong hydrogen bonds,[1–4] and there is evidence[3] that those at the lower end of this range (900—600 cm^{-1}) are genuinely symmetrical, *i.e.* they possess a single potential minimum. Nearly all known examples are of types (**1**) and (**2**),[2,3,5] *viz.* the cations and anions of 'hemi-salts.' We report an example of extreme D-type bonding in a quite unexpected context.

$(BHB)^+$

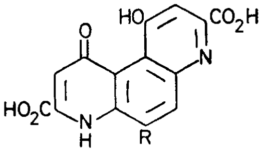
(1)

$(AHA)^-$

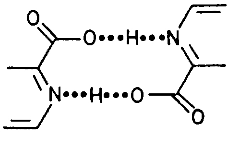
(2)



(3)



(4)



(5)

Cyclisation of the bis-anils derived from substituted *p*-phenylenediamines and acetylenedicarboxylic esters yields the tetrahydro-1,10-dioxo-4,7-phenanthroline-3,8-dicarboxylic esters [*e.g.*, (**3**)]† from which the acids (**4**) may be prepared by hydrolysis.[6] The tautomeric form shown for the ester (**3**, R = Br) is demonstrated by three features: (a) the doubling of ester carbonyl, also found for (**3**, R = H) and otherwise inexplicable in a symmetrical molecule, (b) the co-existence in the 6 μm region (see Table) of vibrations due to separate pyridine- and pyridone-like species, and (c) broad shallow B- and C-type bands[2] centred near 2600 and 1850 cm^{-1} and assigned to the strong intramolecular O–H · · · O hydrogen bond whose ^{1}H n.m.r. signal [in $(CD_3)_2SO$] at δ 16·7 is concentration-independent. Pyridone ν_{NH} is at 3290 cm^{-1} (broad, δ *ca.* 12). This

TABLE

Assignment of i.r. bands in the 6 μm region.

(**3**, R = Br)	(**4**, R = Br)	Assignment
1738	1748	Ester or acid $\nu_{C=O}$
1712		
1633	1614	Pyridone $\nu_{C=O}/\nu_{C=C}$[a]
1605	1599	ν_{ring}
1563	1546	Pyridone $\nu_{C=O}/\nu_{C=C}$[a]
1511	1506	ν_{ring}
1484		

[a] *Cf.* B. D. Batts and E. Spinner, *Austral. J. Chem.*, **1969**, **22**, 2581.

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† All compounds described possess satisfactory elemental analyses. The alternative linear structure can be eliminated despite a report to the contrary (S. V. Khetan and M. V. George, *Canad. J. Chem.*, **1969**, **47**, 3545) because of i.r. and n.m.r. spectral features, some of which are discussed here. Some of these isomeric pyrido[2,3-*g*]quinolinedione acids and esters have been synthesised unambiguously (ref. 6) and are distinct; in particular, they do not possess two different, very low-field proton signals.

tautomeric form plausibly results from strong dipolar repulsion between the otherwise expected[7] twin carbonyls; a similar rationalisation explains[8] the (quite different) tautomeric equilibria in the sterically contrasted 10-hydroxy-1,7-phenanthrolines. The i.r. spectra of (**3**, R = Br) and (**4**, R = Br) are shown in Figures 1 and 2, respectively.

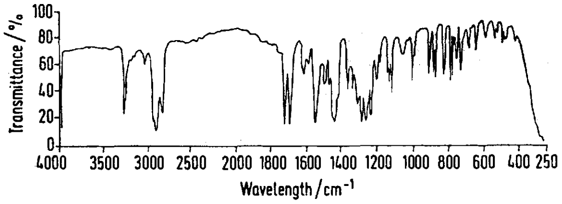

FIGURE 1. I.r. spectrum (Nujol) of (**3**, R = Br).

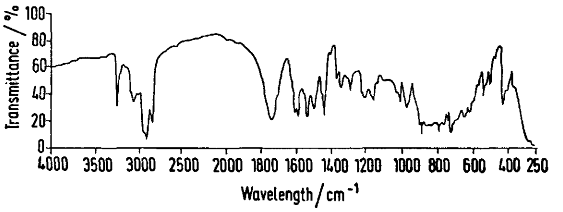

FIGURE 2. I.r. spectrum (Nujol) of (**4**, R = Br).

The tautomeric form is clearly unchanged in the corresponding acid (**4**, R = Br), while ν_{NH} and the type B and C bands are still present (Figure 2; contrast Figure 1). This spectrum however is dominated by an enormously strong and broad D-type band, clearly showing the characteristic 'transmission windows'[2] and centred below 800 cm^{-1}. There is also a new, broad band near 3050 cm^{-1}. If the latter is due, as is plausible,‡ to the $\nu_{NH}{}^{+}$ of a zwitterion, the 800 cm^{-1} band being assigned to its anion in the form (**2**, A = CO_2), one would expect[9] a sharp rise (20—40 cm^{-1}) in the *ca.* 1600 cm^{-1} pyridine ring mode, with acid $\nu_{C=O}$ in the 1710—1640 cm^{-1} region.[3] Neither feature is found. As an alternative we suggest that, while one acid group per molecule takes part in the usual dimer, the other forms an intermolecular bond to the ring nitrogen of a neighbouring molecule, these being responsible for the 3050 and 800 cm^{-1} bands, respectively.

There are difficulties in this interpretation too; 3050 cm^{-1} is high for carboxylic ν_{OH}, while the very broad 1750 cm^{-1} band has to be interpreted as an envelope covering bonded (dimer, near 1720 cm^{-1}) and unbonded [as in (**5**)] acid carbonyl groups. Nevertheless we regard these objections as less serious. We therefore postulate as the origin of the D-type band a hydrogen bond with the asymmetric single potential minimum indicated in the part-structure (**5**). This situation is rare, but may be foreshadowed by a recent study[10] which shows that exceptionally strong hydrogen bonds, with ν_{XH} as an A,B,C continuum, are formed in solution between amines and carboxylic acids when the populations of (OH $\cdots$ N) and ($O^{-}\cdots HN^{+}$) are nearly in balance. Possibly in (**4**) an even balance could result from exceptional electron donor properties induced in aza-nitrogen by the intramolecular OH $\cdots$ O bond. Since the D-type bands of species (**1**) can move to 2400 cm^{-1} in solution,[11] our results, and those of Lindemann and Zundel,[10] may represent solid-state and solution aspects of the same phenomenon.

In view of the above speculations and the universality of D-type bands throughout series (**4**), a crystal structure would be of great interest. Unfortunately, all attempts to grow suitable crystals have failed. Solubilities in common solvents are extremely low and m.p.s (*ca.* 300 °C) are correspondingly high, as is compatible with the infinite chains which can be drawn on either theory.

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‡ We thank a referee for this suggestion.

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[5] See, *e.g.* D. Cook, *Canad. J. Chem.*, 1963, **41**, 2575; A. L. MacDonald, J. C. Speakman, and D. Hadži, *J.C.S. Perkin II*, 1972, 825; Z. Dega-Szafran, M. Z. Naskret-Barciszewska, and M. Szafran, *ibid.*, 1974, 763.

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