The Ion-pair Reinforced, Hydrogen-bonding Molecular Ribbon

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A hydrogen transfer potential is programmed into the components of a self-organising system, and cocrystallisation gives a molecular ribbon in which a triple hydrogen-bonding motif is reinforced by ion pairing.

The application of hydrogen bonding as a design principle in the construction of 'supermolecules' is in these days commonplace. Hydrogen bonding drives host–guest complexation, controls states of aggregation, and pervades approaches to 'crystal engineering'.[1] Despite this, the relative weakness of this interaction must eventually limit the practical utility of simple H-bonded solids as materials. Indeed, in the absence of a multiplicity of hydrogen bonds acting cooperatively, there is little basis for uncommon physical properties.

To counter this there have been moves towards the application of the stronger ionic, metal–ligand, and Lewis acid–base type interactions in component design.[2] Another approach is the exploitation of noncovalent interactions to template the assembly of a molecular aggregate which is subsequently rendered permanent in a 'covalent fixing' step.[3]

In nature, however, the forces which stabilise higher order structures are often combinations of two or more electrostatic, H-bonding, or van der Waals type interactions. The DNA double helix, for example, benefits from both multiple H-bonding and aromatic stacking, while proteins make extensive use of salt bridges, H-bonding, and π–π interactions, not to mention hydrophobic domain-oriented behaviour. Thus, we became interested in the prospect of coupling ion pairing with hydrogen bonding in polymeric self-associates of the type recently described by Lehn[4] and Whitesides,[5] and popularised in the work of Kunitake,[6] Ringsdorf,[7] and others.[8] The motivation for this was twofold: firstly this would reinforce the H-bonding network which stabilises such assemblies,[9] thus potentially improving their material properties; secondly it introduces the possibility of directional proton conduction through molecular ribbons oriented to a particular crystal plane.[10]

We now report the solid state structure of a triply hydrogen-bonded molecular ribbon which is self-reinforcing by ion pairing. Because molecular ribbons can be assembled using either barbituric or cyanuric acid derivatives as the 'acidic component' and either melamine or triaminopyrimidine as the 'basic component', consideration of the relative acidities of these subunits led us to choose the combination which would give the most effective possible interaction. Intercomponent proton transfer, if it could be made to take place, would by necessity involve a cyanuric acid and triaminopyrimidine pair, because: (*a*) the NH of cyanuric acid is a better H-donor and the C=O groups better H-acceptors than in barbituric acid derivatives,[11] which are already known *not* to transfer a proton to a triaminopyrimidine partner,[4] and (*b*) the popular melamine recognition unit is insufficiently basic to accept a proton from either of the above species. Our own study of pK_a values supports our choice of subunits.† Derivatives which eventually gave suitable crystals were found in *N*-(3-hydroxypropyl)cyanuric acid **1** and 5-butyl-2,4,6-triaminopyrimidine **2**, which were synthesised by known methods.[12] As can be seen in the X-ray crystal structure‡ (Fig. 1), the infinite chain consists of alternating pyrimidinium *cations* and cyanurate *anions* triply hydrogen bonded to each other, on one side in the traditional alternate A–D–A : D–A–D§ sense, but on the other side in the A–A–A : D–D–D sense. The hydrogen bonding in the latter case is more effective than in the former (compare O–N, N–N, O–N distances of 2.820, 2.814, 2.903 Å *vs.* 2.853, 2.942, 3.008 Å, respectively). This is a clear manifestation of the effect of secondary electrostatic relationships between diagonally situated partial charges as defined by Jorgensen and Pranata[13] and later supported by Murray and Zimmerman.[14] This phenomenon probably also facilitates the proton transfer from **1** to **2** against a slight pK_a gradient.[15] The crystal plane is defined by the stacking of individual ribbons at the van der Waals contact distance (3.4–3.5 Å) additionally stabilised by hydrogen bonding between the hydroxypropyl tailgroup of **1** and an NH in **2**. Interestingly, this requires like-charged species to be located directly over each other. Matched pairs of chains are then offset relative to neighbouring pairs to allow opposite charges to stack in the next layer. These sheets of ribbons are only loosely associated with adjacent planes, and thus when made to grow quickly, highly birefringent plates 100–150 nm thick by about 40 μm square are observed, in accordance with the molecular packing.

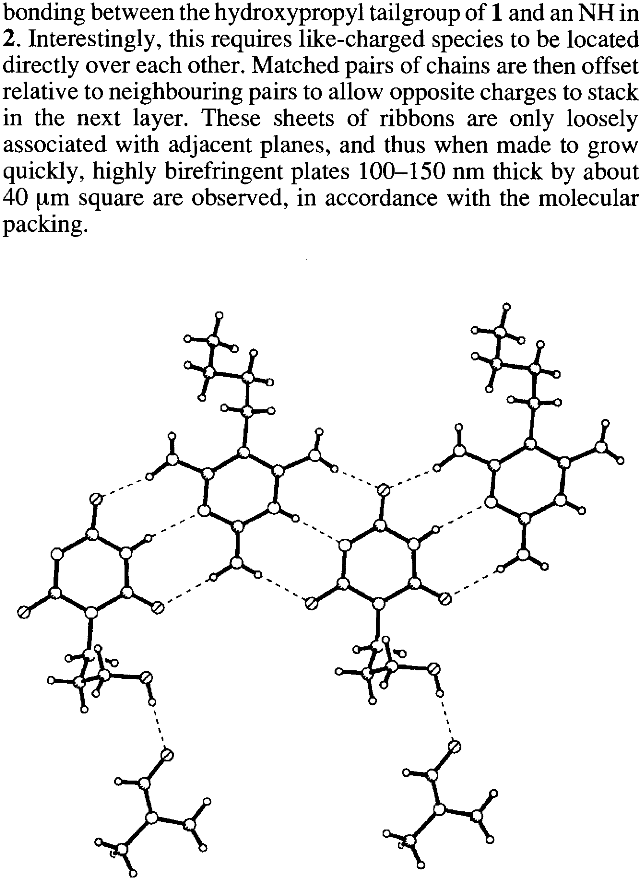

Fig. 1 Crystal structure of **1**·**2**·DMF [projection on the (1$\bar{1}$1) plane]

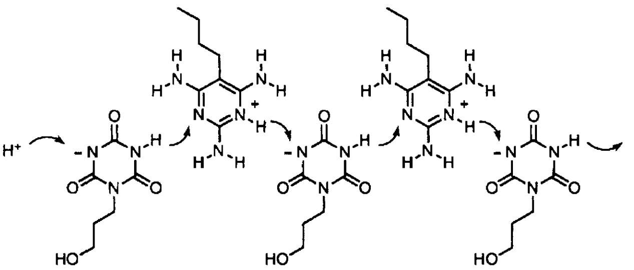

Fig. 2 Classic Grotthuss-type charge transport mechanism for (**1**·**2**)$_n$. The arrows represent the direction of protonic rather than electronic movement.

As is demonstrated in Fig. 2, each strand formally represents a directional, reversible single-proton translocation path insulated by a layer of solvent. This constitutes a pH responsive gate, where a proton delivered to one side of the strand causes the emergence of a proton on the other, in the same sense that crystalline imidazole and ice are believed to conduct, but with superior mechanical properties (*cf.* melting point 267 °C *vs.* 90 °C and 0 °C).¶ Interestingly, the proton mobility in an ionic system such as $(\mathbf{1}\cdot\mathbf{2})_n$ differs fundamentally from the above-mentioned molecular crystals since the protons must tunnel not only through hydrogen bonds, but also fall through electrostatic potentials. Conduction where the proton acts as charge carrier is unusual for organic materials, and such substances have potential applications in high density solid-state fuel cells and supercapacitors.[10]

It should also be possible to alter the properties of composites of the $(\mathbf{1}\cdot\mathbf{2})_n$ type by introducing a second ion-pairing interaction between the sidechains of components where there are now only alkyl and hydroxyalkyl substituents. Further work along these lines is now in progress.

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Footnotes

† p*K*a values (UV method)—acids: 5,5-diethylbarbituric acid (barbital), 7.97 ± 0.02; **1**, 7.29 ± 0.02; bases: *N,N′*-dibutylmelamine, 5.78 ± 0.03; **2**, 7.06 ± 0.10.

‡ *Crystal data*: $C_{17}H_{31}N_9O_5$, $M = 441.51$, triclinic, space group $P\bar{1}$, $a = 9.173(1)$, $b = 9.439(1)$, $c = 14.156(1)$ Å, $\alpha = 90.40(1)$, $\beta = 97.85(1)$, $\gamma = 117.10(1)°$, $V = 1077.6(2)$ Å^3, $Z = 2$, $D_c = 1.36$ g cm^{-3}, Ni-filtered Cu-Kα radiation, $\lambda = 1.54178$ Å, $\mu = 8.6$ cm^{-1}, crystal dimensions 0.11 × 0.25 × 0.45 mm, CAD4 diffractometer, $2\theta/\omega$ scans, $\theta \leqslant 70°$, 4076 unique reflections. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least squares methods (SHELXL-93) on F^2 of 4061 reflections ($R = 0.113$, for 2538 reflections with $I > 2\sigma(I)$, $R = 0.054$, non-H atoms anisotropic, N- and O-bound H isotropic, other H riding, 317 variables), $\Delta\rho_{max} = 0.31$, $\Delta\rho_{min} = -0.22$ e Å^3. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ A = H-bonding acceptor group, D = H-bonding donor group.

¶ Reliable proton conductivity measurements will require single crystals large enough for the attachment of a dedicated hydrogen–palladium electrode to specific faces. It is however worth noting at this point that Thomas *et al.* observed phenomenal conductivity in single crystals of the isocytosine–isocytosine tautomer where a translocation path comparable to **1**·**2**·DMF was available. This could only be detected with the Pd/H electrode, otherwise the material appeared not to conduct (J. M. Thomas, J. R. N. Evans, T. J. Lewis and P. Secker, *Nature*, 1969, **222**, 375).