

## A Molecular Approach to Solid-state Synthesis: Prediction and Synthesis of Self-assembled Infinite Rods

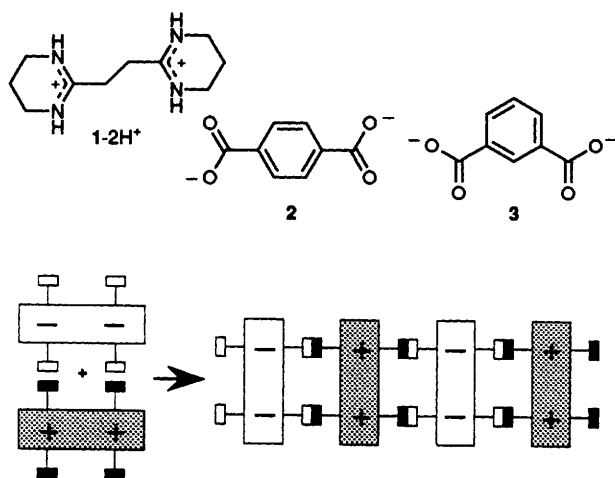
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Strict self-assembly of complementary dianionic and dicationic tetrahydrogen bond donors and acceptors leading to infinite molecular chains in the solid state is achieved in aqueous solution using both directionally controlled hydrogen bonding and ion-pairing electrostatic interactions.

The control of assembly processes in the solid state still remains a challenge for chemists. Using molecular concepts, the manufacture of strictly programmed and controlled solids can be envisaged through the assembly of structurally well-defined subunits.<sup>1,2</sup> The driving force for the assembly processes may be directional hydrogen bonding<sup>3-5</sup> or less directional electrostatic and/or van der Waals and  $\pi$ -stacking interactions.<sup>6</sup> Most of the results obtained so far deal with non ionic hydrogen bonding pattern. Thus, finite assemblies,<sup>3</sup> low-dimensional infinite assemblies,<sup>4</sup> and three-dimensional networks<sup>5</sup> have been reported. Although most biological systems self-assemble in water, it is worth noting that, excepting the organic nanotubes composed of cyclic peptides assembled from aqueous solution,<sup>5a</sup> all the other cases mentioned above were obtained from solvents incapable of hydrogen bonding and thus unable to compete with the solutes.

Our aim was to assemble molecular entities in protic solvents using both hydrogen bonds and electrostatic ion pairing interactions. Our approach to the synthesis of solids was based on iterative, both in terms of interaction and symmetry, assembly processes between complementary units. Thus, control of the directionality of the assembly process by appropriate positioning of interaction sites within the framework of the basic units should produce geometrically defined structures. In order to allow iterative assembly processes to take place, the basic units must contain complementary interaction sites oriented in a divergent fashion towards the exterior of the unit's backbone. Our first attempt consisted of assembling centrosymmetric dicationic molecular 'bricks' possessing four acidic protons with dianionic bricks capable of accommodating four hydrogen bonds (Scheme 1).

For this purpose, the bis(cyclic amidine) **1**<sup>7</sup> seemed to be the candidate of choice, since in its diprotonated form (**1-2H**<sup>+</sup>), all four N-H protons are acidic and equivalent. Thus, **1-2H**<sup>+</sup> should act as a dicationic H-bond donor unit in which all four N-H interaction sites bearing each half-positive charge are oriented outwardly in a divergent and centrosymmetric



Scheme 1 The general strategy used to build infinite chains from complementary units (see text)

fashion. The crystal structure of the di-*p*-toluenesulfonate salt of **1-2H**<sup>+</sup> indeed showed the above mentioned features.<sup>8</sup> In solution, the centrosymmetric nature of **1-2H**<sup>+</sup> was also established by both <sup>1</sup>H and <sup>13</sup>C NMR studies. As the complementary anionic brick, tere(2)- or iso-phthalate (**3**) dianions bearing two negative charges distributed over four oxygen atoms and thus capable of accepting four hydrogen bonds were chosen.

Due to the difference in the p*K*<sub>b</sub> values between **1**, **2** and **3** the mixing of the free base **1** with **2-2H**<sup>+</sup> and with **3-2H**<sup>+</sup> in water gave rise to an acid-base reaction leading exclusively to (**1-2H**<sup>+</sup>, **2**) and to (**1-2H**<sup>+</sup>, **3**) salts as colourless crystalline solids. Recrystallization from EtOH-MeOH-H<sub>2</sub>O mixture afforded air- and moisture-stable translucent crystals suitable for X-ray studies.<sup>†,‡</sup>

As predicted, the solid-state analysis of the mono-crystals of (**1-2H**<sup>+</sup>, **2**)<sup>†</sup> revealed infinite linear chains exclusively composed of **1-2H**<sup>+</sup> dication and **2** dianion interconnected through hydrogen bonds and arranged in an alternating manner [Fig. 1(a)]. On the other hand, in the case of isophthalate **3**, in principle linear and cyclic arrangements may be envisaged. However, the X-ray study<sup>‡</sup> again showed that infinite linear chains exclusively composed of **1-2H**<sup>+</sup> dication and **3** dianion

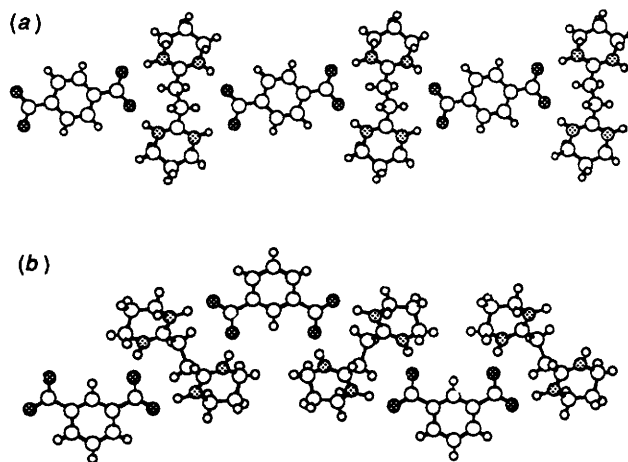


Fig. 1 Infinite chains assembled in the solid state using (a) **1-2H**<sup>+</sup> and terephthalate **2**, and (b) **1-2H**<sup>+</sup> and isophthalate **3** (● = O, ⊙ = N)

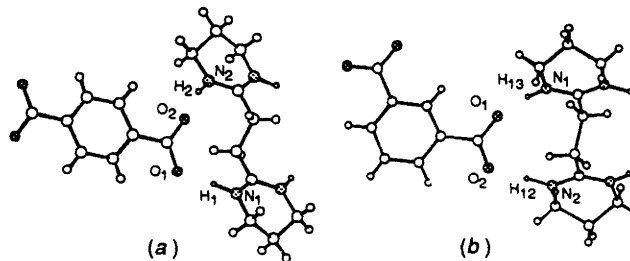


Fig. 2 The repeating unit in (a) (**1-2H**<sup>+</sup>, **2**) infinite chains distances: H(1)-O(1) 1.698, H(2)-O(2) 1.766 Å, angles: H(1)-N(1)O(1) 3.81, H(2)-N(2)-O(2) 7.82°; and (b) (**1-2H**<sup>+</sup>, **3**) infinite chains, distances: H(13)-O(1) = 1.801, and H(12)-O(2) 1.594 Å, angles: H(13)-N(1)-O(1) 1.52, H(12)-N(2)-O(2) 6.14° (● = O, ⊙ = N)

interconnected through hydrogen bonds and arranged in an alternating manner were formed [Fig. 1(b)].

The analysis of the unit cells both in the case of (1-2H<sup>+</sup>, 2) [Fig. 2(a)] and (1-2H<sup>+</sup>, 3) [Fig. 2(b)] revealed the following features: (i) all four acidic protons were localised on 1 with an average N-H distance of *ca.* 1.03 Å; (ii) the dicationic unit 1-2H<sup>+</sup> and the dianionic 2 or 3 were interconnected through hydrogen bonds with an average N...O distance of *ca.* 2.74 Å and of NH...O distance of *ca.* 1.71 Å. The average bond angle for NHO hydrogen bonds was *ca.* 172.4°. Due to the fully extended *trans* conformation of the ethylene chains connecting the two amidines in 1, N(1), N(2), C(1) and N'(1), N'(2), C'(1) planes were almost parallel but not coplanar. On the other hand, in 2 and 3 the carboxylate groups were essentially coplanar with the aromatic ring. Consequently, in the solid state the main planes for 2 and 3 were tilted by *ca.* 28 and 18° respectively with respect to the plane containing N(1), N(2), N'(1) and N'(2) atoms in 1-2H<sup>+</sup>.

Comparison of geometrical factors (NH...O distances and angles) with those compiled and analysed by Kennard *et al.*<sup>9</sup> clearly shows that the H-bonds involved in (1-2H<sup>+</sup>, 2)<sub>n</sub> or in (1-2H<sup>+</sup>, 3)<sub>n</sub> assemblies are strong. Moreover, due to the distribution of positive and negative charges upon 1, 2 and 3, the assemblies are reinforced by strong coulombic interactions involving all four positive and negative charges.

Analysis of the lattices (Fig. 3) showed several interesting features. Both infinite linear chains were found to be discrete with no specific interactions between them. Indeed, the average distances between the centroids of the aromatic rings in consecutive layers were 7.39 and *ca.* 4 Å respectively for 2 and 3. On the other hand, due to the absence of specific interaction sites, the shortest C-C distances between two adjacent chains were *ca.* 4.5 and 3.7 Å respectively for 2 and 3.

It is interesting to note that both tere-<sup>10</sup> and iso-phthalic<sup>11</sup> acids, which are self complementary units, form linear chains composed of either 2-2H<sup>+</sup> or 3-2H<sup>+</sup> interconnected by H-bonds in the solid state. By analogy, the (1-2H<sup>+</sup>, 2)<sub>n</sub> or (1-2H<sup>+</sup>, 3)<sub>n</sub> assemblies may be considered as infinite chains of terephthalate 2 or isophthalate 3 dianions strictly interconnected in a linear fashion by dicationic 2-2H<sup>+</sup> units. Conversely,

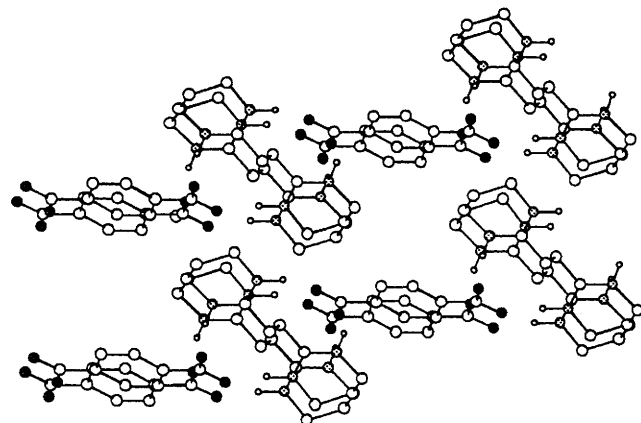


Fig. 3 Tridimensional representation of the lattice for (1-2H<sup>+</sup>, 2). The distances between two consecutive layers and between two adjacent chains are 7.39 and *ca.* 4.5 Å, respectively (● = O, ○ = N).

the (1-2H<sup>+</sup>, 2)<sub>n</sub> or (1-2H<sup>+</sup>, 3)<sub>n</sub> chains may be also seen as infinite chains of 1-2H<sup>+</sup> interconnected by terephthalate 2 or by isophthalate 3 dianions.

In conclusion, the following points may be emphasized: (i) compound 1 is well suited for binding of carboxylate anions through both oxygen atoms; (ii) using both electrostatic interactions and directionally controlled H-bonding, positive and negative units may be assembled in the solid state with predictable linear structures; (iii) although in the present study we used tetrahydrogen bond donor and acceptor units, one may extend the same strategy to other units, in particular, 1-2H<sup>+</sup> could be assembled in a bidimensional network with hexa H-bond acceptors such as disulfonate anions.<sup>8</sup>

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### Footnotes

† Crystallographic data for (1-2H<sup>+</sup>, 2) (colourless crystals, -100 °C): C<sub>18</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>, *M* = 360.4, triclinic, space group *P* $\bar{1}$ , *a* = 7.392(2), *b* = 11.034(3), *c* = 6.146(2) Å,  $\alpha$  = 98.08(2),  $\beta$  = 113.06(2),  $\gamma$  = 98.13(2)°, *Z* = 1,  $\rho_{\text{calc}}$  = 1.342 g cm<sup>-3</sup>, Cu-K $\alpha$  graphite monochromated, 830 data with *I* > 3 $\sigma$ (*I*), *R* = 0.036, *R*<sub>w</sub> = 0.057.

‡ Crystallographic data for (1-2H<sup>+</sup>, 3) (colourless crystals, -100 °C): C<sub>18</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>, *M* = 360.4, monoclinic, space group *P*2<sub>1</sub>/*m*, *a* = 6.236(2), *b* = 21.554(7), *c* = 7.346(2) Å,  $\beta$  = 112.29(2)°, *Z* = 2,  $\rho_{\text{calc}}$  = 1.310 g cm<sup>-3</sup>, Cu-K $\alpha$  graphite monochromated, 895 data with *I* > 3 $\sigma$ (*I*), *R* = 0.036, *R*<sub>w</sub> = 0.059. The structure was solved using MULTAN. 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.

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