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Molecular Tectonics II : Synthesis of Molecular Sheets By Self-Assembly of Complementary Molecular Units In The Solid State

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Abstract. Using both directional hydrogen bonding and electrostatic interactions, the self assembly of diprotonated 1,2-Bis(2'-tetrahydropyrimidyl)ethane **1**-$2H^+$ with dihydrogenopyrophosphate in the solid state leads to infinite discreet sheets composed of **1**-$2H^+$ and dihydrogenopyrophosphate ribbons interconnected through $H_2P_2O_7^{2-}$ anions by hydrogen bonds.

The strict control of solid state structures is currently under active investigation.[1-2] The understanding of processes involving the formation of crystalline materials by assembly of specific molecular units possessing individual magnetic, electronic or photonic properties should lead to millimetre to centimetre scale solid devices showing predicted and/or unusual behaviour. Passage from the molecular level to the large solid state assemblies with strictly controlled structures and thus properties may be achieved by iterative assembling processes.[3-6] For the construction of organic solids, these processes in the solid state require an assembling algorithm based on : i) elementary units with complementary interaction sites oriented outwardly (exoreceptors), ii) precise positioning of the interaction sites within the structure of the basic units as a function of the desired overall topography. Dealing with the latter aspect, the geometrical features of the basic units are of crucial importance, since, due to the iterative nature of the process, any deviation from the desired structure during the first assembling steps will be strongly amplified in the final structure.

Our approach to the design and synthesis of organic crystals was based on the simultaneous use of weak but directional hydrogen bonding along with strong but less directional electrostatic charge-charge interactions. As a first building block, we considered as unit the cyclic bisamidine **1** (Figure 1).[7] Indeed, in its diprotonated form (**1**-$2H^+$), this unit offers the possibility of forming four hydrogen bonds in a divergent fashion as observed in the solid state analysis of its *para*-toluenesulfonate salt.[8]

Using the strategy mentioned above, we have succeeded in assembling (**1**-$2H^+$) with tere- or iso-phthalate dianions into discrete infinite rods and ribbons.[9] In order to extend the topography of the assembly from discrete rods to discrete sheets, the individual rods or ribbons must be interconnected. This may be achieved by the addition of another dimension within the structure of the building blocks involved in the assembling process. While keeping the centrosymmetric dicationic unit **1**-$2H^+$, in which each side is capable of forming two hydrogen bonds, one may use instead of tere- or iso-phthalate dianions possessing two sets of two oxygen acceptor sites in a planar arrangement, a dianionic partner with trigonal arrangement of two oxygens and a hydroxyl group, hydrogen bond acceptor and donor sites respectively, as in phosphate derivatives. We report here our success in forming discrete sheets in the solid state by assembling (**1**-2H$^+$) with the dihydrogenopyrophosphate dianion (Figure 1).

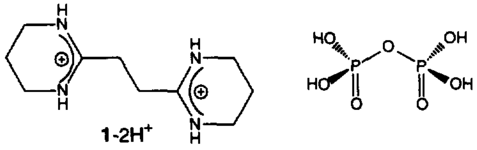

Figure 1: Chemical structures of the bisamidinium 1-2H+ (left) and pyrophosphoric acid (right)

Although pyrophosphoric acid is able to liberate four protons, since **1** is a strong dibase, the acid-base reaction between equimolar amounts of these two compounds takes place instantaneously in aqueous or alcoholic solution leading to **1**-2H$^+$ with dihydrogenopyrophosphate ($H_2P_2O_7^{2-}$) as the counter anion. Crystallisation of the salt from EtOH/H_2O 3/2 mixture affords stable colourless crystals suitable for X-ray studies.[10] The (**1**-2H$^+$, $H_2P_2O_7^{2-}$) salt cocrystallizes with a water molecule. Since the hydrogen atoms on the latter could not be localized we were not able to analyse the possible interaction of the water molecule with other components. Nevertheless, the water molecule was found in the proximity of the pyrophosphate with only one short O-O distance of 2.78 Å.

The analysis (Figure 2) of the individual components $H_2P_2O_7^{2-}$ and **1**-2H$^+$ revealed the following features: i) in the solid state, the dihydrogenopyrophosphate dianions adopt a staggered conformation with a gauche disposition of the OH moieties (POH-POH angle = 77.04°) and with a syn relationship between the two protons (Figure 2b) ii) for the bisamidinium **1**-2H$^+$, all four protons are localized on nitrogen atoms with N1-H1 and N2-H2 distances of 1.002 and 1.102 Å respectively thus yielding, as predicted, a centrosymmetric dicationic unit in which all four NH groups, each bearing half of a positive charge, are pointing outwardly. Due to the fully extended trans conformation of the ethylene chains connecting the two amidines in **1**-2H$^+$, N1, N2, C1 and N'1, N'2, C'1 planes were almost parallel but not coplanar (Figure 2a).

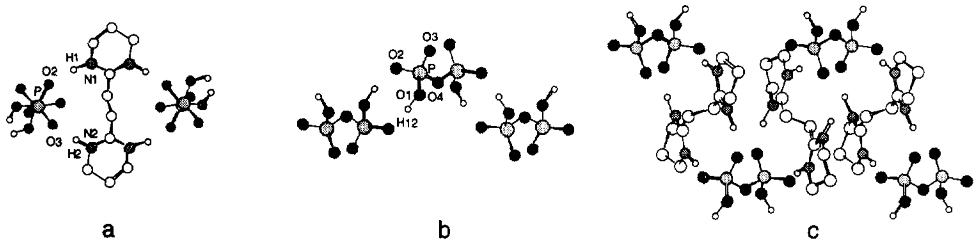

Figure. 2: The molecular unit (a), N1-H1 = 1.002 Å, N2-H2 = 1.102 Å, H1-O2 = 1.834 Å, H2-O3 = 1.701 Å; N1H1O2 = 152.98 °, N2H2O3 = 162.89 °; a portion of the $H_2P_2O_7^{2-}$ infinite chain (b), O1-H12 = 1.017 Å, O2-H12 = 1.608 Å, O2H12O1 = 163.34 °; and the repetitive unit in the (**1**-2H$^+$, $H_2P_2O_7^{2-}$) showing the formation of infinite ribbons (c). H atoms, except those involved in H-bonding, are not presented.

The analysis of the lattice revealed the following features: i) due to the ability of dihydrogenopyrophosphate to act as both hydrogen bond donor (OH) and acceptor (O$^-$) and to the disposition of the two hydroxy groups, in the lattice this self-complementary unit forms infinite ribbons in which two adjacent pyrophosphate units are interconnected in a head-to-tail fashion by two hydrogen bonds with a OH---O$^-$ distance of 1.607Å and a (OH, O) angle of 163.34° (Figure 2b). ii) each centrosymmetric dicationic bisamidine unit **1**-$2H^+$ interconnects by two sets of two hydrogen bonds localized on its both sides, in a alternate fashion, two dianionic pyrophosphates belonging to two consecutive ribbons formed exclusively by dihydrogenopyrophosphate units (Figure 2c). Each set of two hydrogen bonds (distances N1H1$^+$---O2$^-$ = 1.834 Å, N2H2$^+$---O3$^-$ = 1.701 Å, angles (N1H1, O2) = 152.98°, (N2H2, O3) = 162.89°) takes place between the two cationic NH$^+$ groups localized on the same side of the bis amidinium ion and the two negatively charged oxygen atoms of one of the phosphate moiety of dihydrogenopyrophosphate dianion. Alternatively, each dihydrogenopyrophosphate unit interconnects two different bisamidinium units through four hydrogen bonds between its four negatively charged oxygen atoms and two sets of two NH$^+$ groups belonging to two different **1**-$2H^+$ units. Among the four oxygen atoms involved in the binding, two of them are shared between other pyrophosphate units and **1**-$2H^+$. iii) the dianionic pyrophosphate units and the cationic bisamidinium moieties form ribbons composed of both units interconnected by hydrogen bonds (Figure 2c).

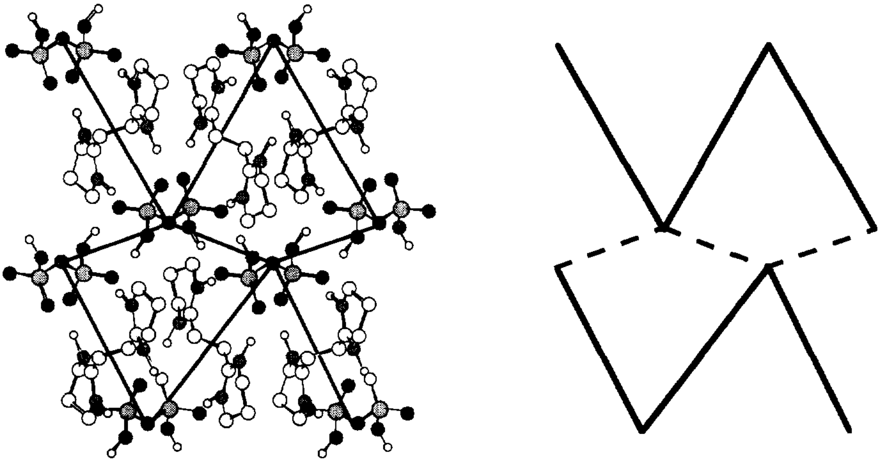

Figure 3: The repetitive unit in the (**1**-$2H^+$, $H_2P_2O_7^{2-}$) showing the formation of infinite sheets composed of **1**-$2H^+$ and $H_2P_2O_7^{2-}$ (left), and a schematic representation of the connection of the two constituents (right) : interconnections of $H_2P_2O_7^{2-}$ by **1**-$2H^+$ are presented by filled lines, whereas the chain composed of $H_2P_2O_7^{2-}$ is presented by a dashed line.

The overall structure in the solid state is composed of discrete sheets composed of **1**-$2H^+$ and dihydrogenopyrophosphate units. Indeed, on the one hand **1**-$2H^+$ and dihydrogenopyrophosphate units form ribbons through hydrogen bonds, on the other hand dihydrogenopyrophosphate anions also self-assemble into ribbons using hydrogen bonding. Consequently, all ribbons composed of **1**-$2H^+$ dication and $H_2P_2O_7^{2-}$ dianions, are interconnected by hydrogen bonds between the dihydrogenopyrophosphate units (Figure 3). The same type of sheets was also obtained using **1**-$2H^+$ and HSO_4^-.

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10 *Crystal data* for **1**-2H$^+$, $H_2P_2O_7^{2-}$: $C_{10}H_{22}N_4O_7P_2.H_2O$, M = 390.3, monoclinic, a = 8.068(3), b = 19.823(5), c = 10.976(3) Å, β = 110.00(2)°, U = 1649.5 Å^3, space group C2/c, Z = 4, Dc = 1.571 g cm^{-3}, μ(Cu-$K\alpha$) = 28.653 cm^{-1}. Crystal dimensions 0.20x0.12x0.06 mm. Data were measured at 173 K on a Philips PW1100/16 automatic diffractometer with graphite monochromated Cu-Kα radiation using ω scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.044, Rw = 0.063 for 748 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 102$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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