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Molecular Tectonics IV : Molecular Networks Based on Hydrogen Bonding and Electrostatic Interactions

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Abstract: Whereas diprotonated **1** (1,2-Bis(2'-tetrahydropyrimidyl)ethane) forms a discrete exobinuclear complex with a dihapto mode of hydrogen bonding with 4-methylbenzoate anion **2**$^-$ in the solid state, with 4,4'-biphenyldicarboxylate **3**$^{2-}$ an α-network composed of **1**-2H$^+$ dication and **3**$^{2-}$ dianion interconnected through strong hydrogen bonds and arranged in an alternating manner was obtained. The interconnection of the linear chains by water molecules affords a β-network.

The preparation of molecular networks, a subject of current interest, has been explored intensively over the last decade. In terms of strategy, the one followed by the molecular tectonics[1] approach seems to be viable for the construction of such networks. Molecular tectonics is based on molecular recognition between complementary tectons (building modules) and on the translation of the recognition pattern which may be termed the assembling core. Whereas endo-receptors in the presence of appropriate substrates afford discrete molecular endo-complexes, tectons or exo-receptors possessing interaction sites oriented outwardly, lead either to discrete molecular exobinuclear complexes in the presence of stopper substrates unable to permit the translation of the assembling core (figure 1a), or to molecular networks in the presence of connectors (figure 1b). In terms of interaction energy, any type of weak interactions may be used. Although recently the formation of α-networks using mainly van der Waals interactions has been achieved[2], H-bonding[3], in the majority of cases reported, was shown to be the most viable and used construction tool for the synthesis of organic crystals made by self-assembly[4] of complementary molecular modules.

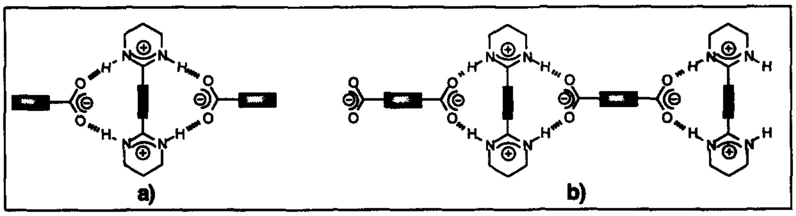

Figure 1 : Schematic representation of a discrete exobinuclear molecular complex formed between an exo-receptor and a stopper substrate (a) and of an α-network (one-dimensional network) obtained between an exo-receptor and a connector (b).

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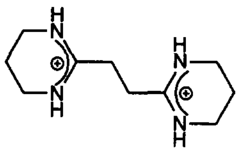
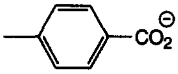
Our approach to organic crystal engineering is based on the simultaneous use of directional hydrogen bonding and electrostatic charge-charge interactions between complementary units. Bis cyclic amidines such as the compound **1**[5] are interesting tectons for crystal engineering of molecular solids.[6] Indeed, due to the conjugated nature of the amidine group, their diprotonated form possesses four acidic N-H protons pointing outwardly and thus capable of donating four hydrogen bonds. Protonated amidines have been used as hydrogen bonding recognition sites for carboxylate anions.[6a,b,7], sulphonate[6c] and phosphate[6d] derivatives. α-[6a] and β-molecular networks[6b] using dications such as **1** have previously reported in the solid state.

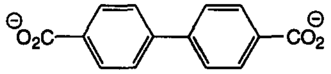
In the present paper we demonstrate that in order to obtain molecular networks, in particular α-networks in the present case, both partners the tecton and the connector must possess, in addition to interaction energy, geometrical features allowing the translation of the assembling core. Whereas the compound **1**-2H$^+$ was used as the dicationic tecton, for the anionic partner on the other hand, the monocarboxylate **2**$^-$ was used as stopper and the dicarboxylate **3**$^{2-}$ was used as connector. Compound **1** is a rather strong base and therefore, due to the difference in the pK$_b$ values between **1**, **2**$^-$ and **3**$^{2-}$ the mixing of the free base **1** with the **2**-2H$^+$ or with **3**-2H$^+$ affords in water an acid-base reaction leading exclusively to (**1**-2H$^+$, 2**2**$^-$) and to (**1**-2H$^+$, **3**$^{2-}$) salts as colourless air and moisture stable crystalline solids.



1-2H$^+$



2$^-$



3^{2-}

Whereas in the presence of monocarboxylate anions such as **2**$^-$, acting as stoppers, discrete binuclear molecular complexes, with a dihapto mode of coordination between the anionic and dicationic units may be expected for **1**-2H$^+$(figure 1a), in the presence of dicarboxylate anions (1/1 ratio) such as **3**$^{2-}$, the dicationic tectons may be interconnected by hydrogen bonding, again in a dihapto mode of interaction, by dianionic modules affording thus α-networks or unidimensional solids (figure 1b).

As predicted, in the solid state the (**1**-2H$^+$, 2**2**$^-$) salt formed discrete molecular units without any repetition of the interaction core. The (**1**-2H$^+$, 2**2**$^-$) salt crystallised in the monoclinic crystal system with P2$_1$/c as the space group. The **1**-2H$^+$ unit was centrosymmetric. The unit cell was composed of **1**-2H$^+$, and 2**2**$^-$ entities. The solid state analysis[8] of mono crystals, obtained upon mixing the free base **1** and 2 eq of the monoacid **2**-H$^+$ in a water/EtOH mixture, revealed the following features (figure 2) : 1) All four acidic protons were localised on **1** with an average N-H distance of *ca* 1.01 Å; 2) In each NCN fragment, the average C-N distance (1.31 Å) and N-C-N angle (122.5°) were close to those observed for **1**-2TsOH (1.30 Å, 122. 7°)[6c]; 3) The ethylene chain connecting the two cyclic amidinium moieties was in a *trans* extended conformation; 4) Both 6 membered cycles adopted a half chair conformation; 5) The two NCN planes of the two amidinium moieties were almost parallel but not coplanar ; 6) The carboxylate unit was tilted by 3° with respect the phenyl ring; 7) A dihapto mode of interaction between the dication and the monocarboxylate anion with strong H-bonds was observed. The average N··O distance of 2.74 Å and H··O distance of 1.74 Å as well as the average NHO angle of ca 166.1° clearly demonstrated the strong nature of the hydrogen bonding pattern.

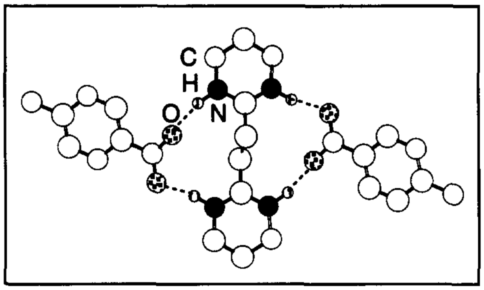


Figure 2 : X-ray structure of (1-2H$^+$, 22$^-$) complex. For the sake of clarity all other hydrogen atoms expect those involved in H-bonding were omitted.

As predicted, the solid state analysis[9] of mono crystals, obtained upon mixing the free base **1** and 1 eq of the diacid **3**-2H$^+$ in a water/EtOH mixture, revealed that (**1**-2H$^+$, **3**$^{2-}$) salt formed infinite linear chains exclusively composed of **1**-2H$^+$ dication and **3**$^{2-}$ dianion interconnected through hydrogen bonds and arranged in an alternating manner (figure. 3). The (**1**-2H$^+$, **3**$^{2-}$) salt crystallised also in the monoclinic crystal system with P2$_1$/c as the space group. The **1**-2H$^+$ unit was not centrosymmetric. The unit cell was composed of **1**-2H$^+$, **3**$^{2-}$ and two water molecules.

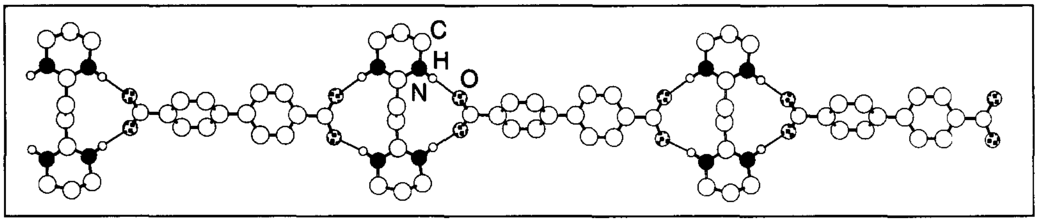


Figure 3 : X-ray structure of the α-network formed between **1**-2H$^+$ and 3^{2-}. For the sake of clarity all other hydrogen atoms expect those involved in H-bonding were omitted.

The X-ray analysis showed the following features (figure 3) : 1) Again all four acidic protons were localised on **1** with an average N-H distance of *ca* 1.01 Å; 2) In each NCN fragment, the average C-N distance (1.31 Å) and N-C-N angle (122.5°) were close to those observed for the above mentioned (**1**-2H$^+$, 22$^-$) salt and for **1**-2TsOH (1.30 Å, 122. 7°)[6c]; 3) The ethylene chain connecting the two cyclic amidinium moieties was in a *trans* extended conformation; 4) Both 6 membered cycles adopted a half chair conformation; 5) The two NCN planes of the two amidinium moieties were almost parallel but not coplanar ; 6) For the dianionic fragment, the two carboxylate moieties were not coplanar but tilted by 17.5° and -14° with respect to their connecting phenyl ring; 7) The two interconnected aromatic groups were tilted by 38° with respect to each other; 8) A dihapto mode of interaction between the dication and the dicarboxylate anion with strong H-bonds was observed. The average N··O distance of 2.76 Å and H··O distance of 1.80 Å as well as the average NHO angle of ca 169.2° clearly demonstrated the strong nature of the hydrogen bonding pattern; 9) Not predicted but observed was the formation of a β-network resulting from the interconnection of the linear chains formed between **1**-2H+ and **3**$^{2-}$ by two water molecules (figure 4). The interconnection of α-networks was found to be between the carboxylate moieties. The two water molecule (O_{w1} and O_{w2}) were hydrogen bonded ($dO_{w1}O$ = 2.82 Å, $dO_{w2}O$ = 2.93 Å) to two carboxylate moieties belonging to two different chains composed of (**1**-2H$^+$, **3**$^{2-}$) units. The formation of the β-network resulted from the hydrogen bonding ($dO_{w1}O_{w2}$ = 2.79 Å) between the two water molecules (figure 4).

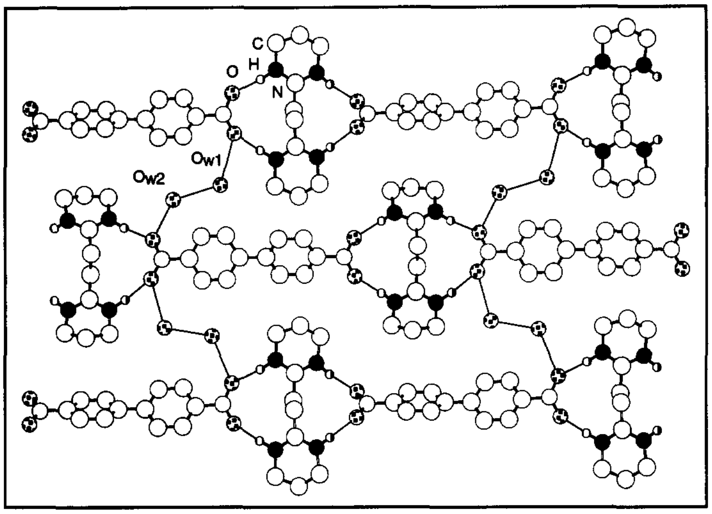


Figure 4 : Formation of a β-network resulting from interconnection by hydrogen bonds of α-networks formed between 1-2H$^+$ and 3^{2-} by two water molecules. For the sake of clarity all other hydrogen atoms expect those involved in H-bonding were omitted.

In conclusion we have demonstrated that an appropriate choice, both in terms of geometry and energy of interaction, of molecular modules indeed leads to the formation of predicted molecular networks in the solid state.

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8 *X-ray data* for **1-22H$^+$** : $C_{10}H_{20}N_4 \cdot 2C_8H_7O_2$, *M* = 466.6, monoclinic, *a* = 15.758(4), *b* = 5.876(1), *c* = 14.165(4) Å, β = 112.35(2)°, *U* = 1213.1 Å^3, space group $P2_1/c$, Z = 2, *Dc* = 1.277 gcm^{-3}, μ(Mo-*K*α) = 0.815 cm^{-1}. Crystal dimensions 0.35x0.30x0.25 mm. Data were measured at 293 K on a Enraf-Nonius CAD4-F diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give *R* = 0.045, *R*w = 0.063 for 1094 independent observed reflections [$|F_o| > 3\sigma(|F_o|$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

9 *X-ray data* for **1-32H$^+$**: $C_{10}H_{20}N_4 \cdot C_{14}H_8O_4 \cdot 2H_2O$, *M* = 472.5, monoclinic, *a* = 13.582(4), *b* = 16.315(4), *c* = 10.410(3) Å, β = 97.58(2)°, *U* = 2286.5 Å^3, space group $P2_1/c$, Z = 4, *Dc* = 1.373 gcm^{-3}, μ(Mo-*K*α) = 0.931 cm^{-1}. Crystal dimensions 0.35x0.30x0.30 mm. Data were measured at 293 K on a Enraf-Nonius MACH3 diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give *R* = 0.058, *R*w = 0.077 for 1573 independent observed reflections [$|F_o| > 3\sigma(|F_o|$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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