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Molecular Tectonics V : Molecular Recognition in the Formation of Molecular Networks Based on Hydrogen Bonding and Electrostatic Interactions

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Abstract: The formation of α-molecular networks based on dihapto mode of H-bonding was investigated in the solid state using bis-cyclic amidinium dications and acetylenedicarboxylate dianion. It has been demonstrated that the formation of networks depends strongly on the structure of the components. A proper disposition of H-bond donor and acceptor sites indeed leads to the formation of infinite molecular assemblies in the crystalline phase.

Molecular tectonics[1] deals with the design of molecular networks.[2] It is based on molecular recognition between complementary tectons or construction modules and on the translation of the recognition pattern. In terms of interaction energy, although other types of weak interactions such as van der Waals[3] have been used, H-bonding[4] seems to be the most viable and used interaction for the synthesis of organic crystals.[5] In principle, molecular networks are obtained when both composing tectons fulfil geometrical as well as energetical criteria.

Our approach to organic crystal engineering is based on the simultaneous use of directional hydrogen bonding, in a dihapto mode of interaction, and less directional electrostatic charge-charge interactions between complementary units (figure 1).[6]

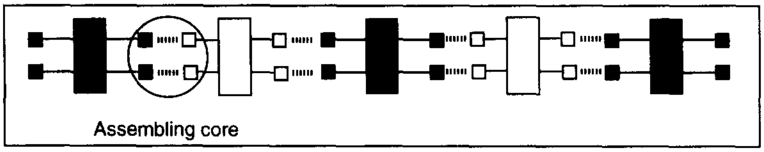
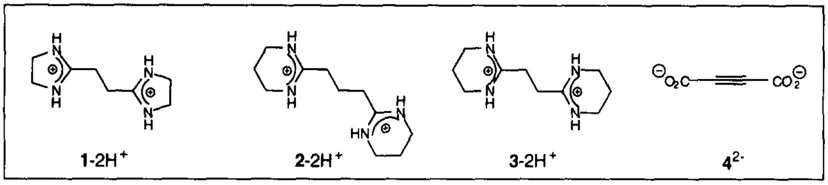


Figure 1 : Schematic representation of an α-network formed between complementary tectons. White and black squares represent H-bond donor and acceptor sites.

Bis cyclic amidines[7] such as the compound **1-3** are interesting tectons for crystal engineering of molecular solids. 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. α-[6a] and β-molecular networks[6b] using dications such as **3** have previously reported in the solid state.

In the present paper we demonstrate the structural effect of tectons on the formation of α-networks.

As dicationic molecules diprotonated compounds **1-3** were used. Whereas the structural difference between compounds **1** (5 membered ring) and **3** (6 membered ring) is due to the size of their cyclic amidinium moieties, the difference between **2** ($(CH_2)_3$) and **3** ($(CH_2)_2$) resides on the length of the spacer connecting the two cyclic amidinium fragments. On the other hand, the dianionic partner 4^{2-}, capable of a dihapto mode of interaction (acceptor of two H-bonds) at its both carboxylate moieties, was chosen because of its compactness and rigidity. Compounds **1**-**3** are a rather strong bases and therefore, due to the difference in the pK_b values between **1**-**3** and 4^{2-} the mixing of the free base **1** with the **4**-$2H^+$ leads in H_2O/EtOH mixture to an acid-base reaction affording exclusively (**1**-$2H^+$, 4^{2-}), (**2**-$2H^+$, 4^{2-}) and (**3**-$2H^+$, 4^{2-}) salts as air and moisture stable crystalline solids.



1-$2H^+$ **2**-$2H^+$ **3**-$2H^+$ 4^{2-}

The (**1**-$2H^+$, 4^{2-}) salt crystallises in monoclinic crystal system in C2/c space group.[8] The unit cell was composed of (**1**-$2H^+$, 4^{2-}) and two water molecules. The X-ray analysis (figure 2) revealed the following features : 1) All four acidic protons are localised on **1**; 2) For the NCN fragments, the average C-N distance is 1.31 Å with the N-C-N angle of 112.4°; 3) Both 5 membered cycles are almost coplanar; 4) The ethylene chain connecting the two cyclic amidinium moieties is in a *trans* extended conformation; 5) The two OCO (average CO distance of 1.24 Å) fragments in 4^{2-} are not coplanar but tilted by 79.5°; 6) The interaction between **1**-$2H^+$ and the dianion 4^{2-} takes place in a monohapto mode of interaction, through strong hydrogen bonds (d_{NO} = 2.73 Å, θ_{NHO} = 166.9°) between two out of four NH^+ groups of **1**-$2H^+$ and two out of four oxygen atoms of the dianions 4^{2-} (figure 2b). The remaining two NH^+ groups are hydrogen bonded (d_{NO_w} = 2.81 Å, θ_{NHO_w} = 164.5°) to water molecules (figure 2b). The remaining two oxygen atoms of 4^{2-} are again H-bonded (d_{OO_w} = 2.77 Å) to water molecules (figure 2c).

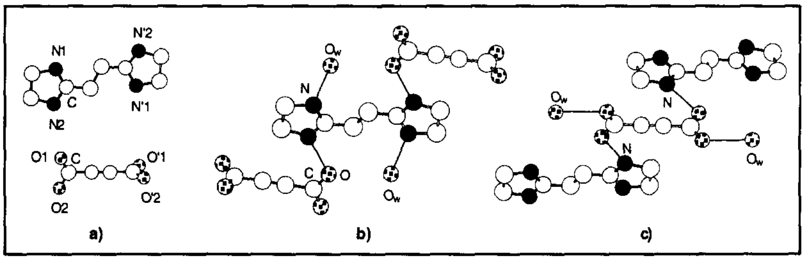


Figure 2 : X-ray structure of (**1**-$2H^+$, 4^{2-}) salt. Numbering (a), surrounding of **1**-$2H^+$ (b), and of 4^{2-} (c).

The (**2**-$2H^+$, 4^{2-}) salt crystallised in the monoclinic crystal system with C2/c as the space group.[9] The unit cell was composed of **2**-$2H^+$, and 4^{2-} entities. The solid state analysis of mono crystals, obtained upon mixing the free base **2** and 1 eq of the monoacid **4**-$2H^+$ in a water/EtOH mixture, revealed the following features (figure 3) : 1) All four acidic protons are localised on **2**; 2) In each NCN fragment, the average C-N distance is 1.32 Å with the N-C-N angle of 122.6°; 3) The propylene chain connecting the two cyclic amidinium moieties adopts a gauche conformation with dihedral angle of -68.1°; 4) Both 6 membered cycles adopted a half chair conformation; 5) The two NCN planes of the two amidinium moieties are not coplanar but tilted by -108.8°; 6) The two OCO fragments (average CO distance of 1.23 Å) in 4^{2-} are coplanar; 7) The interaction between the dicationic unit **2**-$2H^+$ and the dianion 4^{2-} takes place again in a monohapto mode of interaction, through strong hydrogen bonds (d_{N1O2} = 2.84 Å and d_{N2O1} = 2.77 Å) between all four NH^+ groups of **1**-$2H^+$ (figure 3b) and oxygen atoms of the dianions 4^{2-} (figure 3c).

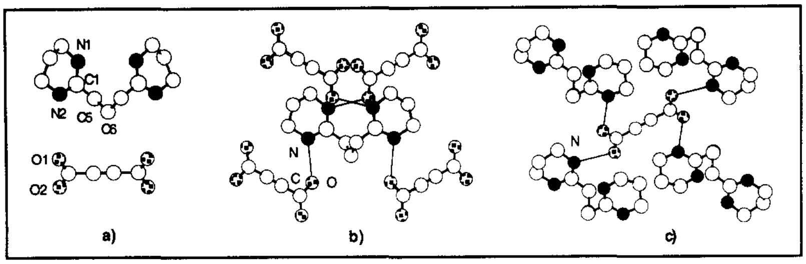


Figure 3 : X-ray structure of ($2\text{-}2H^+$, 4^{2-}) salt. Numbering (a), surrounding of $2\text{-}2H^+$ (b), and of 4^{2-} (c).

As predicted and previously observed for other dicarboxylates[6a,6b], the solid state analysis[10] of mono crystals, obtained upon mixing the free base **3** and 1 eq of the diacid $4\text{-}2H^+$ in a water/EtOH mixture, revealed that ($3\text{-}2H^+$, 4^{2-}) salt formed infinite linear chains (α-network) exclusively composed of $3\text{-}2H^+$ dication and 4^{2-} dianion interconnected with a dihapto mode of interaction through four strong hydrogen bonds between the NH^+ groups of $3\text{-}2H^+$ and oxygen atoms of 4^{2-} and arranged in an alternating manner (figure. 4). The ($3\text{-}2H^+$, 4^{2-}) salt crystallised also in the monoclinic crystal system with $P2_1/c$ as the space group. Both $3\text{-}2H^+$ and 4^{2-} components are centrosymmetric. The unit cell was exclusively composed of $3\text{-}2H^+$ and 4^{2-}. The X-ray analysis showed the following features (figure 4) : 1) Again all four acidic protons are localised on **3** ; 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 ($1\text{-}2H^+$, 4^{2-}) 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 (average CO distance of 1.23 Å) are almost coplanar

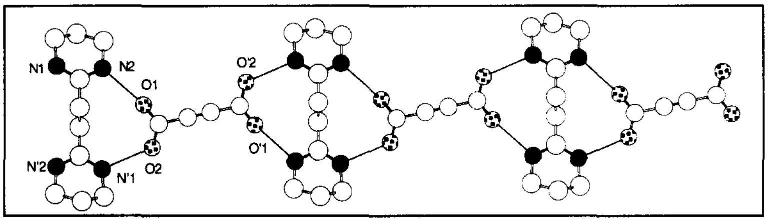


Figure 4 : X-ray structure of the α-network formed between the dication $3\text{-}2H^+$ and the dianion 4^{2-}.

with a tilte angle of 1.4° ; 7) A dihapto mode of interaction between the dication and the dicarboxylate anion with strong H-bonds is observed. The average N··O distance of 2.75 Å clearly indicates the strong nature of the hydrogen bonding pattern.

The comparison between all three structures revealed the following features : among compounds **1**-**3**, only the diprotonated form of $3\text{-}2H^+$ leads to the formation of an α-network with predicted dihapto mode of hydrogen bonding between the dication and the dianion. In addition to the charge complementarity between $3\text{-}2H^+$ and 4^{2-}, the dihapto mode of interaction results from the proper disposition, in terms of distance and geometry, of all four NH hydrogen donors sites on $3\text{-}2H^+$. Size contraction from the 6 membered rings in **3** to the 5 membered rings in **1** causes dramatic changes in the ability of their protonated forms to recognise carboxylate groups in the solid state. Indeed, although, due to the extended conformation of the ethylene chain, the distance between the two amidinium cycles in both compounds is almost the same, the NCN angle drops from 122.4° in $3\text{-}2H^+$ to 112.4°

for **1**-2H^{+} leading to an increase, from 5.00 Å for **3**-2H^{+} to 5.21 Å for **1**-2H^{+}, in the N-N distance between the two nitrogen atoms belonging to two different amidinium cycles but located on the same side. As a consequence of the elongation of the distance between the two hydrogen bond donors, the hydrogen bonding pattern between the dicationic and the dianionic modules switches from a dihapto mode for (**1**-2H^{+}, **4**$^{2-}$) to a monohapto mode for (**1**-2H^{+}, **4**$^{2-}$). It seems that in the latter case, two water molecules compensate by hydrogen bonding the increase in the distance between NH^{+} groups. The difference between **2** and **3** resides on the aliphatic chains connecting the two 6 membered cycles. Whereas in **3**-2H^{+} the ethylene fragment adopts a *trans* elongated conformation, in **2**-2H^{+} the propylene chain adopts a gauche conformation inducing a strong asymmetry in the molecule and, thus, leading to two sets of NN distances (3.62 Å and 5.72 Å) between nitrogen atoms situated on the same side of the molecule. Consequently, the only viable mode of H-bonding between **2**-2H^{+} and **4**$^{2-}$ seems to be the monohapto type of interaction.

In conclusion we have demonstrated that an appropriate choice of molecular tectons indeed leads to the formation of predicted molecular networks in the solid state. Whereas so far the majority of molecular networks deals with structural features, a further step, under investigation, is to shift from structural to functional aspects by using molecular tectons possessing specific properties.

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8 *X-ray data* for (**1**-2H^{+}, **4**$^{2-}$): $C_{12}H_{20}N_4O_6$, M = 316.3, monoclinic, a = 22.187(0), b = 5.397(0), c = 14.597(0) Å, β = 123.20(2)°, U = 1462.5 Å^3, space group C2/c, Z = 4, Dc = 1.437 gcm^{-3}, μ(Mo-$K\alpha$) = 0.710 cm^{-1}. Crystal dimensions 0.30x0.25x0.20 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 = 0.063, Rw = 0.107 for 1143 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 (**2**-2H^{+}, **4**$^{2-}$): $C_{15}H_{22}N_4O_4$, M = 322.4, monoclinic, a = 6.995(2), b = 14.589(4), c = 16.939(5) Å, β = 100.74(2)°, U = 1698.3 Å^3, space group C2/c, Z = 4, Dc = 1.261 gcm^{-3}, μ(Mo-$K\alpha$) = 7.332 cm^{-1}. Crystal dimensions 0.40x0.30x0.20 mm. Data were measured at 173 K on a Philips PW1100/16 diffractometer with graphite monochromated Cu-Kα radiation. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.055, Rw = 0.081 for 799 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.

10 *X-ray data* for (**3**-2H^{+}, **4**$^{2-}$): $C_{14}H_{20}N_4O_4$, M = 308.3, monoclinic, a = 5.954(1), b = 10.338(3), c = 12.677(3) Å, β = 103.04(2)°, U = 760.2 Å^3, space group P2$_1$/c, Z = 2, Dc = 1.347 gcm^{-3}, μ(Mo-$K\alpha$) = 7.332 cm^{-1}. Crystal dimensions 0.35x0.30x0.30 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 = 0.057, Rw = 0.085 for 1032 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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