Cocrystals of Melamine and Succinimide: Supramolecular Lattice Structure Constructed with Both Self and Not-self Intermolecular Hydrogen Bonds

Hideyuki Tukada* and Yasuhiro Mazaki†
Graduate School of Integrated Science, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236
†*Department of Chemistry, Faculty of Science, Kitasato University, 1-15-1 Kitasato, Sagamihara 228*

(Received January 22, 1997; CL-970047)

Melamine (**M**) and succinimide (**S**) give cocrystals in a 1:1 ratio, in which a supramolecular network is formed by multiple hydrogen bonds. The network is composed of two kinds of infinite links based on four molecular units, **S-M-M-S**; hydrogen bonds between the units to the **a** direction, and the π–π stacks in the **c** direction.

Molecule-based architectures [1] have received considerable attention in recent years. One of the intelligent ways to obtain such a supramolecular assembly is the use of self-organization of small molecules with weak intermolecular bonds. The molecular assemblies can be constructed with not only one component, but also two (or more) components, and the latter will give an affluent diversity for the molecular architectures.

Among the many molecular combinations in two-component systems, a pair of 2,6-diaminopyridines and imides has given fruitful results for crystal engineering and molecular recognition. [2] For example, Whitesides has generated many rosette motifs from complementary hydrogen bonded melamines and cyanuric acid derivatives as shown in Figure 1-(a).

We describe here a unique cocrystalline system, melamine **1**-succinimide **2**, in which π–π interactions and both complementary and self-intermolecular hydrogen bonds give a supramolecular lattice structure.

Cocrystals of **1-2** suitable for X-ray crystallography were obtained from aqueous solutions (mol ratio of **1/2** is 1: 4 - 1:1). From a ^{1}H NMR spectrum of the cocrystals dissolved in DMSO-d_6, a 1:1 ratio [3] is indicated instead of the expected 1: 3 from complete complementary molecular association of (a) in Figure 1. X-ray structural determination [4] for the single crystal also confirms the molecular ratio (1:1), and reveals unique supramolecular structures for **1-2**.

A melamine molecule (**M**) complementarily connects to a succinimide molecule (**S**) with three cyclic hydrogen bonds [two $R_2^2(8)$; according to a notation of graph-theory [1]]. The melamine also joins to another melamine molecule with two hydrogen bonds [$R_2^2(8)$]. Thus the melamine molecule exhibits both complementary and self molecular coupling [5] to give a quadruple molecular slab **S--M--M--S** (Figure 1-b) with an almost planar structure (Figure 2; the supramolecular plane is slightly kinked at the **M-M** junction; Figure 2-b; dihedral angle $\theta_{M\text{-}M}$ = 7.6°).

Further hydrogen bonds are recognized among the slabs. One amino-hydrogen atom and a triazine nitrogen atom in **M** make a cyclic hydrogen bond [$R_2^2(8)$] between the slabs. Thus the slabs infinitely link each other in the **a** axis (arrows in the Figure 2-a).

The molecular slabs, **S--M--M--S**, stack translationally to the **c** axis, and are inclined by 7° to the **a** axis and 19° to the **b**

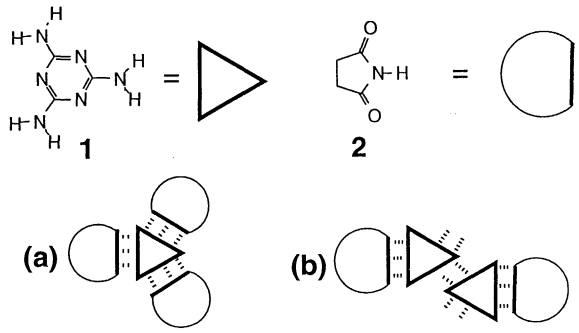

Figure 1. Schematic representation of the possible supramolecular structures of complex **1** (shown as a triangle) and **2** (as a half circle). Dotted lines indicate a hydrogen bond.

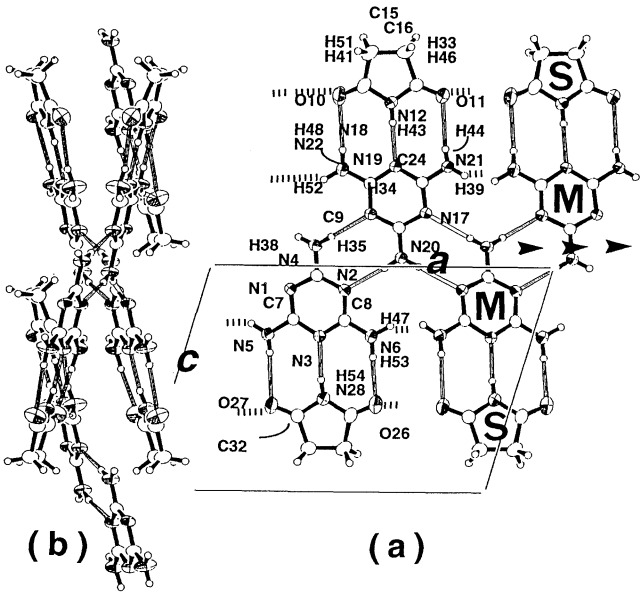

Figure 2. The molecular structure of melamine–succinimide projected along the **b** axis(a), and the **a** axis(b). Some molecules are omitted for clarify. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths and angles: N1-C7= 1.339(3), N1-C9=1.342(3), N4-C9=1.338(3), N4-H35=0.875 (27), N4-H38=0.822(25), N6-C8=1.341(3), N6-H47=0.942 (33), N6-H53=0.954(33), N12-H43= 0.895(33), N28-H54= 0.879(36), C9-N4-H35=119.1(1.8), C7-N5-H50=119.0(2.2), C14-N12-H43=124.1(2.1), C9-N1-C7-N3 = -0.1(0.4), H43-N12-C14-C16=177.4(2.5), H35-N4-C9-N2 =-7.6(2.1), H34-N20-C23-N18=-0.5(2.2).

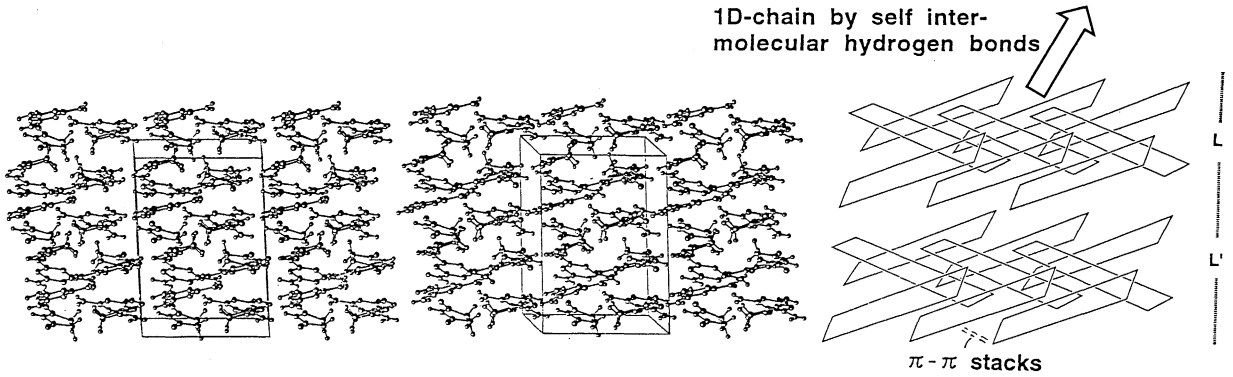

Figure 3. Stereo view of the cocrystals of the 1:1 molecular component (**1-2**). Right; schematic drawning of supramolecular structures.

axis. The stacks are sufficient for the close π–π contact (face to face distance=3.40 Å) of a melamine in one slab with a succinimide in another slab, and make infinite stacks. Projection along the **b** axis gives a good superposition between **S** and **M** molecules. Such the packing are favorable to minimize dipole-dipole repulsion between succinimide molecules.

The slabs link together along the **a** axis with alternative inclination to the **b** axis. Therefore one slab contacts with three slabs at each side of adjacent stacks(Figure 2-b). An amino hydrogen atom show a weak interaction to a carbonyl oxygen atom in the neighboring stacks[$R_4^2(8)$, dashed lines in the Figure 2-a], thus all of the amino hydrogen atoms participate in the hydrogen bonding network.

Consequently, the π–π contacts and hydrogen bonds form a layer which has a lattice structure by translationally stacked slabs, and the layer(L) stacks in the **b** direction without no particular interactions or bonds (Figure 3). The layers stack slightly offset to each other in the **a** direction as to avoid steric repulsion between ethylenes at the edge of the slabs, and pile up in the following manner, L/ L'/ L/ L' - -.

In summary, among the several possible association patterns, the cocrystal of melamine and succinimide selects both complementary (**M-S**) and self(**M-M**)-recognition, and forms the lattice-like supramolecular structure owing to multiple hydrogen bonds and selective π–π interactions.

References and Notes

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3 mp= 354-360° (partial sublimation). IR(nujor mull); 3478, 3458, 3346, 3236, 3130, 1703, 1624 cm^{-1}. The ^1H NMR spectrum [11.07 (NH of **1**), and 5.96 ppm (NH_2 of **2**)] indicated no sign of complexation of **1** and **2** in DMSO-d_6 by varying the ratio of **1** / **2**.

4 Crystal data for **1-2**: ($C_7H_{11}N_7O_2$), molecular weight = 450.42 , 0.3 x 0.2 x 0.7 mm^3, colorless, monoclinic, space group P21/a, a= 14.550 (2), b= 14.116(2), c=10.160(1), β=106.23(1), U=2003.6(5)A^3, Dc=1.494 gcm^{-3}, Z=4, μ(MoKα)=0.71073cm^{-1} (graphite monochromated). A total of 3047 reflections were collected[$I>2.5\sigma(I)$] at rt in a 2θ range 4 - 55 degrees using a Rigaku AFC-5 automatic diffractometer. The structure was solved by a direct method using the SAPI85 program package and refined to R= 0.053, R_W= 0.063 by the UNICS-III program.

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