

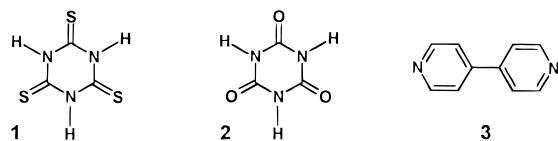
## Noncovalent Synthesis of Layered and Channel Structures Involving Sulfur-Mediated Hydrogen Bonds

V. R. Pedireddi, Swati Chatterjee,  
Anupama Ranganathan, and C. N. R. Rao\*

Chemistry & Physics of Materials Unit  
Jawaharlal Nehru Centre for Advanced  
Scientific Research  
Jakkur P. O., Bangalore 560 064, India

Received July 9, 1997

The hydrogen bond has emerged to be a powerful tool for the design of supramolecular organic systems based on noncovalent synthesis.<sup>1,2</sup> There are many examples of such synthesis in the recent literature, that of cyanuric acid-melamine aggregates being a superb case in point.<sup>1</sup> Supramolecular weaving and nanotube structures are other examples.<sup>3</sup> Channel structures and large hexagonal networks have been prepared by the cocrystallization of trimesic acid with other molecules.<sup>4</sup> All of these systems inevitably possess N–H···O, N–H···N, or O–H···O hydrogen bonds, and it appears that efforts toward noncovalent synthesis based on hydrogen bonds formed with sulfur donors have been limited. Considering that cyclic amides,<sup>5</sup> in particular cyanuric acid,<sup>1,6</sup> are good substrates for noncovalent synthesis, we have attempted to design new supramolecular systems formed by trithiocyanuric acid, hoping that some of them would have novel layered and channel structures. We have carried out a comparative study of the supramolecular assemblages obtained on crystallization of trithiocyanuric acid, **1**, and cyanuric acid, **2**, from different solvents and with chosen donor molecules to explore how the structures formed by N–H···S bonds differ from those formed by N–H···O bonds. We report some of the novel structures derived from **1** through the sulfur-mediated hydrogen bonds in this paper.



Crystallization of **1** and **2** from highly polar, hydrogen-bond breaking solvents yields comparable structures. Thus, crystallization of **1** and **2** from dimethyl sulfoxide (DMSO) gives tapes of molecules held together by N–H···S (H···S, 2.56, 2.51 Å) and N–H···O (H···O, 1.97–2.0 Å) bonds respectively with the DMSO molecules between the tapes forming N–H···O bonds; neighboring DMSO molecules interact through C–H···O bonding. Crystallization of **2** from acetone or methanol yields a structure with linear chains held together by two-dimensional

sheets, similar to that reported in the literature,<sup>7</sup> with no solvent of crystallization in the structure. Crystallization of **1** from methanol, on the other hand, gives a 1:1 adduct where the molecules of **1** are held together by N–H···S bonds (H···S, 2.32, 2.51 Å) forming a tape, with the methanol molecules forming N–H···O bonds with **1**. The tapes arrange in the form of crossed ribbons to form a three-dimensional network, involving C–H···S and S···S interactions. The difference between the hydrogen bonded assemblages formed by **1** and **2** becomes even more evident in the acetone-crystallized samples.

Crystallization of **1** from an acetone solution gave a 1:1 adduct of **1** with acetone with two molecules in the asymmetric unit.<sup>8</sup> The structure consists of essentially planar  $\alpha$ -networks of hexagons formed by six molecules of **1**, the hexagonal units being hydrogen bonded to acetone molecules as shown in Figure 1a. An examination of the figure shows that, in each hexagon, the symmetry-dependent pairs of molecules are held together through N–H···S hydrogen bonds with an H···S distance of 2.54 Å. In turn, these pairs are connected to each other through symmetry-independent molecules by N–H···S hydrogen bonds. The H···S distances in the adduct are 2.47, 2.49, 2.50, and 2.52 Å, characteristic of weak hydrogen bonds. To our knowledge, this is one of the first examples of a designed supramolecular assemblage of sulfur-mediated hydrogen bonds. Although Figure 1a gives the impression that open channels are present along an axis, such channels do not actually exist, as cavities are capped by the methyl group of acetone from the adjacent (see Figure 1b). The acetone molecules are bound to **1** by N–H···O bonds (H···O, 1.89 Å). The arrangement is reminiscent of pillared inorganic layered structures, the acetone molecules pillaring the layers formed by **1** in the present instance.

Cocrystallization of **1** with 4,4'-bipyridine, **3**, from a 1:1 chloroform/methanol solution resulted in the formation of a  $\beta$ -network structure incorporating molecules of **3** in the network<sup>9</sup> of the type shown in Figure 2a. Cocrystallization of **1** with **3** from a benzene solution also gave an adduct consisting of such sheets, but with a difference. These crystals<sup>10</sup> had **1**, **3**, and benzene in the molar ratio of 2:1:1, and the benzene molecules were present in the channels formed by the cavities. An examination of the sheet structure in Figure 2a reveals the existence of enlarged cavities (relative to those in Figure 1a) enabled by the N–H···N hydrogen bonds (H···N, 2.77 Å) between **1** and **3**. In addition, there are weak C–H···S bonds (H···S, 2.91, 2.93 Å) between these units. Between molecules of **1**, however, there are N–H···S hydrogen bonds, with an

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(8) Crystal data for **1**:  $2(C_3H_3S_3N_3) \cdot C_3H_6O$ ,  $M_w = 412.61$ , triclinic, space group  $P1$ ,  $a = 8.945(1)$ ,  $b = 9.999(1)$ , and  $c = 10.464(1)$  Å,  $\alpha = 95.14(1)^\circ$ ,  $\beta = 96.78(1)^\circ$ ,  $\gamma = 107.29(1)^\circ$ ,  $V = 879.7(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.558$ ,  $\lambda(\text{Mo K}\alpha) = 0.785$  mm<sup>-1</sup>,  $F(000) = 424$ ,  $\lambda = 0.710$  73, Smart CCD area detector, Siemens,  $\omega - 2\theta$  scan,  $1^\circ < \theta < 24^\circ$  ( $-9 \leq h \leq 6$ ,  $-11 \leq k \leq 11$ ,  $-9 \leq l \leq 11$ ), 3422 total reflections, 2441 independent reflections with 2433 reflections at  $I > 2\sigma(I)$ , which were used for refinement. The structure was solved by direct methods (SHELXTL-PLUS) and refined by full-matrix least-squares on  $F^2$  (SHELX-93; G. M. Sheldrick, Göttingen, 1993) to  $R_1 = 0.035$  and  $wR_2 = 0.090$ . Residual density, min/max  $-0.356/0.340$  e. Å<sup>-3</sup>.

(9) Triclinic, space group  $P1$ ,  $a = 11.294(1)$ ,  $b = 13.020(1)$ , and  $c = 16.623(1)$  Å,  $\alpha = 72.48(1)^\circ$ ,  $\beta = 72.04(1)^\circ$ , and  $\gamma = 64.73(1)^\circ$ .

(10) Crystal data for **1** and 4,4'-bipyridine adduct:  $2(C_3H_3S_3N_3) \cdot (C_{10}H_8N_2) \cdot C_6H_6$ ,  $M_w = 588.82$ , triclinic, space group  $P1$ ,  $a = 7.018(1)$ ,  $b = 10.344(1)$ , and  $c = 10.757(1)$  Å,  $\alpha = 63.75(1)^\circ$ ,  $\beta = 75.78(1)^\circ$ ,  $\gamma = 73.82(1)^\circ$ ,  $V = 665.8(1)$  Å<sup>3</sup>,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.469$ ,  $\lambda(\text{Mo K}\alpha) = 0.543$  mm<sup>-1</sup>,  $F(000) = 304$ ,  $\lambda = 0.710$  73, Smart CCD area detector, Siemens,  $\omega - 2\theta$  scan,  $2^\circ < \theta < 24^\circ$  ( $-7 \leq h \leq 7$ ,  $-11 \leq k \leq 7$ ,  $-11 \leq l \leq 11$ ), 2581 total reflections, 1838 independent reflections with 1830 reflections at  $I > 2\sigma(I)$ , which were used for refinement. The structure was solved by direct methods (SHELXTL-PLUS) and refined by full-matrix least-squares on  $F^2$  (SHELX-93; G. M. Sheldrick, Göttingen, 1993) to  $R_1 = 0.032$  and  $wR_2 = 0.077$ . Residual density, min/max  $-0.217/0.162$  e. Å<sup>-3</sup>.

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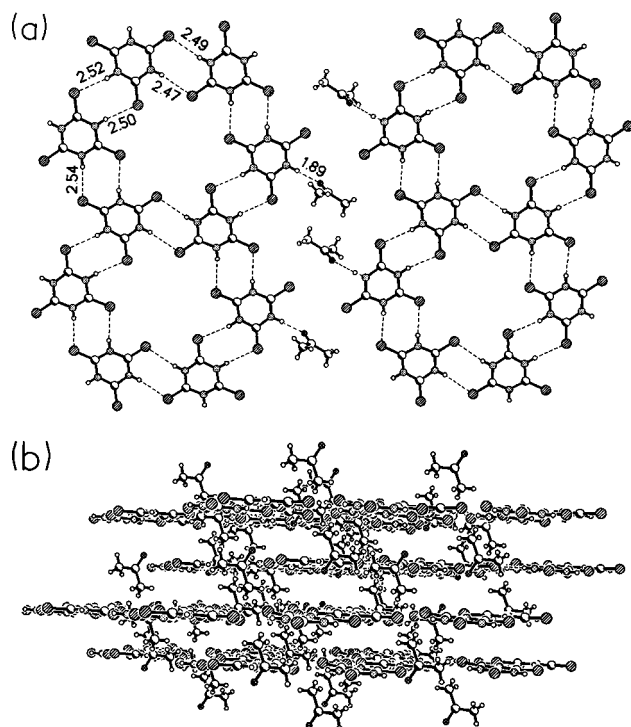
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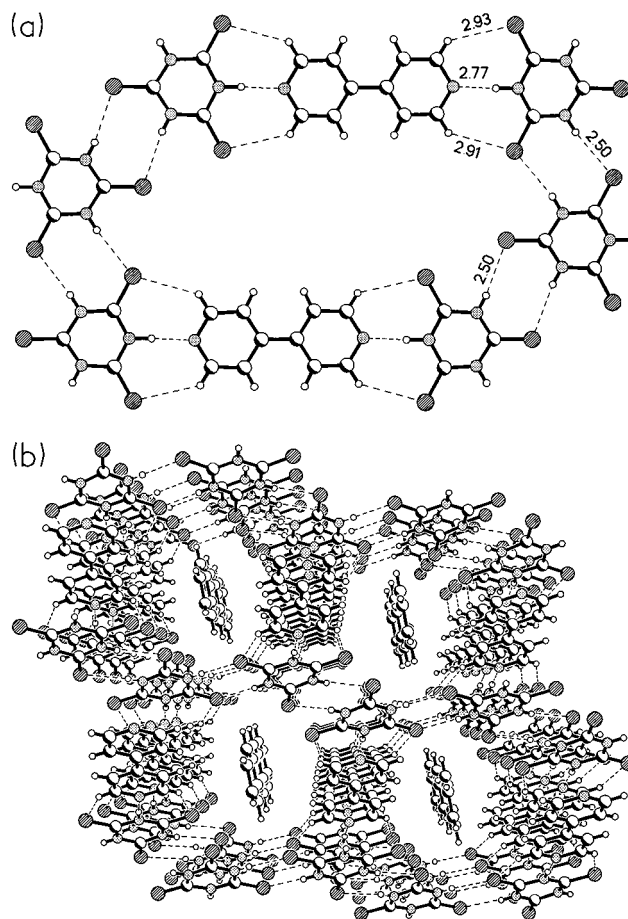
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**Figure 1.** (a) A two-dimensional sheet showing the self-assembly of molecules of **1**. Dashed lines represent hydrogen bonds. (b) Stacking of four layers of the planar sheets of **1**. Notice the pillaring of the layers by acetone molecules.

H $\cdots$ S bond length of 2.50 Å, just as in the **1**–acetone adduct (Figure 1a). In Figure 2b, we show the stacking arrangement of the two-dimensional sheets and the location of benzene molecules in the channels. In principle, it should be possible to incorporate other molecules, including planar aromatic molecules, in the channels. Cocrystallization of **2** with **3** from methanol as well as benzene gave a 2:1 adduct which does not possess a layered structure or channels. Molecules of **2** and **3** also form N–H $\cdots$ N bonds, but the assemblage in three-dimensions involves crossed ribbons wherein molecules of **2** form layers *via* an  $\alpha$ -network (with N–H $\cdots$ O bonds). The molecules of **3** are actually present in between the  $\alpha$ -networks forming C–H $\cdots$ O bonds.

The present study demonstrates how, by simple cocrystallization of trithiocyanuric acid, **1**, with different molecules, it is possible to obtain a layered structure consisting of hexagonal units of **1**, a structure with enlarged cavities as well as a structure with the three-dimensional channels filled by other molecules. Furthermore, major differences are found in the structures formed by **1** and **2** when they are crystallized from less-polar solvents. This arises not only because of the differences in the



**Figure 2.** (a) Self-assembly of **1** and **3** molecules forming a layered network with larger cavities than in Figure 1. (b) Representation of channels, in three-dimensional arrangement, noticed in the adduct of **1** and **3**. The channels are filled by benzene molecules.

N–H $\cdots$ S and N–H $\cdots$ O bond strengths but also possibly due to certain structure-directing effects specific to the former bonds. In conclusion, the present study demonstrates how the sulfur-mediated bonds formed by **1** give rise to structures entirely different from those obtained from **2**.

**Supporting Information Available:** Figures (molecular structure drawings of the adduct **1** with acetone and of the adduct of **1** with 4,4'-bipyridine and benzene with labeling scheme and their ORTEP drawings) and tables containing general crystallographic information, fractional coordinates of nonhydrogen atoms, list of bond lengths and angles, anisotropic displacement parameters, and fractional coordinates of hydrogen atoms (15 pages). See any current masthead page for ordering and Internet access instructions.

JA972289Z