

### Solid-State Structures of "Rosette" and "Crinkled Tape" Motifs Derived from the Cyanuric Acid–Melamine Lattice<sup>1</sup>

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We are using the pattern of hydrogen bonds present in the 1:1 complex formed from cyanuric acid and melamine (CA·M) as the basis for the design of self-assembling structures.<sup>2-5</sup> We have described a solid-state structure based on a "linear" tape motif taken from this lattice (3, Figure 1),<sup>3</sup> and we have inferred the existence of cyclic aggregates containing three melamine and three isocyanurate moieties in solution.<sup>4,5</sup> Here we report solid-state structures of a new type of tape format (a "crinkled tape", 4) and a cyclic structure (a "rosette", 5), both obtained by combination of *N,N'*-bis(*p*-substituted phenyl)melamine (1) and 5,5-diethylbarbituric acid (2). We believe that the three solid-state structures 3–5 are the most plausible structural motifs that can be derived from the CA·M lattice: other, more collapsed tape or cyclic structures (e.g., 6 and 7, and larger cyclic structures containing these units) are destabilized by nonbonded steric interactions (indicated by arrows in Figure 1). These two new structures, together with the structure of a linear tape (X = H) already described,<sup>3</sup> serve as paradigms for use in the design of self-assembling structures based on the CA·M lattice and provide structural parameters applicable to evaluation of the energetics of these structures using molecular mechanics.<sup>6</sup>

Figure 2 (middle) shows the structure of the 1:1 complex of 1a (X = CO<sub>2</sub>CH<sub>3</sub>) and 2.<sup>7</sup> This crinkled format occurs commonly: of 15 structures we have determined in the series of cocrystals incorporating substituted diphenylmelamines and 2, three are crinkled tapes. The complex 1a·2 crystallizes from

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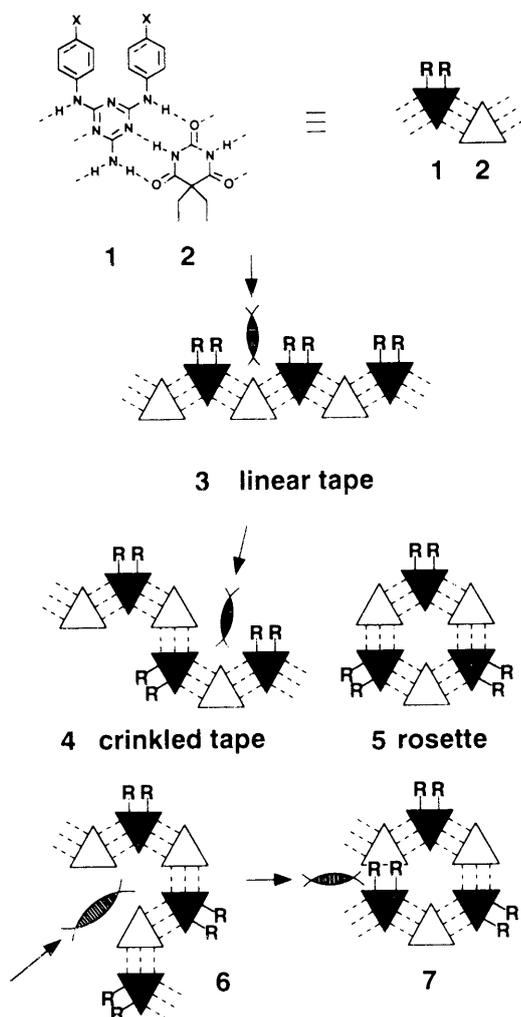
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(7) Crystal data for 1a·2 (X = CO<sub>2</sub>CH<sub>3</sub>): (C<sub>19</sub>H<sub>18</sub>N<sub>6</sub>O<sub>4</sub>)(C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>)·C-H<sub>3</sub>CH<sub>2</sub>OH; space group C2/c; *a* = 23.95 (3) Å, *b* = 16.95 (4) Å, *c* = 14.59 (1) Å, β = 94.4 (1)°, *V* = 5905 (2) Å<sup>3</sup>, *D*<sub>calc</sub> = 1.302 g/cm<sup>3</sup> without a contribution from included solvent, 1.405 g/cm<sup>3</sup> with the solvent; *Z* = 8 1·2 pairs; *R* = 0.14 (further refinement to model the disordered solvent molecule is underway).



**Figure 1.** Schematic representation of structures based on repeating units of **1**·**2**. Melamines are represented by filled triangles, diethylbarbituric acid is represented by open triangles, and the triad of hydrogen bonds is represented by the three connecting dotted lines. Regions of unfavorable steric interactions are indicated by the arrows. The structure of **7** superimposes one pair of R groups on a unit of **2** to show the steric strain.

ethanol as a solvate.<sup>8</sup> Figure 2 (lower) shows the structure of **1b** ( $X = C(CH_3)_3$ ) and **2**.<sup>9</sup> The mean planes of all the rosettes in the crystal are parallel: that is, they do not adopt a herringbone packing motif. No solvent of crystallization is included in the lattice.

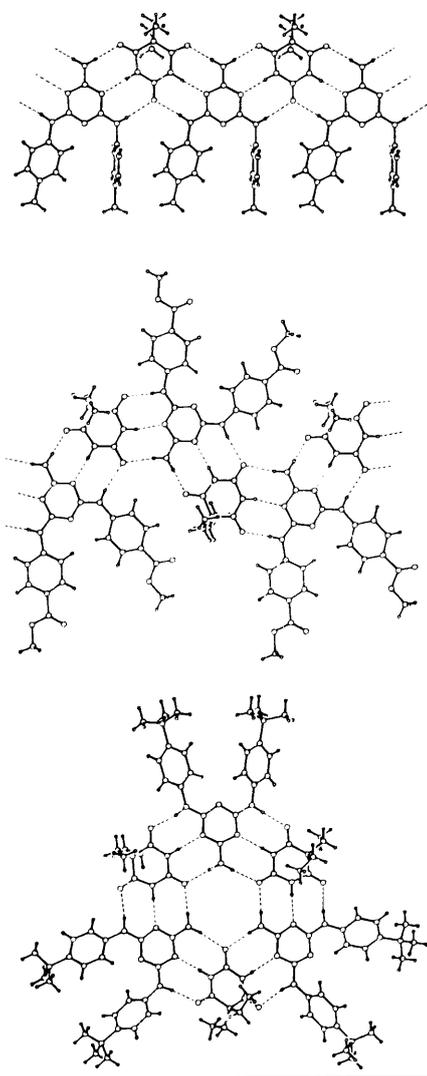
We hypothesize that a competition between nonbonded steric interactions between the X groups and a tendency for a high packing coefficient<sup>10</sup> in the crystal is important in determining which structural motif is adopted by a 1:1 cocrystal of **1** and **2**. We assume that any structure must retain the triad pattern of hydrogen bonds. The linear tape **3** is observed for a number of groups X that are small (F, Cl, Br, I,  $CH_3$ ). When X becomes larger than  $CF_3$  or I,<sup>11</sup> unfavorable lateral nonbonding interactions between X groups on adjacent melamines (Figure 1) are relieved in going to the crinkled structure **4**, but are replaced by unfavorable interactions with the ethyl groups of **2** (Figure 2, bottom).<sup>12</sup> The

(8) All three of the crinkled diphenylmelamine structures we have observed are solvates.

(9) Crystal data for **1b**·**2** ( $X = C(CH_3)_3$ ):  $(C_{23}H_{30}N_6)_3(C_8H_{12}N_2O_3)_3$ ; space group  $P\bar{1}$ ;  $a = 16.471$  (3) Å,  $b = 19.930$  (2) Å,  $c = 15.410$  (4) Å,  $\alpha = 95.10$  (1)°,  $\beta = 99.79$  (2)°,  $\gamma = 97.01$  (1)°,  $V = 4917$  (2) Å<sup>3</sup>,  $D_{\text{calc}}$  = 1.165 g/cm<sup>3</sup>,  $Z = 2$  rosettes (6 **1**·**2** pairs);  $R = 0.112$  (four of the *tert*-butyl groups are disordered; we are continuing to refine the structure with alternative positions for the  $CH_3$  groups).

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**Figure 2.** Top: crystal structures of linear tape ( $X = CH_3$ ),<sup>3</sup> crinkled tape ( $X = CO_2CH_3$ ), and rosette ( $X = C(CH_3)_3$ ) motifs. The crinkled tape crystal contains disordered ethanol that has been deleted from this view for clarity; it is located above and below the planes of the phenyl rings. Bottom: hypothetical space-filling model generated by replacing the ester groups in the crinkled tape with *tert*-butyl groups, without changing any other nuclear positions. The arrow indicates regions of unfavorable steric interaction between the *tert*-butyl group and the ethyl groups of the diethylbarbituric acid.<sup>12</sup>

crinkled structure is sufficiently loosely packed to accommodate one ethanol per dimer unit of **1a**·**2**.<sup>8</sup> Both types of steric interactions are relieved in the rosette **5**.

The structures reported here demonstrate that simple modifications in the molecular structures of a self-assembling system can lead to changes in crystalline architecture that can be rationalized (at least qualitatively) using steric arguments. By

(12) We have not examined these systems for crystalline polymorphism and have not excluded the possibility that some of these structures are kinetically determined, rather than being thermodynamic minima.

varying the steric demands of substituents around the periphery of our hydrogen-bonded components, we expect to be able to select from among alternative geometrical isomers of hydrogen-bonded assemblies in the solid state.

**Supplementary Material Available:** Brief synthetic outline, details of X-ray data collection, tables of crystal data and atomic positional parameters, and ORTEP drawings for both complexes (23 pages). Ordering information is given on any current masthead page.