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ARTICLE *in* CRYSTAL GROWTH & DESIGN · NOVEMBER 2001

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2002
VOL. 2, NO. 1
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Superstructural Variety from an Alkylated Triazine: Formation of One-Dimensional Hydrogen-Bonded Arrays or Cyclic Rosettes

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Received September 25, 2001; Revised Manuscript Received November 1, 2001

ABSTRACT: The propensity of an alkylated 2,6-diamino-1,3,5-triazine to establish dimeric hydrogen bonding motifs has been examined. Either alone, or when partnered with a linear aromatic diimide, the triazine crystallizes in extended one-dimensional hydrogen-bonded arrays. In contrast, the cocrystal with thiophene-2,5-dicarboxylic acid presents closed cyclic hexameric arrays comprised of alternating triazine and diacid units. In all cases, the triazine employs the same hydrogen bond donor and acceptor sites in establishing these extended structures, using only the sites that flank the smallest of the triazine substituents.

Introduction

The use of hydrogen-bonding interactions to direct and control solid-state structure is dependent on both the probability of formation and direction of propagation of specific intermolecular associations.[1–4] Through analysis of the Cambridge Structural Database, Allen et al. have ranked the top 24 most probable patterns of molecular association.[5] The majority of these prevalent structural types involve two adjacent hydrogen bonds, thus four of the top five (Figure 1; motifs 1, 2, 4, and 5) involve a 2-aminopyridine, or related system, that presents adjacent hydrogen bond donor and acceptor sites.[6] However, the use of these molecular types in the design of extended arrays is limited by the presence of only a single acceptor site, in the form of the ring nitrogen. In contrast, a molecule such as 2-aminopyrimidine possesses two acceptor sites and has proven useful in the construction of one-dimensional hydrogen-bonded arrays when combined with linear dicarboxylic acids such as succinic, fumaric, terephthalic, or (+)-camphoric.[7–10]

2,4-Diaminotriazine derivatives bearing non-hydrogen substituents on each amino nitrogen atom have similar potential to 2-aminopyrimidine for one-dimensional chain design. Where 2-aminopyrimidine employs its two amino hydrogen atoms in a chain array (two hydrogen-bond donor atoms and two hydrogen-bond acceptor atoms in total), a 2,4-diaminotriazine, with a possible four amino hydrogen atoms, need use only two of these (one from each amino group) to form associated motifs with appropriate groupings. Thus, one hydrogen atom

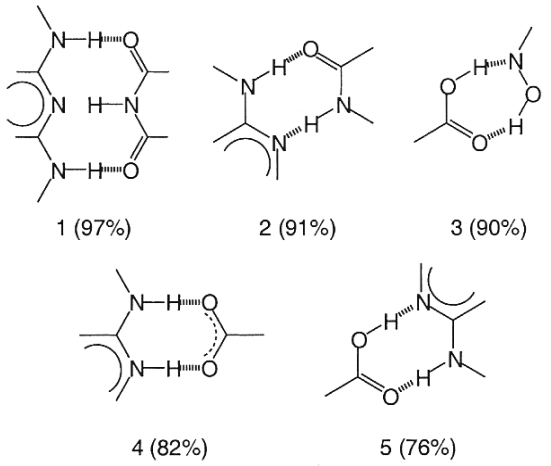

Figure 1. Five most probable hydrogen-bond motifs (ref 5; probability of formation in parentheses).

on each nitrogen may be replaced with a simple organic grouping to prohibit the possibility of competitive hydrogen-bond associations at these sites. Dialkylated *triamino* triazines have been studied by Whitesides and co-workers where a 3-fold hydrogen bonding complementarity with barbiturate derivatives was exploited to prepare a wide variety of systems. In these studies, a large number of derivatives were examined, and fine control of the steric bulk of the *N*-alkyl substituents was employed to control solid-state architecture.[11–15]

For a *diamino* triazine, the positions of the three heterocyclic nitrogen atoms of the 1,3,5-triazine ring system and their relationships to the amino substituents in the 2 and 4 positions allow for three conceivable association motifs, two of which produce binding sites angled at 120° (Figure 2). Motif I does not allow for the formation of extended arrays while both II and III appear well disposed toward this possibility, either in isolation or paired with a complementary component.

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10.1021/cg0155548 CCC: $22.00
Published on Web 11/28/2001

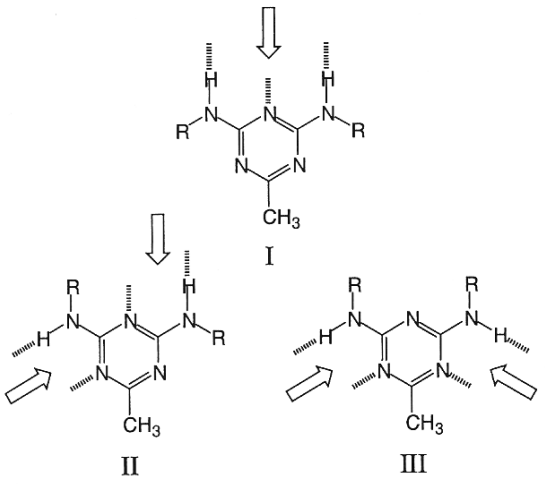


Figure 2. Potential conformations for an *N*-substituted 2,4-diaminotriazine (sites and relative dispositions of hydrogen bond association are indicated by arrows).

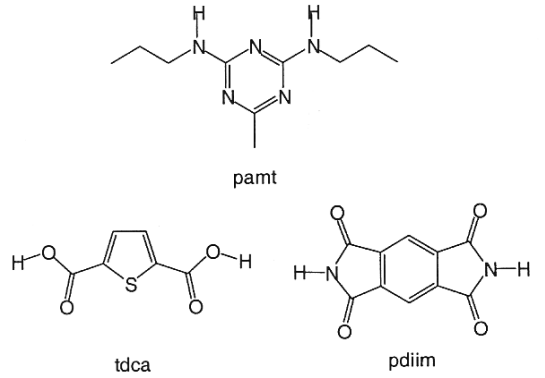


Figure 3. 2,4-Di-*n*-propylamino-6-methyl-*s*-triazine (pamt), thiophene-1,5-carboxylic acid (tdca), and pyromellitic diimide (pdiim).

Adoption of motif III appears the most attractive option since it allows for the establishment of extended structure at sites removed from the bulky *N*-propyl substituents. Only those sites flanking the smallest (methyl) substituent of the triazine are employed.

The synthetic background to this study was provided by a series of papers published in 1959 by Shapiro and co-workers wherein were reported the syntheses of a large number of substituted biguanide derivatives as part of a study of potential hypoglycemic agents.[16−19] A number of diaminotriazine derivatives were also prepared by condensation reactions of these various substituted biguanides with carbonyl compounds, typically esters. As a part of a program of research aimed at utilizing common recognition motifs in the solution self-assembly of large ordered structures, we prepared a model diaminotriazine for preliminary solid and solution state investigation.[20] We report here X-ray crystal structures of this model triazine (Figure 3; pamt), its 1:1 cocrystal with thiophene-2,5-dicarboxylic acid (tdca), and its 2:1 cocrystal with pyromellitic diimide (pdiim). The hydrogen-bonding preferences observed in the solid-state structures may prove important in terms of predicting, designing, and managing solution self-assembly processes based on similar structures.

Experimental Procedures

All materials were obtained from the Aldrich Chemical Co. and were used as received. The preparations are modeled on published procedures for related materials.[16−19]

***N*¹-*n*-Propyldicyandiamide 1.** A mixture of propylamine hydrochloride (10.00 g, 0.10 mol) and sodium Dicyandiamide (10.00 g, 0.11 mol) in *n*-butanol (100 mL) containing water (10 mL) was heated with stirring to reflux for 16 h. After the sample was cooled, the precipitated NaCl was removed by filtration, and the mixture was evaporated to dryness. Trituration of the residue with water gave a white crystalline solid (11.12 g, 88%): mp 45−46 °C; ^{13}C NMR (63 MHz, DMSO-d_6) δ 161.17 (0), 118.38 (0), 42.57 (2), 22.31 (2), 11.23 (3) ppm; ^{1}H NMR (270 MHz, DMSO-d_6) δ 5.91 (br s, 1H), 5.76 (br s, 2H), 2.12 (q, J = 8 Hz, 2H), 0.54 (sextet, J = 8 Hz, 2H), −0.07 (t, J = 8 Hz, 3H) ppm.

***N*¹,*N*⁵-Di-*n*-propylbiguanide Hydrochloride 2.** A mixture of N^1-*n*-propyldicyandiamide (10.11 g, 0.08 mol) and propylamine hydrochloride (7.70 g, 0.81 mol) was fused at 150 °C on an oil bath for 30 min. Acetonitrile (80 mL) was added to the cooled residue, and the suspension was heated to reflux for 30 min, the cooled suspension was filtered to give a white crystalline solid (11.37 g, 63%): mp 225−227 °C; ^{13}C NMR (63 MHz, DMSO-d_6) δ 158.38 (0), 42.71 (2), 22.27 (2), 11.37 (3) ppm; ^{1}H NMR (270 MHz, DMSO-d_6) δ 6.25 (br s, 2H), 5.95 (br s, 3H), 2.15 (q, J = 8 Hz, 4H), 0.56 (sextet, J = 8 Hz, 4H), −0.02 (t, J = 8 Hz, 6H) ppm.

2,4-Di-*n*-propylamino-6-methyl-*s*-triazine 3 (pamt). To a solution of the hydrochloride salt of N^1,N^5-di-*n*-propylbiguanide (1.00 g, 4.5 mmol) in MeOH (30 mL) was added freshly cut sodium (0.13 g, 5.5 mmol). After 5 min stirring, the reaction was filtered to remove the precipitate of sodium chloride, ethyl acetate (0.60 mL, 0.54 g, 6.3 mmol) was added, and the mixture was brought to reflux for 16 h. The reaction was subsequently cooled, and the white residue was crystallized from acetonitrile to yield the triazine as a white crystalline solid (0.93 g, 99%): mp 167−169 °C; ^{13}C NMR (63 MHz, DMSO-d_6, 60 °C) δ 173.30 (0), 165.33 (0), 41.49 (2), 24.58 (3), 22.03 (2), 10.95 (3) ppm; ^{1}H NMR (270 MHz, DMSO-d_6, 60 °C) δ 6.76 (br s, 2H), 3.23−3.15 (m, 4H), 2.08, 2.07 (2 × s, 3H; from free and self-complexed forms), 1.51 (sextet, J = 8 Hz, 4H), 0.86 (t, J = 8 Hz, 6H) ppm.

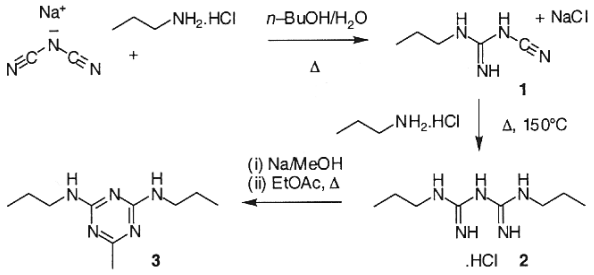
Crystallography. Crystals of pamt were grown by total evaporation from MeCN, while crystals of [(pamt)(tdca)] and [(pamt)$_2$(pdiim)] were grown by vapor diffusion of water into DMF solutions containing equimolar amounts of the two components. Intensity data for the three crystals were collected at room temperature on a Nonius Kappa CCD area detector diffractometer using monochromatized Mo Kα X-radiation; λ = 0.71073 Å. Crystallographic details are given in Table 1. Data were corrected for Lorentz and polarization effects, but no absorption corrections were applied. All of the data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least-squares. Refinements were based on F^2 and computations were performed using SHELXS-86 for solution and SHELXL-97 for refinement.[21] All hydrogens not involved in the strong hydrogen-bonding associations were included in the refinement at calculated positions as riding models. All amino hydrogen atoms, the carboxylic acid hydrogen atoms of tdca, and the alkyl hydrogen atoms attached to the first nondisordered carbon atom in the disordered propyl chains of pamt in the parent structure, and in [(pamt)(tdca)], were located by Fourier difference methods and both positional and thermal parameters were refined. In [(pamt)(tdca)], only one hydrogen atom was located on the first nondisordered carbon atom. The last two carbon atoms of the 4-position propyl chain in pamt are disordered across two sites per atom and were each assigned 50% site occupancies as determined from the refinement. Similar disorder occurs on the last carbon atom of the only symmetry-unique propyl chain in [(pamt)(tdca)] with the site occupancies of the two carbon positions being 77 and 23%. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center,

Table 1. Crystallographic Data and Refinement Details

	pamt	[(pamt)(tdca)]	[(pamt)$_2$(pdiim)]
formula	$C_{10}H_{19}N_5$	$C_{16}H_{23}N_5O_4S$	$C_{30}H_{42}N_{12}O_4$
M_r	209.30	381.45	634.76
crystal size, mm	0.65 × 0.50 × 0.05	1.00 × 0.01 × 0.01	0.45 × 0.25 × 0.10
crystal system	triclinic	trigonal	triclinic
space group	$P\bar{1}$	$R\bar{3}c$	$P\bar{1}$
a, Å	5.2485(2)	21.9918(6)	8.8726(2)
b, Å	10.2130(4)	21.9918(6)	9.0394(2)
c, Å	12.4377(6)	20.8670(4)	11.2704(3)
α, deg	107.012(2)	90	69.733(1)
β, deg	97.765(2)	90	75.546(1)
γ, deg	99.730(2)	120	84.268(2)
V, Å^3	616.19(4)	8740.0(4)	821.03(3)
Z	2	18	1
D_{exptl}, g cm^{-3}	1.128	1.305	1.284
μ, mm^{-1}	0.073	0.197	0.090
no. of rflns measd	2158	1698	2869
no. of refined params	174	143	223
no. of rflns with $I > 2.0\sigma(I)$	1647	1294	2307
R^a	0.053/0.071	0.060/0.080	0.052/0.065
$R_w{}^a$	0.139/0.153	0.154/0.173	0.147/0.136

[a] Using data with [$F > 4\sigma(Fo)$]/all data.

Scheme 1. Synthesis of Triazine 3



deposition numbers: pamt CCDC 171356, [(pamt)(tdca)] CCDC 171357, [(pamt)$_2$(pdiim)] CCDC 171358.

Results and Discussion

Synthesis. Reaction of approximately equimolar amounts of propylamine hydrochloride and sodium dicyandiamide afforded the biguanide precursor **1** in good yield (Scheme 1). Fusion of this material with a second equivalent of propylamine hydrochloride gave symmetrical substituted biguanide **2** as the hydrochloride salt. Conversion of **2** to the free base form by treatment with sodium, and subsequent condensation with ethyl acetate, led to triazine **3** in essentially quantitative yield. All materials were readily purified by recrystallization. Self-associative behavior of **3** in solution complicated the assignment of its proton NMR spectra, although low concentration experiments allowed unambiguous assignments to be made.[20]

Solid-State Structure of pamt. Pamt (Figure 4) has two hydrogen-bond donor and three hydrogen-bond acceptor sites, yet access to the heterocyclic nitrogen acceptor atom situated between the propylamino substituents is hindered by these groups. In essence, therefore, pamt is self-complementary since the accessible faces of this system each present one donor site and one acceptor site, self-association will ensure that all accessible hydrogen-bond donor or acceptor sites are satisfied.

Long range ordering in crystals of pamt is controlled by association in conformation III (Figure 5). The propyl chains are directed away from the sites of self-complementary hydrogen bonding contact, facilitating the establishment and propagation of infinite one-dimensional hydrogen-bonded ribbons along the *ab* axis diagonal (see Table 2 for hydrogen bond parameters and geometry). These infinite ribbons pack in parallel rows and allow for one of the propyl chains to interdigitate with opposing 6-methyl substituents of triazine rings in an adjacent ribbon. In contrast, the 4-position propyl

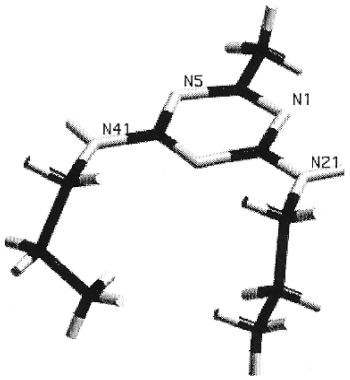


Figure 4. Molecular configuration of pamt (hydrogen bond donor/acceptor sites labeled, see Table 2).

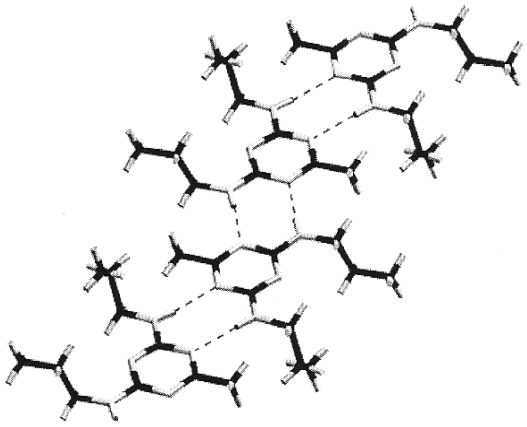


Figure 5. Part of the continuous one-dimensional array of triazines within crystals of pamt (dashed lines indicate hydrogen bonds).

Table 2. Hydrogen Bond Distances and Angles[a]

crystal	donor (D)	hydrogen (H)	acceptor (A)	D−H	H- - -A	D- - -A	∠D−H- - -A
pamt	N21	H21	N1	0.86(2)	2.19(2)	3.047(2)	176(2)
	N41	H41	N5	0.84(2)	2.25(2)	3.093(2)	175(2)
[(pamt)(tdca)]	N21A	H21A	O20B	0.75(4)	2.29(4)	3.008(5)	162(4)
	O21B	H21B	N1A	0.98(5)	1.61(5)	2.577(4)	171(4)
[(pamt)$_2$(pdiim)]	N5	H5	O1	0.86(3)	2.11(3)	2.960(2)	174(2)
	N4	H4	N2	0.90(2)	2.14(3)	3.029(2)	170(2)
	N6	H6	N2	0.89(3)	2.03(3)	2.914(2)	173(2)

[a] For atom labels see Figures 4, 6, and 9.

chains of adjacent ribbons find themselves co-aligned and are thus forced to adopt a conformation in which they fold over one another. This somewhat hindered situation may be the cause of some disorder in the end two carbons of these chains.

Adoption of associative motif III is likely to be largely controlled by issues relating to the accommodation of the propyl side chains. As previously mentioned, the studies of Whitesides and co-workers demonstrated the degree to which cocrystalline architecture could be controlled by subtle steric modification. Although these studies concerned 1:1 triaminotriazine−barbiturate systems, i.e., a mixed system of two complementary components, an identical argument concerning the availability of the heterocyclic nitrogen atom between the aminoalkyl substituents can be applied to pamt, and the prediction made that this site will be disfavored, thus forcing adoption of motif III.[14] The homocomplementarity of pamt leads to an important superstructural difference with the work cited above—the infinite ribbons within pamt crystals are perfectly linear, whereas the specific association geometry required in triaminotriazine−barbiturate systems, although controlled by the same factors, necessarily leads to the formation of crinkled tapes.

Solid-State Structure of [(pamt)(tdca)]. Both components of this cocrystal are self-complementary; therefore, a possible structure might have involved the formation of discrete, homomolecular ribbons of pamt and tdca. However, our expectation, based on the aforementioned work concerning probabilities of motif formation, was that some form of heteromolecular superstructure would be observed. Alternating units of pamt and tdca must associate via establishment of motif 5 (Figure 1), the fifth most common arrangement in this ranking and one placed much higher than either of the homomolecular arrangements for this particular system. The question remained open of whether the expected alternating arrays of components would, because of the turn inherent in the thiophene dicarboxylic acid, lead to crinkled (i.e., substantially nonlinear) tapes, or to a closed cyclic rosette.

The latter situation is that observed in crystals of [(pamt)(tdca)]. Figure 6 reveals the molecular configuration of the hydrogen bonded components. Figure 7 presents a plan view of the planar six-component hydrogen-bonded [(pamt)$_3$(tdca)$_3$] rosette (see Table 2 for hydrogen bond parameters and geometry). The dihedral angle between the triazine and thiophene ring systems is 0.6(1)°. The symmetry of the two component molecules, combined with the high symmetry of the rosette motif, dictate a high symmetry space-group, with each component molecule asymmetrically halved by mirror planes (the disorder in the end carbon atoms of

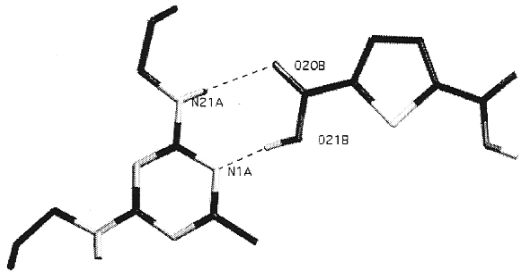


Figure 6. Molecular configuration of [(pamt)(tdca)], non-hydrogen-bonded hydrogen atoms omitted for purposes of clarity (dashed lines indicate hydrogen bonds, hydrogen bond donor/acceptor sites labeled, see Table 2).

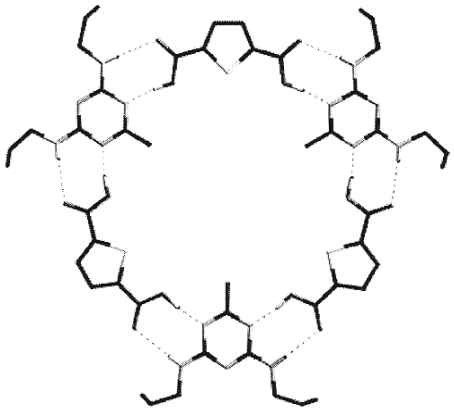


Figure 7. Plan view of the cyclic, hexameric rosette within crystals of [(pamt)(tdca)], non-hydrogen-bonded hydrogen atoms omitted for purposes of clarity (dashed lines indicate hydrogen bonds).

the propyl chains is thus mirrored across the pamt molecule). The propyl side chains line the exterior of the rosettes, the proximity of adjacent hexameric rings causing them to fold back toward the tdca rosette constituents. The in-plane packing of adjacent rosettes in the crystal is illustrated in Figure 8. Individual rosettes do not stack one upon another to create channels.

The melamine−cyanurate system studied by the Whitesides group has provided a reliable vehicle for A_3B_3 cyclic rosette formation.[15] In its most minimal form, i.e., unsubstituted melamine and cyanuric acid, Rao and co-workers have revealed a rare example of channel formation from a structure adopting the hexameric rosette motif.[22] In these systems, both molecular components possess angles of exactly 120° between their associative faces; hence, all angles are perfectly set for hexamer formation. It is interesting to note that although this situation is true for pamt, the corresponding angle for tdca is around 150°. This more open structure

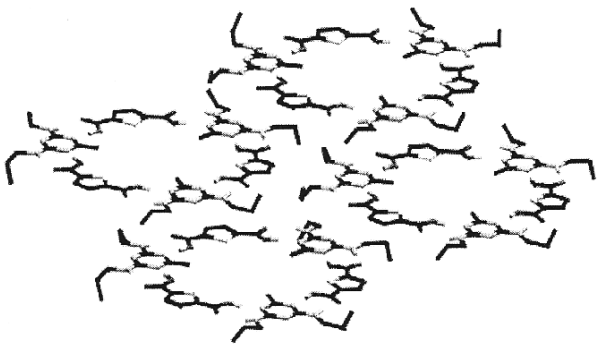


Figure 8. Packing of adjacent rosettes within crystals of [(pamt)(tdca)], non-hydrogen-bonded hydrogen atoms omitted for purposes of clarity.

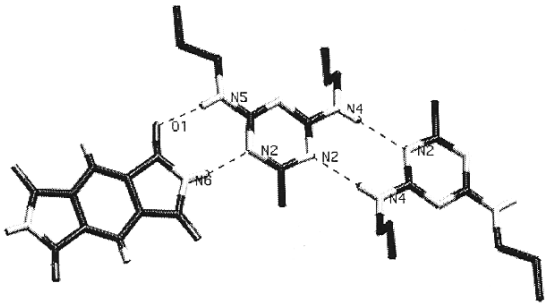


Figure 9. Molecular configuration of [(pamt)$_2$(pdiim)], non-hydrogen-bonded hydrogen atoms omitted for purposes of clarity (dashed lines indicate hydrogen bonds, hydrogen bond donor/acceptor sites labeled, see Table 2).

is compensated by the hydrogen bonds defining the hexamer which are set at angles of considerably less than 180° (see Table 2).

Solid-State Structure of [(pamt)$_2$(pdiim)]. Rebek and co-workers were among the first to recognize the potential of diaminotriazine-imide association by demonstrating that this recognition process could be used to direct and drive a self-replication cycle.[23,24] At the outset of this project, we anticipated that the result of mixing pamt with the linear aromatic diimide pdiim, in a 2:1 ratio, would be formation of a 2:1 cocrystal via the establishment of triple hydrogen-bond arrays via associative conformation I. However, the crowding of the face of pamt required for adoption of this conformation ensured an alternative outcome.

The 2:1 stoichiometry is retained in crystals of [(pamt)$_2$(pdiim)], but the units are arrayed in continuous AABAAB chains, not discrete ABA triads (see Figure 9 for molecular configuration). Adjacent triazines associate via conformation III (Figure 2), while their outer faces contact the ends of the diimide subunits (motif 2, Figure 1). Thus, the structure may be viewed as a variant of that of pure pamt, where the diimide has been inserted at every second triazine into the infinite ribbon structure (Figure 10; see Table 2 for hydrogen bond parameters and geometry). The observed combination of hydrogen-bonding arrangements, the associative conformation selected by pamt, and the apparent maximization of molecular symmetry, must represent the pathway to the most favorable lattice structure. The subsequent packing of the hydrogen-bonded ribbons, and the necessary accommodation of the propyl chains,

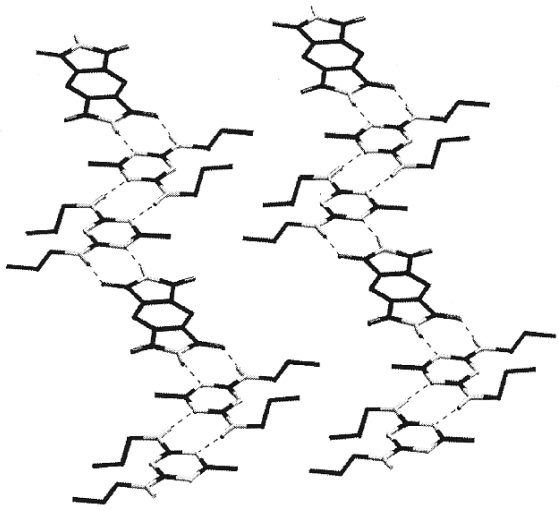


Figure 10. Part of the continuous one-dimensional array of triazines within crystals of [(pamt)$_2$(pdiim)], non-hydrogen-bonded hydrogen atoms omitted for purposes of clarity (dashed lines indicate hydrogen bonds).

does not give rise to any disorder. Finally, the π-electron-rich triazine rings maintain substantial overlap with the π-electron deficient diimide units [the perpendicular centroid−centroid distance is 3.411(5) Å, with an angle between the planes of the respective ring systems of 4.7-(1)°].

The structure of the melamine-succinimide 1:1 cocrystal shares a number of features with that of [(pamt)$_2$(pdiim)].[25] Succinimide, of course, cannot propagate extended structure in the manner of pdiim, but when crystallized with melamine ABBA tetrads are formed where succinimide units (A) act as terminating caps at the ends of melamine dimers that are held together by the same array of hydrogen bonds as seen in our structures. Meijer and co-workers have demonstrated a remarkable degree of stoichiometric control in a related system where variation in the level of substitution of an imide component led to the formation of 1:1, 1:2, or 1:3 cocrystals with melamine.[26] This study represents another example of steric control of cocrystalline architecture. The current study may be seen as complementary to this work as the superstructures we observe involving pamt are dictated, to some extent, by the presence of the aminopropyl substituents and their role in inhibiting a potential acceptor site.

Conclusion

The potential of pamt as a crystal synthon to produce either one-dimensional hydrogen-bonded arrays or cyclic rosettes is clearly demonstrated in the three example structures presented in this paper. The triazine favors associative conformation III, an observation in broad agreement with predictions based on the probability of formation of various hydrogen-bonded motifs when concession is made to the lack of availability of the heterocyclic nitrogen atom situated between the aminopropyl substituents. These groups direct themselves in such a manner as to allow access to two equivalent sites for dimer formation via N−H···N hydrogen bonds. These sites are angled at 120° to one another and are therefore ideally disposed toward the formation of ribbons, with

or without a companion complementary molecule, or closed cyclic aggregates when appropriately partnered.

Acknowledgment. We thank Mount Holyoke College for financial support of this work and the NSF (Grant CHE-9974648) for support of the X-ray Structural Characterization Laboratory at the University of Massachusetts, Amherst.

Supporting Information Available: X-ray structural information in CIF format for pamt, [(pamt)(tdca)], and [(pamt)$_2$(pdiim)], including tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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CG0155548