1250 *Chem. Mater.* **1994,** *6,* 1250–1257

Investigations into the Robustness of Secondary and Tertiary Architecture of Hydrogen-Bonded Crystalline Tapes

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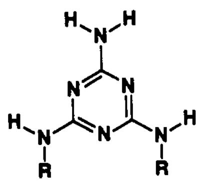
Received May 6, 1994. Revised Manuscript Received June 10, 1994[⊗]

Five crystal structures of hydrogen-bonded complexes (*N*-(*p*-iodophenyl)-*N*′-(*p*-cyanophenyl)-melamine•barbital, *N,N*′-diphenylmelamine•5,5-dimethylbarbituric acid, 2-amino-4-((*m*-bromophenyl)amino)-6-chloro-1,3,5-triazine•barbital, melamine•5,5-dibromobarbituric acid, and melamine•barbituric acid) are presented. These particular components represent perturbations on the molecules that were previously used to construct crystallographic hydrogen-bonded tapes (Zerkowski, J. A.; MacDonald, J. C.; Seto, C. T.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994,** *116,* 2382). Four of the complexes pack in the solid state as linear tapes, while the diphenylmelamine•dimethylbarbituric acid complex packs as a crinkled tape due to the closer stacking of tapes permitted by the small methyl substituents. The triad of hydrogen bonds that forms tapes is apparently robust to this sort of variation, even though some of the substituents introduce noncovalent intertape interactions, such as halogen–nitrogen contacts, ionic forces, and other hydrogen bonds. The potential of such intertape interactions for designing crystalline architecture is discussed.

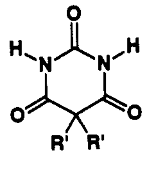
Introduction

To probe the modifiability and robustness of hydrogen-bonded cocrystalline "tapes", we have begun investigating the effects that major structural changes have on the formation and packing of tapes. We have shown that crystalline architecture[1] could be constructed and rationalized from complexes of 1 and 2. In particular, by varying the steric properties of the substituents R of 1, we have obtained three structural motifs. When R was a phenyl ring substituted in the para position with CF_3 or a smaller group, we obtained linear tapes.[2] When the para substituent on the phenyl group was CO_2Me,[3] the meta substituent was Cl or Br,[4] or when R was *tert*-butyl,[5] crinkled tapes were obtained. When the para substituent was *tert*-butyl, a pseudo-C_3 cyclic structure (a "rosette") was obtained.[3] **Bar(Et)$_2$** (barbital) has been the barbiturate that we used most frequently, although other substituents on the barbiturate have also generated crystalline tapes.[5]



1

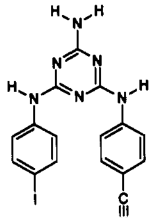
Mel(R)$_2$



2

Bar(R′)$_2$

In the research presented in this paper, we examined the influence of larger variations in the structures of both components on the structure of the 1:1 cocrystals. With an unsymmetrically substituted melamine (**3**, R_1 = *p*-iodophenyl, R_2 = *p*-cyanophenyl), a non-melamine (**4**), *un*substituted melamine (**5**), or significantly truncated substituents on the barbiturate (R′ = Br (**6**) or H (**7**)), linear tapes are still obtained. With the seemingly minor perturbation of shortening the ethyl groups of **Bar(Et)$_2$** to methyl groups (**8**), the secondary architecture switched from a linear to a crinkled motif. We were also interested in surveying how substitution patterns of these kinds might be used to control intertape orientation, or tertiary crystalline architecture.



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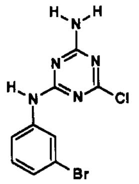

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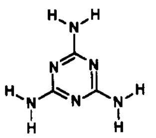

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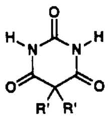

R′ = Br **6**
R′ = H **7**
R′ = Me **8**

Results

Figures 1–5 are conglomerate pictures of the sort we introduced in previous work. These pictures show several

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

(1) To analyze the packing of these complexes, we define hierarchical levels of crystalline architecture: the *primary* level is composition and sequence (formation of 1:1 chains or rings with alternation of melamine and barbituric acid components); the *secondary* level consists of the *motif* describing the 1:1 aggregates (for example linear or crinkled tapes and rosettes); the *tertiary* level consists of the organization and packing of the tapes in the crystal (for example, as sheetlike or dimeric structures).

(2) Zerkowski, J. A.; MacDonald, J. C.; Seto, C. T.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994,** *116,* 2382.

(3) Zerkowski, J. A.; Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992,** *114,* 5473.

(4) Zerkowski, J. A.; Mathias, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994,** *116,* 4305.

(5) Zerkowski, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994,** *116,* 4298.

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Table 1. Crystallographic Data[a]

complex	space group	a (Å)	b (Å)	c (Å)	α (deg)[b]	β (deg)[b]	γ (deg)[b]	R[c]	C_k*[d]	density (g/cm^3)[e]	crystallization solvent
Mel(*p*-I-Ph)(*p*-CN-Ph)·Bar(Et)$_2$	*Fdd2*	30.603	35.760	$\underline{9.711}$				0.052	0.68	1.534	EtOH
4·Bar(Et)$_2$	$P\bar{1}$	7.424	$\underline{9.944}$	13.599	97.34	91.25	95.41	0.059	0.72	1.625	MeOH
Mel·Bar(Br)$_2$	$Ccm2_1$	7.207	$\underline{9.740}$	17.072				0.035	0.81	2.284	H_2O
MelH$^+$·BarH$^-$	*Ccc2*	5.052	$\underline{12.221}$	15.742				0.045	0.79	1.737	H_2O
Mel(Ph)$_2$·Bar(Me)$_2$	$P2_1/a$	9.295	16.911	13.520		96.16		0.058	0.70	1.366	MeOH

[a] The underlined cell dimensions represent the repeat distance in a linear tape. [b] A blank indicates that the angle is constrained to be 90°. [c] This value is the crystallographic reliability index, $R = \sum|(F_o - F_c)|/\sum F_o$. [d] This value is the packing coefficient based on molecular volumes calculated using MacroModel (see Results). For a comparison of our modified, MacroModel-derived C_k* values to "classical" C_k values, see ref 2. [e] Calculated.

different views of the packing of the complexes. Table 1 lists crystallographic data and some geometric parameters describing the packing of tapes.

N-(*p*-Iodophenyl)-N′-(*p*-cyanophenyl)melamine·Barbital, Mel(*p*-I-Ph)(*p*-CN-Ph)·Bar(Et)$_2$ (Figure 1). This complex was investigated to determine whether interactions between iodine and nitrile groups could be used to guide the formation of tertiary architecture. Although –CN and –I have similar linear sizes,[6] the crystal is well ordered with alternating nitrile and iodide moieties along the edge of each tape.[7] Despite abundant evidence for interaction between nitrile groups and the halogen atoms of organic iodides and bromides in the solid state,[8] neither linear nor lateral I- - -NC contacts is important. The closest I- - -N distance involving nitrile groups is that occurring intermolecularly between adjacent melamines within a tape, with a magnitude of 4.0 Å ($\sum_{vdW}$ ~ 3.5 Å).[9] There is, however, a contact at 3.4 Å between perpendicular tapes involving an iodine in tape A in Figure 1 and an NH_2 nitrogen of a melamine in tape B (see Figure 6 for a closeup view of this contact).[10] There are no iodine–iodine contacts.

***N,N′*-Diphenylmelamine·5,5-Dimethylbarbituric Acid, Mel(Ph)$_2$·Bar(Me)$_2$ (Figure 2).** We investigated this complex to study the influence that the protruding ethyl groups of Bar(Et)$_2$ exert on the packing of tapes. Although we assumed that the replacement of ethyl with methyl groups would have no effect on the secondary architecture, the complex packs as a crinkled tape, rather than the linear tape observed for **Mel(Ph)$_2$·Bar(Et)$_2$**.[2] One of the phenyl groups is almost coplanar with the melamine ring, while the other is more twisted out of the plane (torsion angles 11° and 28°, respectively). With no substituents extending very far out of the hydrogen-bonded plane of the tape (relative to tapes with ethyl groups or phenyl groups with larger torsion angles), these crinkled tapes appear "flat" (see the end-on view in Figure 2) and can stack closely on top of each other. Conversely, there are no contacts between adjacent stacks of tapes (e.g., between tapes B and C in Figure 2). There are two intratape CH- - -O contacts under the sum of the van der Waals radii (~2.7 Å).[9] One involves an ortho proton on the nearly in-plane phenyl ring and the neighboring barbituric acid. The other contact involves a meta proton on the other, more twisted phenyl ring and the barbituric acid three units away in the tape (see the top of Figure 2). Both H- - -O distances are ~2.55 Å.

2-Amino-4-((*m*-bromophenyl)amino)-6-chloro-1,3,5-triazine·Barbital, 4·Bar(Et)$_2$ (Figure 3). This melamine analogue (a triazine) was chosen primarily because it has only two amine groups. Chlorine is one of many substituents that might go in the remaining ring position, and the *m*-bromophenyl ring fortuitously gave good crystals; neither of these substituents was chosen to test a specific hypothesis. The linear tape motif is preserved, even though one hydrogen bond has been deleted relative to complexes constructed from melamines. The chlorine and oxygen that occupy the space of the former hydrogen bond are just at van der Waals contact (distance = 3.3 Å, $\sum_{vdW}$ = 3.3 Å). With the removal of one of the NHR groups, the phenyl group of the remaining NHR has room to lie almost coplanar with the triazine ring: the mean planes of the two rings differ by only approximately 3°. Due to this orientation of the phenyl ring, one *ortho*-hydrogen is positioned close to a barbital oxygen at 2.5 Å.

Melamine·5,5-Dibromobarbituric Acid, Mel·Bar(Br)$_2$ (Figure 4). This substituted barbituric acid (and barbituric acid itself, Figure 5) was examined to determine the influence of replacing the ethyl groups of barbital by smaller but more polarizable and/or reactive substituents. The bromine atoms of **Bar(Br)$_2$** are involved in several intertape contacts with nitrogen atoms of melamine at 2.7 and 2.8 Å ($\sum_{vdW}$ = 3.4 Å, see Figure 7 for a closeup view). These intertape interactions are reflected in the high value of C_k* (Table 1).

Melamine·Barbituric Acid, MelH$^+$·BarH$^-$ (Figure 5). Proton transfer from the CH_2 of barbituric acid to a ring nitrogen of melamine has occurred. This complex

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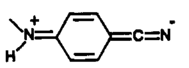
[6] The C_{phenyl}–I bond length in this structure is 2.09 Å; the C_{phenyl}–N distance (skipping over the nitrile carbon) is 2.52 Å.

[7] The bond lengths of the cyanophenyl group do not indicate a significant contribution from the dipolar quinonoid resonance structure i. In particular, the HN-C_{phenyl} bond (1.418 Å) is unchanged from the analogous bonds we have observed in other para substituted diphenylmelamines, which ranged from 1.389 to 1.441 Å.[2]



i

[8] For a review of halogen–nitrile interactions, see: Desiraju, G. R.; Harlow, R. L. *J. Am. Chem. Soc.* **1989,** *111,* 6757. Carter, V. B.; Britton, D. *Acta Crystallogr.* **1972,** *B28,* 945. Britton, D. *Persp. Str. Chem.* **1967,** *1,* 109. For general halogen–nitrogen contacts, see: Xu, K.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1994,** *116,* 105.

[9] The van der Waals radii we are using are isotropic: H 1.20 Å; C 1.70 Å; N 1.55 Å; O 1.52 Å; F 1.47 Å; Cl 1.75 Å; Br 1.85 Å; I 1.98 Å. Bondi, A. *J. Phys. Chem.* **1964,** *68,* 441.

[10] Intuition suggests that the van der Waals radius of an atom should be dependent, to some extent, upon its hybridization state and the identity of the atoms to which it is covalently attached. There is evidence supporting this idea: Bondi[9] cites data purporting that the nitrogen in a nitrile group has a van der Waals radius of 1.4 Å parallel to the CN axis and 1.7 Å perpendicular to it. Some interesting work has appeared on anisotropic van der Waals radii suggesting that halogens in particular undergo "polar flattening" parallel to the C–X axis and expansion perpendicular to it: Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr.* **1985,** *B41,* 274, and Nyburg, S. C.; Faerman, C. H.; Prasad, L. *Acta Crystallogr.* **1987,** *B43,* 106. Nonetheless, many solid-state chemists seem to prefer Bondi's isotropic radii as simple, consistent (and successful) approximations, in the absence of comprehensive studies of different hybridization classes of each element. For a discussion, see: Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: New York, 1989.

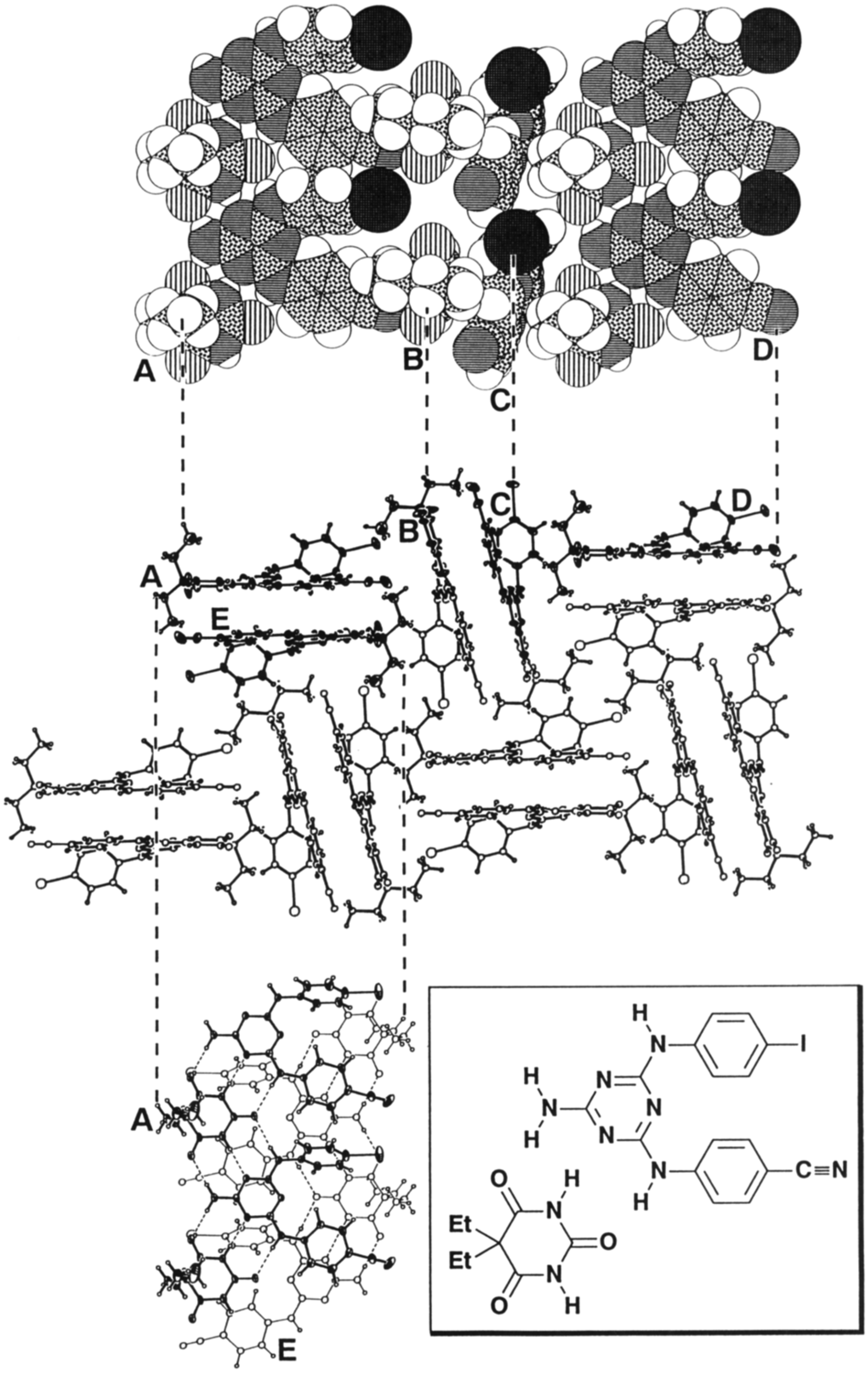


Figure 1. Views of the **Mel(*p*-I-Ph)(*p*-CN-Ph)·Bar(Et)$_2$** complex.

also has a high value of C_k^*. The crystallographically infinite hydrogen-bonded axes of the tapes are parallel within a stack of tapes, but adjacent stacks are twisted by 78° with respect to each other. This structure is the first in which we have observed nonparallel tapes.

Packing Fractions. The values of C_k^*[11] for the complexes incorporating **Bar(Br)$_2$** and **BarH$^-$** are higher than normal for organic molecular crystals.[12] The value for **Mel·Bar(Br)$_2$** is the highest we have observed in any tape. This increase in the efficiency of space filling is probably due to two factors. The first is the presence of

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[11] $C_k = NV_{mol}/V_{cell}$, where N is the number of molecules in a unit cell, V_{mol} is the molecular volume, and V_{cell} is the volume of the unit cell. Kitaigorodsky, A. I. *Organic Chemical Crystallography*; Consultants Bureau: New York, 1961. For a discussion of the relationship between our modified C_k^* values and traditionally calculated C_k values, see ref 2.

[12] Values of C_k usually range from roughly 0.65 to 0.77: Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: New York, 1989; Chapter 2. Some of the highest values listed by Kitaigorodsky[11] are 0.785 (*p*-quaterphenyl), 0.781 (1,2-anthraquinone), and 0.805 (perylene). The value for graphite is 0.887, which can probably be considered an effective upper limit.

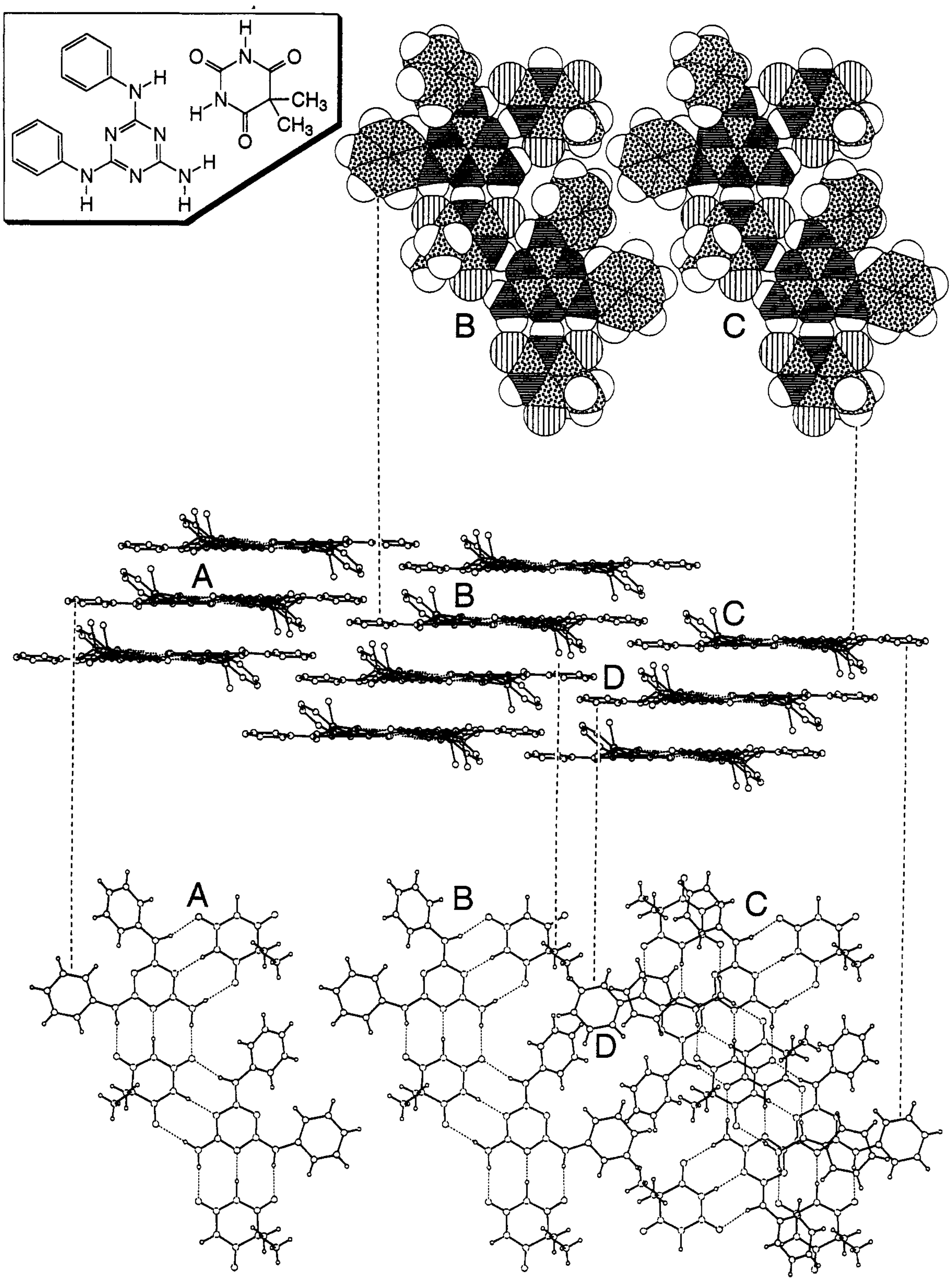

Figure 2. Views of the **Mel(Ph)$_2$·Bar(Me)$_2$** complex. Hydrogen atoms have been omitted from the central, end-on view for clarity.

strong electrostatic intertape forces such as those between bromine and nitrogen atoms in **Mel·Bar(Br)$_2$** and the ionic interactions in **MelH$^+$·BarH$^-$**. Ionic interactions in crystals of the latter compound cause them to have a high density (1.737 g/cm^3) for a material containing only C, H, O, and N.[13] The second factor is geometric: the individual molecules are flatter than melamines and barbiturates substituted with phenyl or ethyl groups; this shape allows the tapes to stack with little empty space between them.

Discussion

The complex of **Mel(*p*-I-Ph)(*p*-CN-Ph)** with **Bar(Et)$_2$** was investigated because it represented a preliminary experiment in the control of tertiary architecture. We hypothesized that this complex might pack analogously to the **Mel(*p*-I-Ph)$_2$·Bar(Et)$_2$** complex (Figure 8).[2] There were extensive I- - -I contacts between tapes in that complex; we thought that replacing one iodine with a nitrile group would allow for virtually isostructural packing and

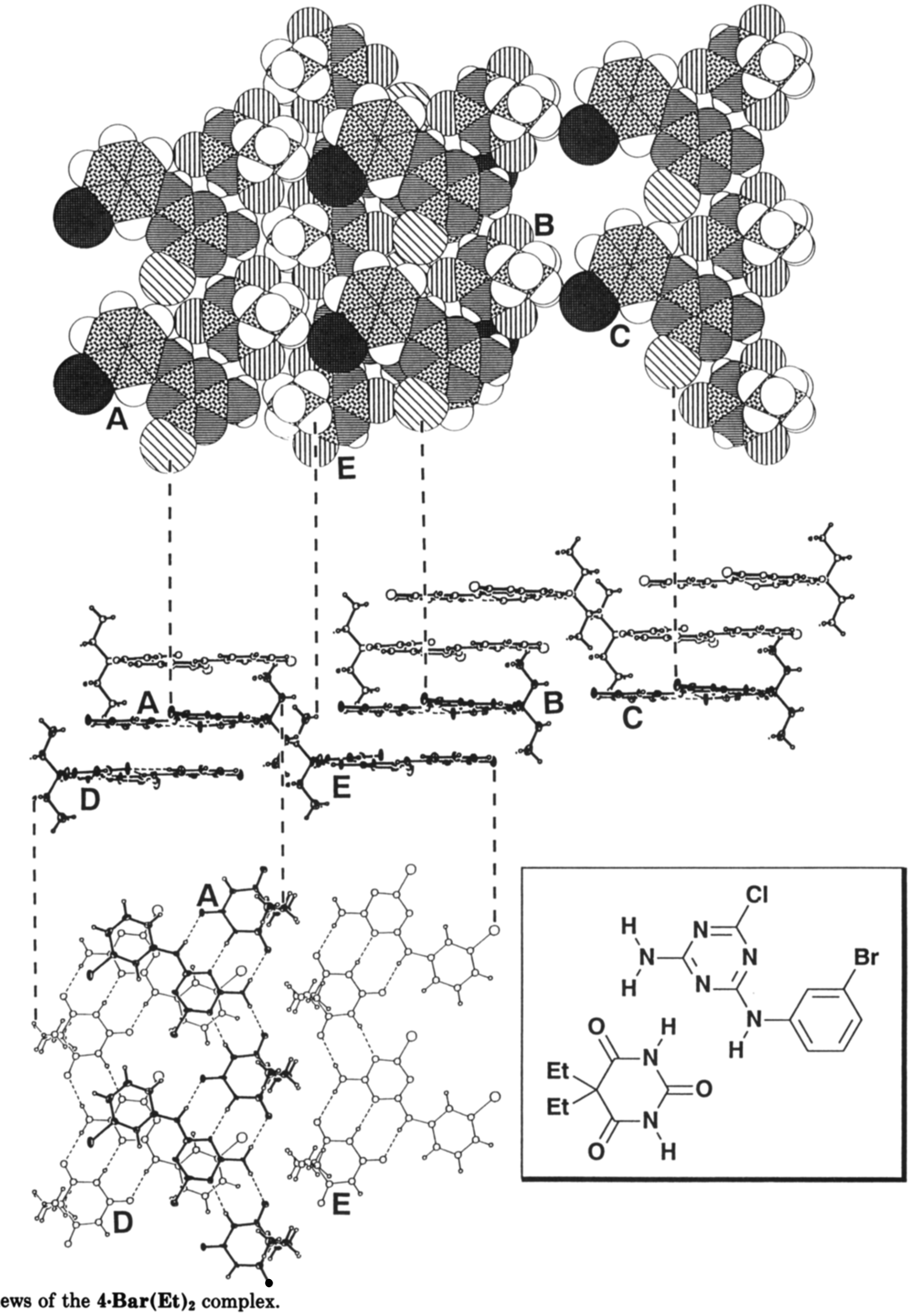

Figure 3. Views of the 4·**Bar(Et)$_2$** complex.

the introduction of I- - -CN interactions.[7,14] Instead, a different kind of packing arrangement occurred, namely, the head-to-tail dimeric orientation of tapes that we have observed in many complexes.[2,4] In this structure, an iodine- - -nitrogen interaction different from the one we expected was formed (Figure 6). This contact, which is only about 0.1 Å under the sum of van der Waals radii, is probably weak, but it may help to stabilize the perpendicular orientation of tapes.[15,16] The intended packing arrangement shown at the bottom of Figure 8 may have

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(13) Extensive hydrogen bonding in the solid state can lead to high densities in organic crystals. For example, the density of cyanuric acid is 1.82 g/cm^3 (Dietrich, H.; Scheringer, C.; Meyer, H.; Schulte, K.-W.; Schweig, A. *Acta Crystallogr.* **1979**, *B35*, 1191); oxalic acid = 1.91 g/cm^3 (Derissen, J. L.; Smit, P. H. *Acta Crystallogr.* **1974**, *B30*, 2240); oxamide = 1.67 g/cm^3 (Ayerst, E. M.; Duke, J. R. C. *Acta Crystallogr.* **1954**, *7*, 588); octahydroxycyclobutane = 1.98 g/cm^3 (Bock, C. M. *J. Am. Chem. Soc.* **1968**, *90*, 2748); squaric acid = 1.90 g/cm^3 (Semmingsen, D.; Hollander, F. J.; Koetzle, T. F. *J. Chem. Phys.* **1977**, *66*, 4405).

(14) We have previously observed an iodine-nitrile interaction in the *N,N'*-bis(*m*-iodophenyl)melamine·barbital·acetonitrile crystalline solvate.[4]

(15) Since the iodine atoms in the **Mel(*p*-I-Ph)$_2$·Bar(Et)$_2$** complex were involved in interactions among themselves, they did not engage in short contacts with nitrogen in that complex.[2]

(16) We have not searched for polymorphs of this complex (nor of any of the structures presented in this paper); other packing arrangements, perhaps even the proposed one shown in Figure 8, could of course occur for this complex.

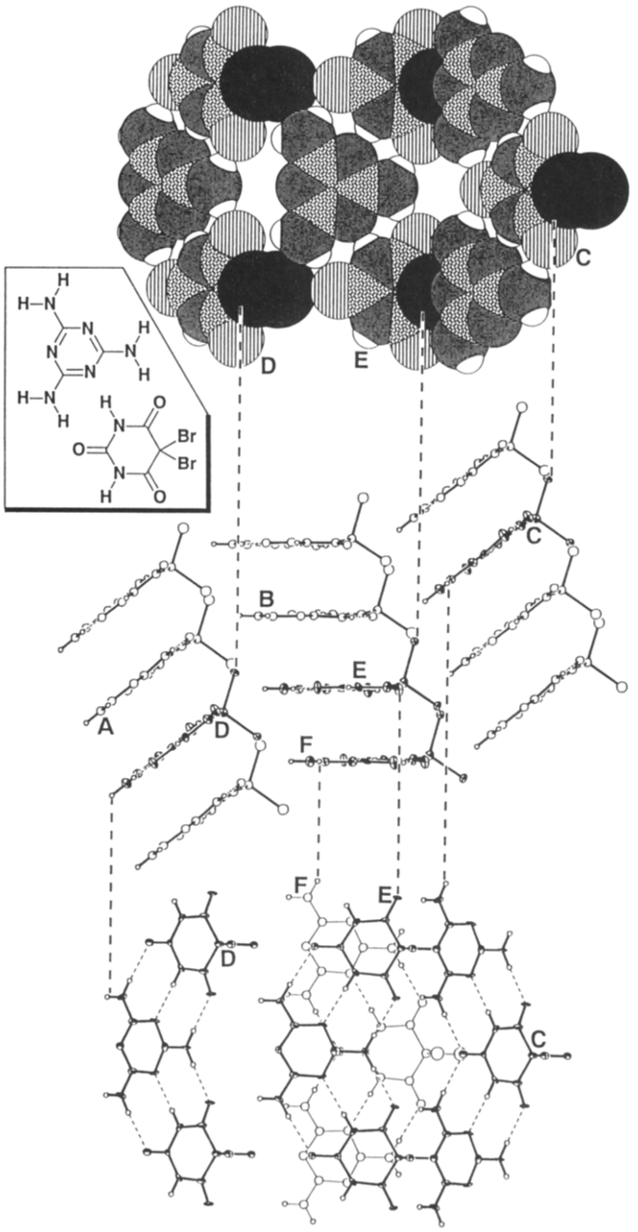

Figure 4. Views of the **Mel·Bar(Br)$_2$** complex. The extensive Br- - -N interactions have been omitted from all these views for clarity; see Figure 7 for a closeup of these interactions.

failed to form because the strong dipoles of the nitriles would have been too close to each other in an unfavorable head-to-head orientation.[17]

The difference between hypothesized and observed structures emphasizes that it is still difficult to predict solid-state structures, even when the prediction is based on a relatively modest change to a known structure.

The hypothesis motivating our study of the **Mel(Ph)$_2$·Bar(Me)$_2$** complex was that small alkyl substituents on the barbiturate component would permit close stacking of tapes. The **Mel(Ph)$_2$·Bar(Et)$_2$** complex packs as linear tapes, its tertiary architecture consisting of dimers of tapes arranged in a herringbone pattern.[2] We suspected that replacement of ethyl groups with methyl groups might alter this dimer-based packing to a sheetlike arrangement, similar to that observed in **4·Bar(Et)$_2$** (Figure 3) or **Mel·Bar(Br)$_2$** (Figure 4), where all the tape backbones in a given stack are parallel.

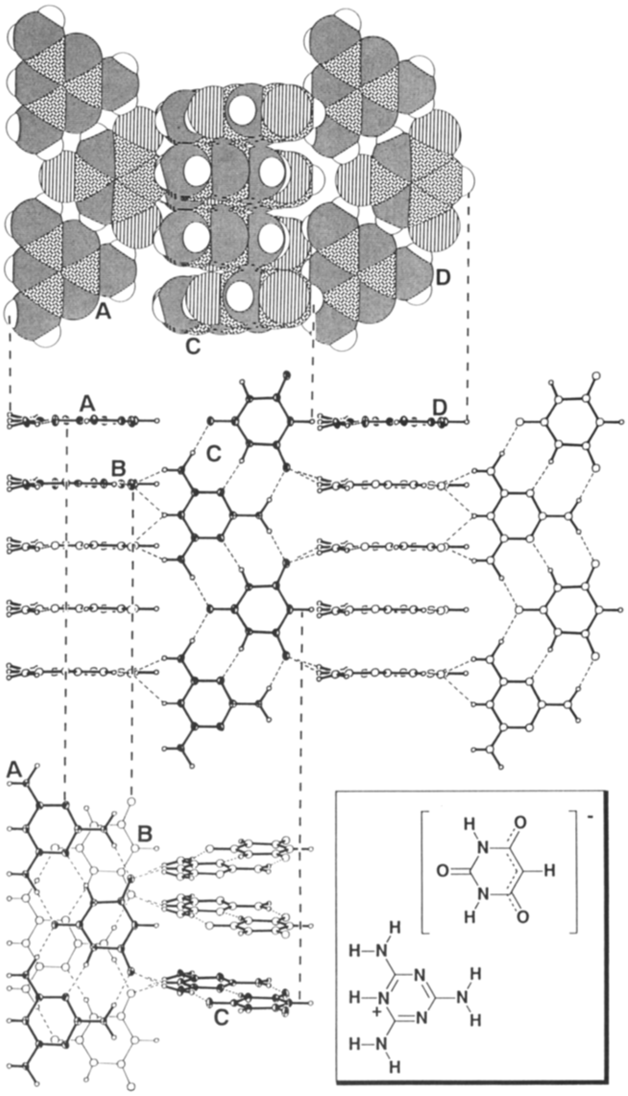

Figure 5. Views of the **MelH$^+$·BarH$^-$** complex.

While the crinkled tape that resulted does display some of the close-stacking features that small barbiturate substituents should allow, the crossover to a crinkled motif was entirely unexpected. On closer examination, however, the factors that favor adoption of a crinkled motif become clearer. One of the phenyl rings of **Mel(Ph)$_2$** is nearly coplanar to the triazine ring. It thus protrudes into the region of space that phenyl groups on a neighboring melamine in a linear tape would need to occupy. The flat, in-plane orientation of this phenyl group is favored by stacking interactions between two tapes (e.g., C and D in Figure 2) involving both the heterocyclic, hydrogen-bonded backbone rings and the aromatic substituents. The intended close stacking of tapes arising from a reduction in the ratio of alkyl to aryl surface area has therefore occurred, but maximal close packing of flat, aromatic and heterocyclic surfaces at the *tertiary* level is apparently energetically favorable enough to dictate the motif of *secondary* architecture that is adopted.

The **4·Bar(Et)$_2$** complex was investigated to see if 3-fold hydrogen bonding is essential to the construction of cocrystalline tapes between barbiturates and derivatives of triazines. Evidently, it is not. We do not know if the approach of the chlorine to the oxygen atom is energetically favorable or repulsive. If repulsive, it is apparently not strong enough to overwhelm the favorable tape-forming

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(17) Gavezzotti, A. *J. Phys. Chem.* **1990**, *94*, 4319.

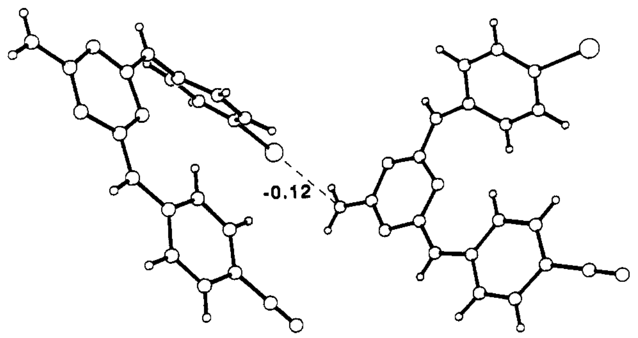

Figure 6. Closeup of the iodine-nitrogen interaction between two perpendicular melamines in **Mel(*p*-I-Ph)(*p*-CN-Ph)·Bar(Et)$_2$**. The melamine on the left belongs to tape A in Figure 1; the melamine on the right belongs to tape B. The number adjacent to the dashed line that indicates this interaction represents the value of the distance of the contact minus the sum of the van der Waals radii (in angstroms).

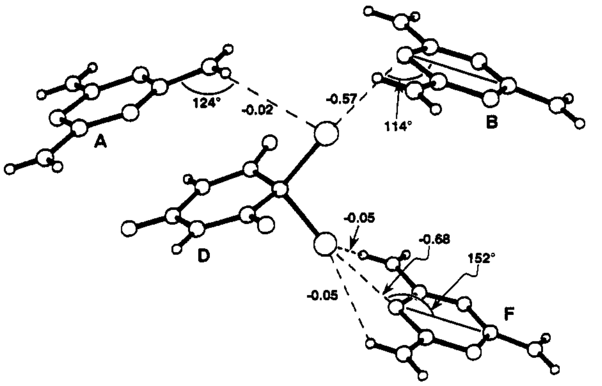

Figure 7. Closeup of the intermolecular interactions involving bromines in **Mel·Bar(Br)$_2$**. The letters indicate to which tape in Figure 4 the molecules belong. The numbers adjacent to the dashed lines that indicate these interactions represent the value of the distance of the contact minus the sum of the van der Waals radii (in angstroms). The hydrogen atoms were placed in calculated positions for crystallographic refinement, with a N–H bond length of 0.9 Å.

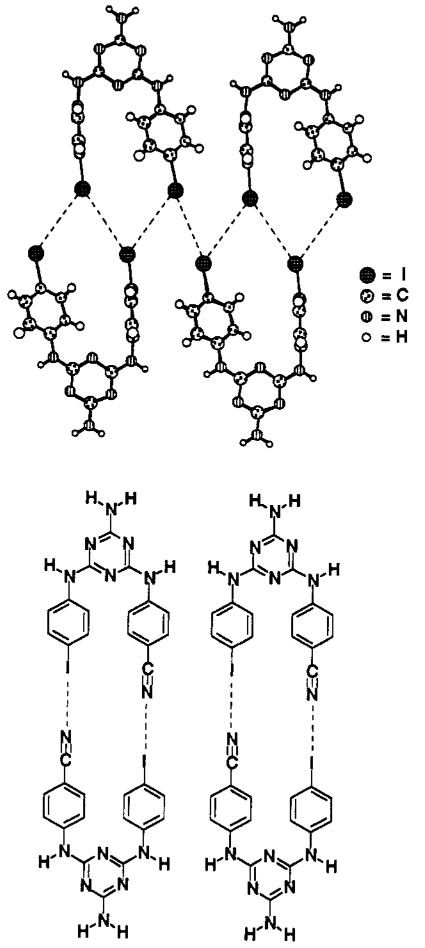

Figure 8. Back-to-back orientations of two tapes linked by noncovalent interactions between substituents in the para positions of the diphenylmelamines. At the top is the *observed* structure of the **Mel(*p*-I-Ph)$_2$·Bar(Et)$_2$** complex.[2] At the bottom is the *hypothetical* structure that we predicted (incorrectly) might result by replacing one iodine with a nitrile group. The observed structure is given in Figure 1.

hydrogen bonds.[18] In a structural sense, we have "mutated" the symmetrically substituted melamine component that we have usually employed for constructing tapes into this kind of chlorotriazine by replacing one NHR group (R = alkyl or aryl) with a chlorine atom.[19] As a result, an indentation or hole has been generated along the periphery of the linear tape (see Figure 3).[20] Note that a nearly coplanar orientation of the bromophenyl and triazine groups can be accommodated by the linear motif when the other substituent on the triazine ring is small (chlorine in 4 compared to NHPh in **Mel(Ph)$_2$**).

The key feature of both complexes incorporating melamine is that some of the hydrogen-bonding sites of the melamine remain unutilized by the formation of linear tapes. That is, one edge of the planar melamine molecule, representing a donor–acceptor–donor triad (HN–N–NH), is uncomplexed. It is therefore free to engage in intertape interactions that can direct tertiary architecture. The occurrence of several close contacts involving bromine and nitrogen atoms in the **Bar(Br)$_2$** complex (Figure 7) is due to the availability of these melamine sites for participation in electrostatic interactions.[8]

In the **MelH$^+$·BarH$^-$** complex, the uncomplexed state of one ring nitrogen of melamine permits proton transfer from the CH$_2$ group of barbituric acid. Protonation creates ionic interactions between **MelH$^+$** and **BarH$^-$** both within and between tapes, and the hydrogen-bonding network throughout the crystal is three-dimensional. To maximize the influence that these strong forces can provide and thereby minimize the lattice energy, stacks of the tapes twist with respect to each other. This crystal structure is the only one in which we have observed tapes with nonparallel axes. We hypothesize that in the absence of such strong intertape forces, the arrangement of tapes that permits the closest possible packing (reflected in a high C_k*) is one in which the hydrogen-bonded axes of all tapes are parallel.

Conclusions

The crystal structures presented in this paper demonstrate that hydrogen-bonded cocrystalline tapes are robust to a wide range of structural variations. Even variations that preclude formation of the full triad of hydrogen bonds, such as replacement of a melamine by a chlorotriazine, do

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[18] The retention of the *linear* motif cannot be ascribed to the Cl···O contact, since a crinkled tape or a rosette would also contain this contact.

[19] In a synthetic sense, the transformation is in the opposite direction: the chlorotriazine is a precursor to the melamine.

[20] Tapes of this general shape may be useful for inducing back-to-back packing of tapes through a knob-into-hole approach; a protruding substituent, perhaps appended to the para position of the phenyl ring, might dovetail efficiently into the cleft on a neighboring tape.

not disrupt the tape motif. Interactions between tapes involving bromine–nitrogen contacts, ionic forces, or hydrogen bonds can lead to close packing of tapes and to high densities. Intertape stacking interactions appear to be able to cause a switch from a linear to a crinkled motif. This phenomenon runs counter to our previous hypothesis that intratape steric effects are most likely to force adoption of a crinkled motif.[5] On the other hand, we have also noted that electrostatic interactions (e.g., CH- - -O contacts) or the packing of tapes around trapped solvent molecules may play a role in crinkling.[4] The **Mel(Ph)$_2$·Bar(Me)$_2$** complex can be viewed as combining these two effects: the immediate cause leading to crinkling is intratape (secondary) steric repulsion involving flat phenyl groups, but the underlying cause is favorable intertape (tertiary) stacking of these groups and the heterocyclic tape backbones. These initial forays into controlling tertiary architecture show that moieties that are capable of engaging in noncovalent interactions can be appended to the peripheries of tapes. Directing those interactions in a specific manner, however, remains a challenge.

Experimental Section

General Methods. *N*-(*p*-Iodophenyl)-*N'*-(*p*-cyanophenyl)melamine (**Mel(*p*-I-Ph)(*p*-CN-Ph)**), 2-amino-4-((*m*-bromophenyl)amino)-6-chloro-1,3,5-triazine (4), *N*,*N'*-diphenylmelamine (**Mel(Ph)$_2$**), and 5,5-dimethylbarbituric acid (**Bar(Me)$_2$**) were prepared according to previously published procedures.[2,4,5] The supplementary material contains spectroscopic details and elemental analyses (see paragraph at end of paper). Melamine and dibromobarbituric acid were obtained from Aldrich Chemicals, barbital from Fisher Scientific, and barbituric acid from Alfa Products. Solvents were reagent grade and were used as received without purification.

Crystallizations. Mel(*p*-I-Ph)(*p*-CN-Ph)·Bar(Et)$_2$, 4·Bar(Et)$_2$, and Mel(Ph)$_2$·Bar(Me)$_2$. These 1:1 complexes were prepared according to procedures described previously.[2,4,5] Crystals of the first two complexes were obtained by room-temperature evaporation of solutions of the complexes in ethanol and methanol, respectively, in 1-dram screw-top vials with the lids resting loosely on top of the vials. Crystals of **Mel(Ph)$_2$·Bar(Me)$_2$** were obtained by room-temperature evaporation of a solution of the complex in methanol in a glass beaker with a watchglass resting on top of the beaker.

Mel·Bar(Br)$_2$ and MelH$^+$·BarH$^-$. Solutions of melamine and the barbituric acid (both 0.1 M) were prepared in distilled H_2O and heated on a steam bath. When the temperature of the solutions was approximately 70 °C, they were combined in an Erlenmeyer flask. This flask was loosely capped and was placed in a Dewar flask that contained approximately 25 mL of water that had also been heated to about 70 °C on a steam bath. The Dewar flask was corked and allowed to rest undisturbed for at least 24 h as it cooled to room temperature. Crystals of the complex developed during this cooling period.

X-ray Crystallography. Data on the **Mel(*p*-I-Ph)(*p*-CN-Ph)·Bar(Et)$_2$** and **Mel(Ph)$_2$·Bar(Me)$_2$** complexes were collected on a Rigaku AFC5R diffractometer equipped with a rotating anode generator by Molecular Structure Corp., The Woodlands, TX. Data on the other complexes were collected on a Siemens P3 diffractometer at Harvard. All structures were solved and refined at Harvard using the SHELXTL-PLUS, SHELXS-86, and SHELXL-93 package of programs. For details of data collection, structure solution, and refinement, see the supplementary material.

Acknowledgment. We acknowledge the support of the National Science Foundation through Grants CHE-91-22331 to G.M.W. and CHE-80-00670 to the Department of Chemistry for the purchase of the Siemens X-ray diffractometer. We thank Dr. Derk Wierda for helpful discussions. J.C.M. acknowledges the Merck Corp. for partial support of this work.

Supplementary Material Available: Experimental details for **Mel(*p*-I-Ph)(*p*-CN-Ph)** and 4 and crystallographic details including tables of atomic positional parameters and bond lengths and angles (56 pages); tables of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.