Steric Control of Secondary, Solid-State Architecture in 1:1 Complexes of Melamines and Barbiturates That Crystallize as Crinkled Tapes

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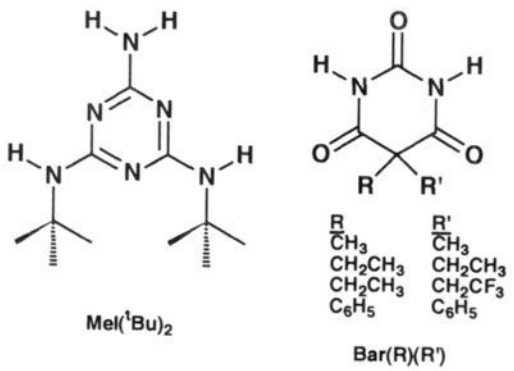
Abstract: This paper describes the single-crystal X-ray structures of four 1:1 complexes between *N*,*N*′-di(*tert*-butyl)-melamine and 5,5-disubstituted barbituric acids (substituents = CH_2CH_3, CH_2CF_3, CH_3, and C_6H_5). These complexes crystallize as infinite "crinkled" tapes having components joined by a triad of hydrogen bonds. The tapes are prevented from adopting a linear motif due to steric repulsion between *tert*-butyl groups on adjacent melamines; the crinkled motif avoids such repulsion. The tape backbones deviate from planarity to permit close packing of the crinkled tapes. Crystals of these complexes of a size and shape suitable for single-crystal X-ray diffraction analysis are readily grown; this system therefore seems well-suited for systematic study of the relationships between molecular and crystalline structure.

Introduction

We are studying the solid-state structures of 1:1 cocrystals of derivatives of melamine and of barbituric acid.[1-3] These cocrystals consist of crystallographically infinite hydrogen-bonded tapes that pack with their long axes parallel. By varying the steric properties of the substituents on the melamine component, we have prepared examples of linear tapes[3] and crinkled tapes.[2,4] We have also obtained one cyclic pseudo-C_3 structure (a "rosette").[2] These three structural motifs are the simplest ones that can be derived from the complex between cyanuric acid and melamine (CA·M).

Our previous work has kept the barbiturate component constant (as barbital, **Bar(Et)$_2$**), and varied the structure of the melamine. In the research reported in this paper, by contrast, we held the melamine component constant (as *N*,*N*′-di(*tert*-butyl)melamine, **Mel(ᵗBu)$_2$**) and varied the barbiturate. One goal of this work was to test the hypothesis that sterically hindered substituents on the melamine would yield crinkled tapes. We chose **Mel(ᵗBu)$_2$** because it is a truncated version of the melamine—*N*,*N*′-bis(4-*tert*-butylphenyl)melamine—that produced a rosette; we have rationalized the formation of the cyclic structure on the basis of the steric demands of the *tert*-butyl group.[2] We also wished simply to explore the influence of the substituents on the barbiturate on the solid-state structure: we are still surveying the range of solid-state structures accessible through manipulation of variants of CA·M, and we expect these data to complement those obtained in other studies.



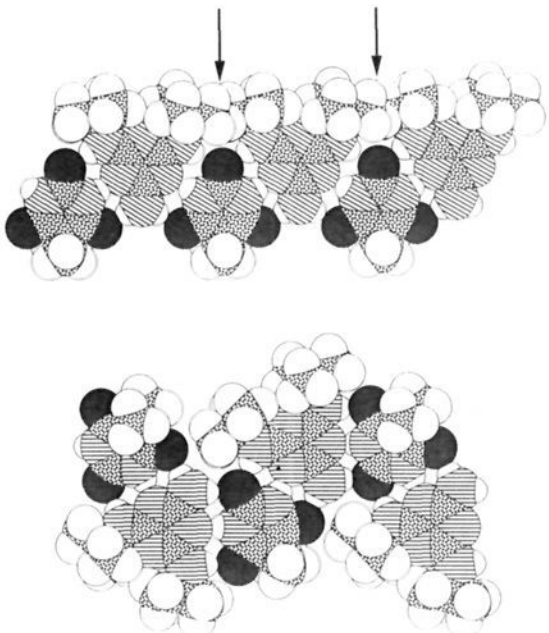


Figure 1. Top: Hypothetical linear tape of the **Mel(ᵗBu)$_2$·Bar(CH$_3$)$_2$** complex, with regions of steric repulsion indicated by arrows. Bottom: The observed crinkled format of this complex, which relieves the steric hindrance.

Results

Formation and Features of Crinkled Tapes. The bulky *tert*-butyl substituent makes formation of linear tapes impossible for steric reasons. Figure 1 (top) shows regions of steric repulsion between the *tert*-butyl groups of adjacent melamines in a hypothetical linear tape incorporating **Mel(ᵗBu)$_2$**. The bottom of the figure shows that the crinkled format avoids such steric repulsion: the *tert*-butyl groups are separated and are disposed on opposite sides of the tape.[5] One crystallographic axis (underlined in Table 1) is the repeat distance in a crinkled tape.

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(1) Zerkowski, J. A.; Seto, C. T.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 9025.

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

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

(4) Zerkowski, J. A.; Mathias, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.*, following paper in this issue.

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Table 1. Crystallographic Data for Mel(ᵗBu)₂·Bar(R)(R′) Complexes

R,R′	space group	*a* (Å)	*b* (Å)	*c* (Å)	*β*[a] (deg)	*R*[b]	C_k*[c]	*ρ*[d] (g/cm³)	solvent[e] of crystallization	deviation from planarity[f] (Å)
Et, Et	$Pna2_1$	13.634	11.708	15.739[g]		0.037	0.62	1.149	MeOH	0.54
Et, CH_2CF_3	$P2_12_12_1$	12.975	15.709	12.796		0.089	0.61	1.214	EtOH	0.78
Me, Me	$P2_1/c$	11.451	16.285	11.665	98.23	0.052	0.66	1.217	MeOH	0.29
Ph, Ph	$P2_1/c$	15.103	15.829	12.642	114.65	0.060	0.68	1.254	MeOH	0.58

[a] A blank indicates that the angle is constrained to be 90°. [b] $R = \Sigma|F_o - F_c|/\Sigma F_o$. [c] This value is the packing coefficient based on molecular volumes calculated with MacroModel (see the Results section for the definition of C_k and ref 3 for a discussion of the relationship between C_k and C_k*). [d] This value is the calculated density. [e] No solvent is included in the crystal lattice in any of these complexes. [f] This value is the average deviation of the atoms in the tape backbone from the mean plane of the backbone. [g] The underlined cell dimensions represent the repeat distance in a tape (see the Results section).

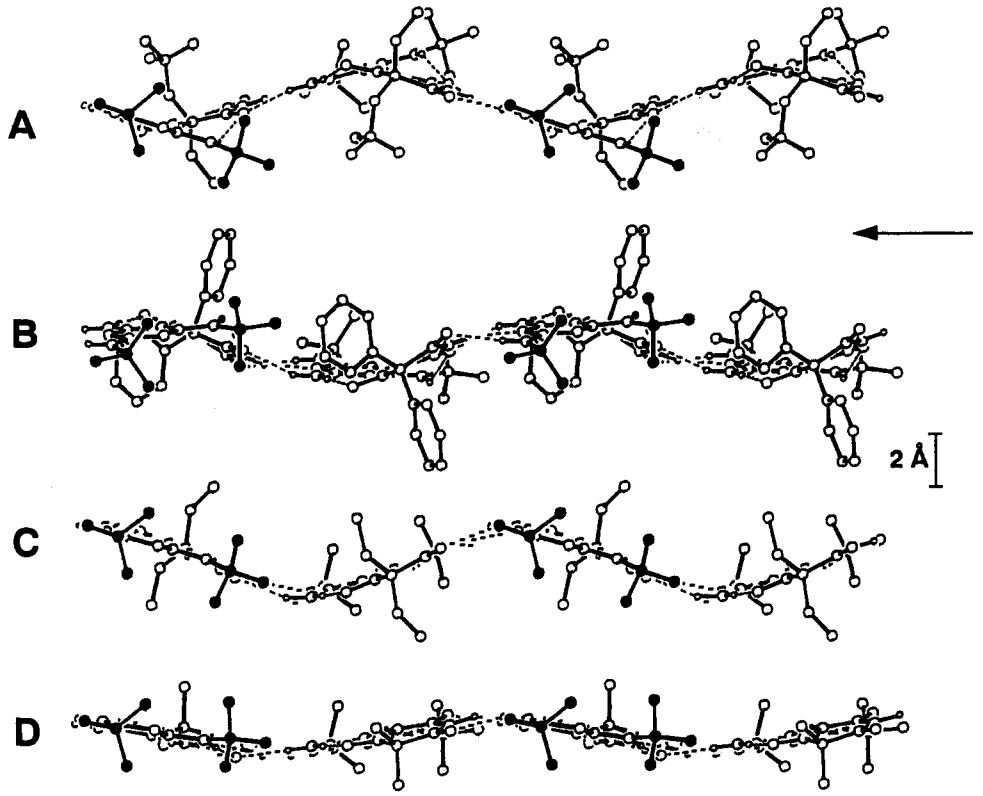

Figure 2. Side views of crinkled tapes of Mel(ᵗBu)₂ complexes showing their deviation from planarity: (A) **Bar(Et)(CH₂CF₃)** complex; (B) **Bar(Ph)₂** complex; (C) **Bar(Et)₂** complex; (D) **Bar(CH₃)₂** complex. The deviation decreases from A to D (see Table 1). The arrow indicates the direction of a view down the long tape axes. The filled-in *tert*-butyl groups are on the edges of the tapes that are nearer to the viewer.

This distance is the length of a screw-related pair of Mel·Bar dimers along the tape axis, illustrated, for example, by the distance between symmetry-equivalent filled-in *tert*-butyl groups in Figure 2. Figure 2 also shows that the crinkled tapes deviate from planarity in a direction perpendicular to the infinite hydrogen-bonded axis. This deformation, or "waviness", turns the crinkled tapes into quasi-three-dimensional structures. To a first approximation, there is a rough trend between the degree of waviness and the size of the axis underlined in Table 1. The tape with the greatest deviation from planarity (the complex with **Bar(Et)(CH₂CF₃)**) has the shortest unit projection (15.709 Å) along the tape axis.

At the macroscopic level, crystals of these crinkled tapes are blocky chunks or plates. Crystals of linear tapes, by contrast, were most frequently obtained as fine needles, a morphology that reflected the parallel packing of the linear tapes.[3] In addition, crystals of crinkled tapes were on average larger than crystals of linear tapes. A fixed-tube X-ray source, rather than a rotating anode generator, could therefore have been used for single-crystal X-ray analysis. Equally importantly, the crystals of these **Mel(ᵗBu)₂** complexes were easier to grow than crystals of complexes of *para*-substituted diphenylmelamines and barbital.[3,6]

Solid-State Structures of Complexes of Mel(ᵗBu)₂·Bar(R)(R′). To convey the important points of intermolecular orientation, we have constructed conglomerate pictures (Figures 3–6) showing several views of tape packing at once. The deviation from planarity of these crinkled tapes makes them appear "thicker" than linear tapes in an end-on view. Nonetheless, such a view (looking down the crystallographically infinite hydrogen-bonded axis) is still useful in showing the relative orientation, or the tertiary architecture, of tapes. Table 1 lists crystallographic data and some geometric parameters of tape packing.

***N,N′*-Di(*tert*-butyl)melamine/Barbital, Mel(ᵗBu)₂·Bar(Et)₂ (Figure 3).** This complex was investigated to provide a comparison to our previous work on systems that contained **Bar(Et)₂** and substituted diphenylmelamines. The only variable structural unit in these cocrystals is thus the melamine, and crinkling can be attributed to its characteristics. The backbone of this tape is wavy (Table 1 and Figures 2 and 3): the average displacement of the atoms in the tape backbone from their own mean plane is

(5) Steric repulsion was also responsible for crinkling in the complex between *N,N′*-bis(4-methoxycarbonylphenyl)melamine and barbital that we reported previously.[2]

(6) This ready crystallization is attested to by the fact that the single crystals of **Mel(ᵗBu)₂·Bar(Et)₂** and **Mel(ᵗBu)₂·Bar(Et)(CH₂CF₃)** used for diffraction were obtained from the very first crystallization attempts made on these complexes.

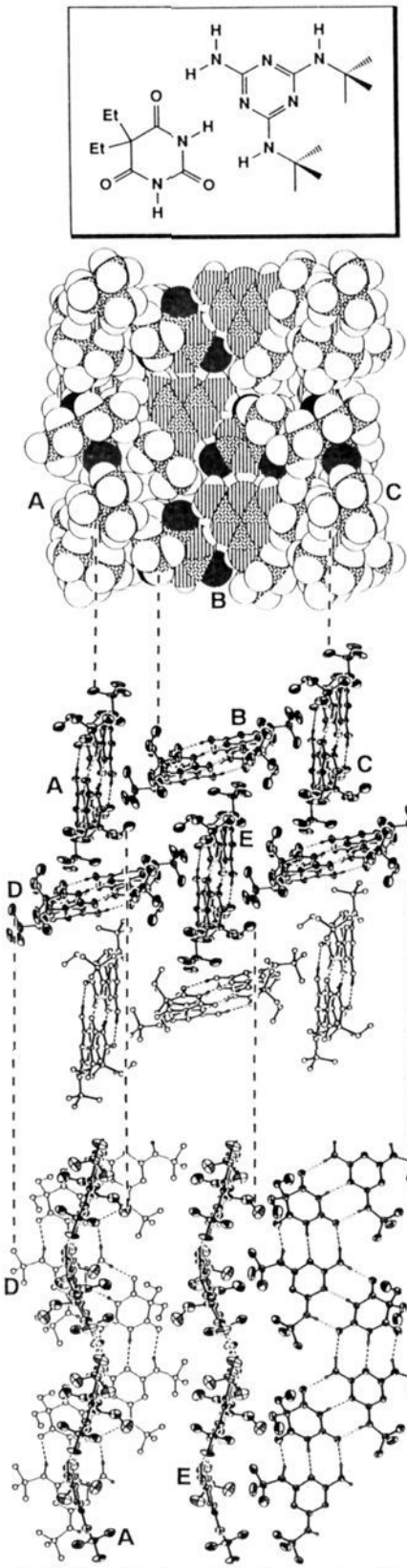

Figure 3. Views of the **Mel(^{t}Bu)$_2$·Bar(Et)$_2$** complex. Alkyl hydrogens have been omitted from the central and bottom views. In this and the following figures, tapes that appear in more than one view are drawn with thermal ellipsoids in the central, end-on view and are connected with vertical dotted lines. In the bottom view, the highlighted tapes are nearer to the viewer.

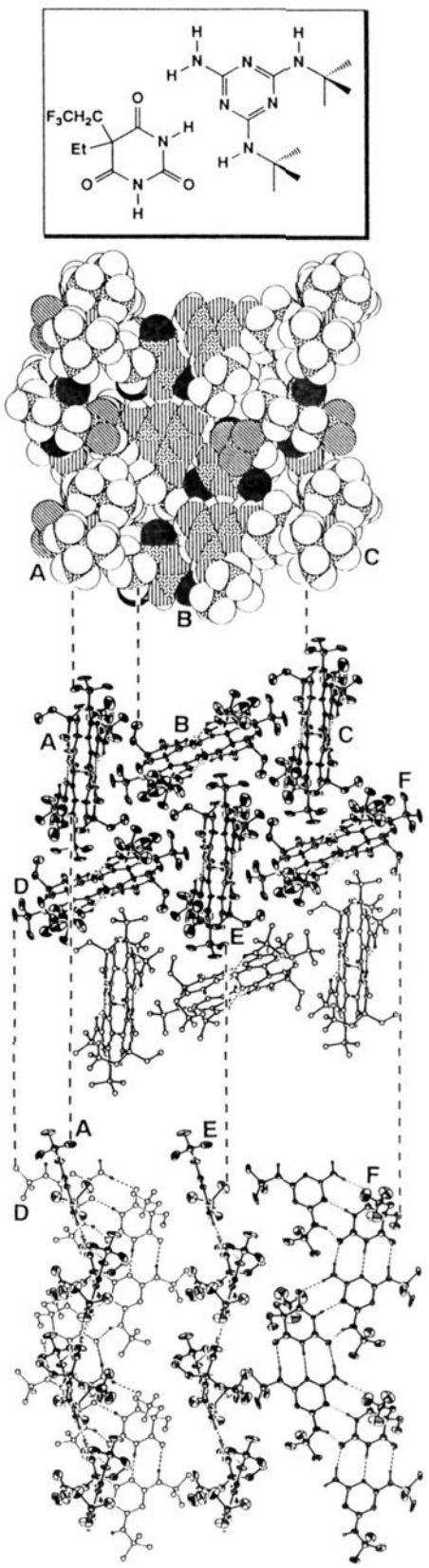

Figure 4. Views of the **Mel(^{t}Bu)$_2$·Bar(Et)(CH$_2$CF$_3$)** complex. Alkyl hydrogens have been omitted from the central and bottom views.

0.54 Å.[7] By contrast, the seven linear tapes of complexes of *para*-substituted diphenylmelamines with barbital that we reported previously are less wavy, with an average deviation from planarity of 0.13 Å.[3]

(7) We define the mean plane of a tape as the six ring atoms of each heterocycle plus the three hydrogen-bonding exocyclic heteroatoms, three nitrogens for the melamine and three oxygens for the barbiturate.

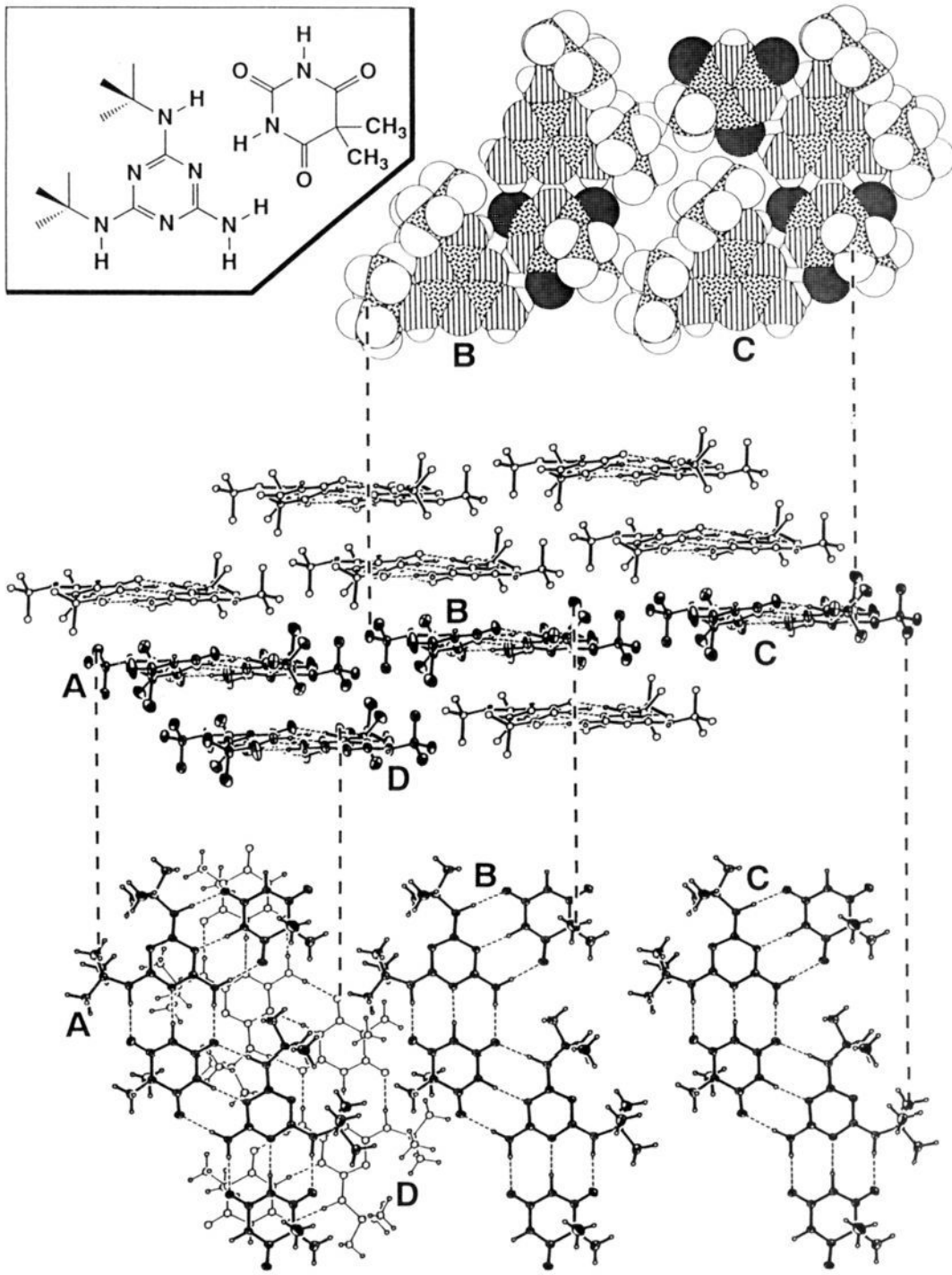

Figure 5. Views of the **Mel(^{t}Bu)$_2$·Bar(CH$_3$)$_2$** complex. Alkyl hydrogens have been omitted from the central view.

***N,N'*-Di(*tert*-butyl)melamine/5-Ethyl-5-(2,2,2-trifluoroethyl)-barbituric Acid, Mel(^{t}Bu)$_2$/Bar(Et)(CH$_2$CF$_3$) (Figure 4).** This complex represents a minimal steric perturbation on the **Bar(Et)$_2$** complex. We are also interested in studying the packing of compounds containing fluorocarbon units, to see if the fluorines segregate away from hydrocarbon regions or exhibit other patterns of behavior that might be used to control solid-state structure. The stacking of the **Mel(^{t}Bu)$_2$·Bar(Et)(CH$_2$CF$_3$)** crinkled tapes is similar to that of the **Mel(^{t}Bu)$_2$·Bar(Et)$_2$** tapes. In this solid-state structure, there are also no fluorine-rich regions and no contacts under the sums of van der Waals radii involving fluorines.

***N,N'*-Di(*tert*-butyl)melamine/5,5-Dimethylbarbituric Acid, Mel(^{t}Bu)$_2$·Bar(CH$_3$)$_2$ (Figure 5).** We investigated this complex because it is an abbreviated analogue of the **Bar(Et)$_2$** complex: that is, the size of the barbiturate substituent has been decreased. The tape backbones are less wavy than in the structures incorporating **Bar(Et)$_2$** and **Bar(Et)(CH$_2$CF$_3$)** (Table 1).

***N,N'*-Di(*tert*-butyl)melamine/5,5-Diphenylbarbituric Acid, Mel(^{t}Bu)$_2$·Bar(Ph)$_2$ (Figure 6).** In this complex, the steric perturbation of the barbiturate substituent is in the opposite direction from **Bar(CH$_3$)$_2$**: the phenyl groups are larger and more rigid than the ethyl groups. The phenyl rings are not packed in either edge-to-face or face-to-face orientations. There is, however, a CH···O contact (2.5 Å, $\Sigma_{vdW} \sim 2.7$ Å) between a barbiturate oxygen on one tape and an *o*-phenyl proton in an overlapping tape (e.g. tapes A and D in Figure 6).[8]

Packing Fractions (Table 1). The packing fraction C_k is a

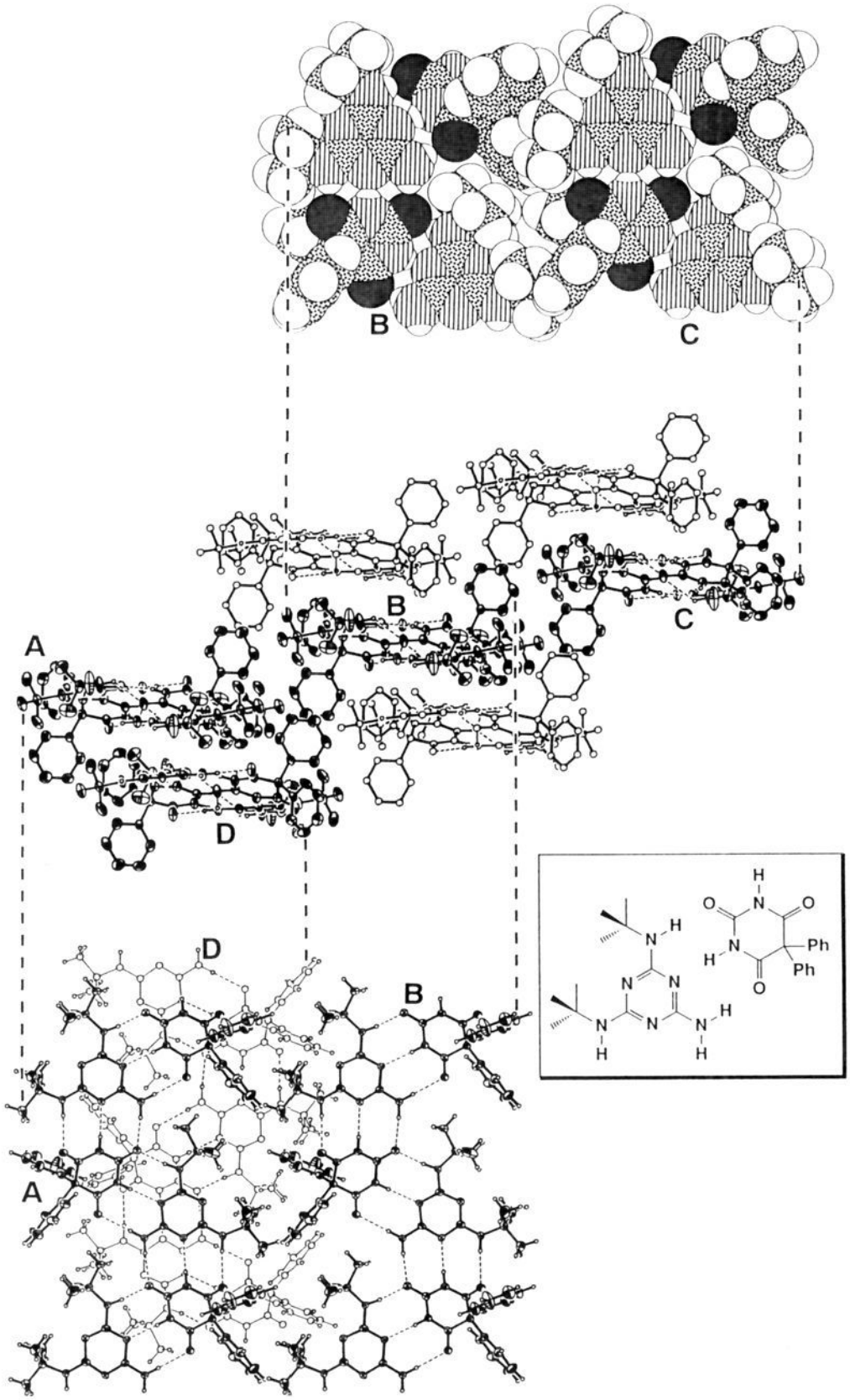

Figure 6. Views of the **Mel(ᵗBu)₂·Bar(Ph)₂** complex. Alkyl and aryl hydrogens have been omitted from the central view.

measure of the completeness with which the molecules of a crystal fill space;[9] our modified value C_k* is based on molecular volumes calculated using MacroModel.[10] The C_k* values for the two herringbone complexes, **Mel(ᵗBu)₂·Bar(Et)₂** and **Mel(ᵗBu)₂·Bar(Et)(CH₂CF₃)**, are at the lower end of the normal range.[11] Nonetheless, there are no discrete cavities large enough to allow inclusion of solvent molecules. The mean value for these four crinkled tape complexes, 0.64, is lower than that (0.69) for the

(8) We do not know if this contact is attractive or repulsive. For a discussion of CH···O contacts, see: Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.

linear tape complexes of *para*-substituted diphenylmelamines with barbital.[3]

Discussion

The results presented here confirm our hypothesis that steric hindrance involving the *tert*-butyl substituents of the melamine would force hydrogen-bonded tapes to pack in a crinkled motif rather than in a linear motif. The most important result of this work, therefore, is that the *secondary* crystalline architecture (the tape motif: *linear*, *crinkled*, or *cyclic*) of complexes of melamines and barbiturates can be predicted and controlled using steric effects. We have not yet searched for polymorphism in these complexes, but we do believe that **Mel(ᵗBu)$_2$** will reliably yield crinkled tapes.

At the level of tertiary architecture (the stacking of tapes in the crystal), we propose that the deviation of crinkled tapes from planarity to produce a wavy shape (Figure 2) occurs to maximize packing efficiency. This observation is consistent with the broad guideline that, in crystals in general, intermolecular contact of van der Waals surfaces tends toward a maximum.[9,11] In these crystals of crinkled tapes, regions of space that would otherwise be voids are filled by the deformation of the hydrogen-bonded backbone of tapes from planarity. The views at the bottoms of Figures 3 and 4 illustrate this increased packing efficiency for the two complexes (those with **Bar(Et)$_2$** and **Bar(Et)(CH$_2$CF$_3$)**) that adopt the herringbone pattern. Two adjacent, perpendicular tapes fit together compactly, by matching the crinkling of one and the waviness of the other. Figure 7 presents a closeup view of these relationships.

In wavy tapes, the hydrogen bonds are bent from linearity. For the N–H···O bonds, the angles at hydrogen are 167°, 145°, 175°, and 157°, and for the N–H···N bonds, the angles are 174° and 173°. The hydrogen atoms involved in these hydrogen bonds were located crystallographically from electron density maps. Bent hydrogen bonds are frequently observed in crystal structures and do not appear to be energetically unfavorable (although there must be a level of deformation beyond which the tapes would not hold together).[12,13]

Conclusions

The four crystal structures of complexes of **Mel(ᵗBu)$_2$** with barbiturates show that the triad of hydrogen bonds that holds together crystallographically infinite tapes is robust to substitutions that cause unfavorable intratape steric interactions. The formation of crinkled tapes can be rationalized using steric arguments: bulky substituents on the melamines (here, *tert*-butyl groups) prevent adoption of a linear format and force tapes to crinkle. In terms of designing organic solids, we expect to be able to use this effect to obtain crystals built from the crinkled structural motif. In fact, the ease of crystallization of these crinkled tapes recommends their use in systematic physical–organic studies of the solid state. Another result instructive for future work is that tapes are tolerant of different classes of substituents (alkyl and aryl groups) on both melamine and barbiturate components. Systematic variation on either component is a valid approach to crystal engineering.

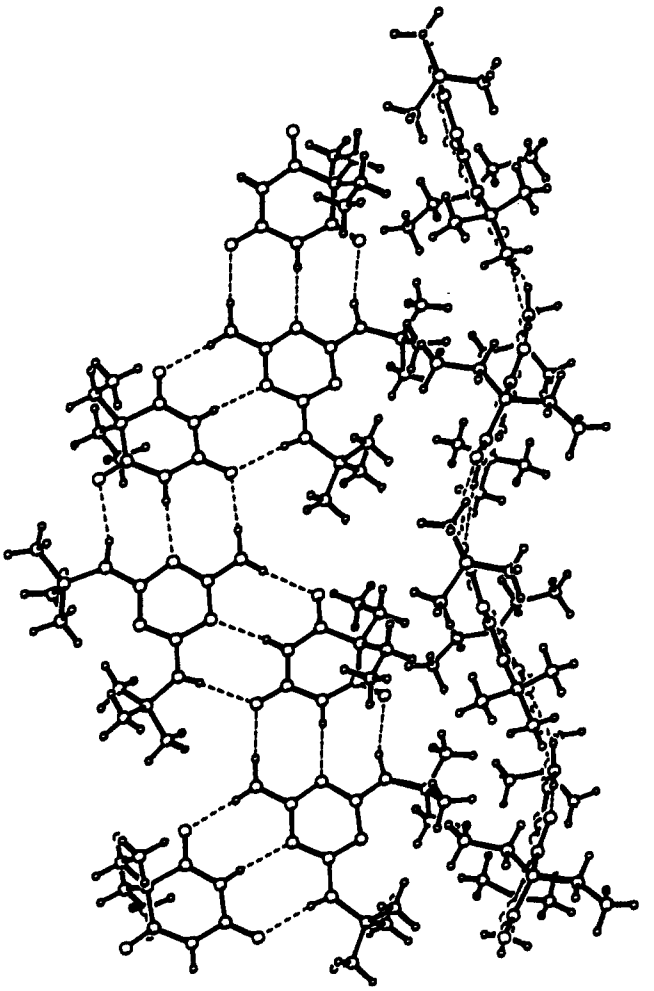

Figure 7. View of two adjacent, roughly perpendicular tapes of **Mel(ᵗBu)$_2$·Bar(Et)$_2$** showing the steric complementarity of their fit. The tape on the right is viewed from the side; the tape on the left is tilted approximately 25° out of the plane of the page (see Figure 3). The deviations from planarity of the tape viewed perpendicularly to the mean plane of its hydrogen bond network (right) clearly are complementary to the protuberances and indentations of the quasiperpendicular tape (left).

While we still have no clear rationalization of intertape packing, we note that it is possible to relate the waviness of a tape—that is, the deviation of its hydrogen-bonded backbone from planarity—to the minimization of voids (and the maximization of the packing fraction, C_k) in the crystal. Crinkled tapes appear to deviate from planarity in order to pack as closely as possible to neighboring tapes. Since our system of tapes appears to be robust enough to tolerate a range of substitutional modifications, we believe that experiments designed to examine the consequences of steric perturbations on packing can be performed in a controlled and consistent fashion.

This system provides another model with which to study the physical–organic chemistry of the solid state. It should provide a consistent molecular framework—parallel, crinkled tapes—with which to probe relations between molecular and crystalline structure.

Experimental Section

General. *tert*-Butylamine was obtained from Aldrich Chemicals. Both 5,5-dimethylbarbituric acid[14] and 5,5-diphenylbarbituric acid[15] were prepared by literature procedures. General techniques were as previously published.[3]

(9) $C_k = N \cdot V_{mol}/V_{cell}$, 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.

(10) See ref 3 for a discussion of the relationship of C_k* to C_k.

(11) 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.

(12) Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320.

(13) Gas-phase studies have shown that linear hydrogen bonds are the most stable (Legon, A. C.; Miller, D. J. *Acc. Chem. Res.* **1987**, *20*, 39). Crystals, however, need to balance a number of intermolecular forces, and hydrogen bonds seem to be able to deform to some extent to permit close packing between other parts of molecules.[11,12]

(14) (a) *Organic Syntheses*; Blatt, A. H., Ed.; Wiley and Sons: New York, 1943; Collect. Vol. II, p 60. (b) Thorne, J. T. *J. Chem. Soc.* **1881**, *39*, 543.

(15) McElvain, S. M. *J. Am. Chem. Soc.* **1935**, *57*, 1303.

2-Amino-4,6-bis(*tert*-butylamino)-1,3,5-triazine (Mel(^{t}Bu)$_2$). A solution of cyanuric chloride (2.0 g, 10.8 mmol) was prepared in 100 mL of freshly distilled THF in a round-bottomed flask and cooled in an ice-water bath. A solution of *tert*-butylamine (1.14 mL, 10.8 mmol) and diisopropylethylamine (1.88 mL, 10.8 mmol) in 20 mL of THF was added from a dropping funnel over the course of 15 min with magnetic stirring. When addition was complete, the ice-water bath was removed and stirring was continued for another hour. The mixture was heated to reflux in an oil bath and another equivalent each of *tert*-butylamine and diisopropylethylamine (in 20 mL of THF) was added. Since the boiling point of *tert*-butylamine is 46 °C, some of this compound was lost to the atmosphere, even with a water-cooled condenser affixed to the reaction flask. Over the course of another 3 h, additional portions of a *tert*-butylamine solution in THF were added to the reaction, amounting to an additional 0.4 equiv. This amount was sufficient to produce primarily one product (2-chloro-4,6-bis(*tert*-butylamino)-1,3,5-triazine) as determined by TLC. The reaction was cooled to room temperature, and solvent was removed by rotary evaporation at aspirator pressure. The residue was slurried in 100 mL of diethyl ether and solids were removed by filtration at aspirator pressure through a short plug of silica gel, which was then washed with more diethyl ether (3 × 30 mL). The ether solutions were combined, and solvent was removed by rotary evaporation at aspirator pressure.

The 2-chloro-4,6-bis(*tert*-butylamino)-1,3,5-triazine was placed in a 15-mL pressure bottle along with a magnetic stirring bar, approximately 8 mL of 2:1 1,4-dioxane/H_2O, and 3 mL of 30% NH_4OH. The pressure bottle was capped and heated in an oil bath to 100–105 °C (**CAUTION: behind a safety shield**). Heating was continued for 5 h, after which the pressure bottle was cooled to room temperature and opened. TLC indicated that some starting material remained, but the most intense spot was the product di(*tert*-butyl)melamine. The reaction mixture was poured into 150 mL of H_2O and stirred well. The precipitated product was collected by vacuum filtration, washed with H_2O (2 × 25 mL), and dried on a vacuum line at 0.1 Torr for several hours. It was then purified by chromatography on silica gel with ethyl acetate as eluant (R_f = 0.3). The product, after rotary evaporation of solvent, was a white solid (1.57 g, 61%): melting point 166–7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.85 (br s, 2 H), 4.5 (br s, 2 H), 1.4 (s, 18 H); HRMS-EI (M^+) calcd for $C_{11}H_{22}N_6$ 238.1906, found 238.1913.

5-Ethyl-5-(2,2,2-trifluoroethyl)barbituric acid. The precursor 2,2,2-trifluoroethyl trifluoromethanesulfonate was prepared by a literature procedure from 2,2,2-trifluoroethanol, $(CF_3SO_2)_2O$, and pyridine in $CFCl_3$.[16] A solution of this trifluoromethanesulfonate (2.46 g, 10.6 mmol) in 10 mL of freshly distilled diethyl ether was added over the course of 30 min from a dropping funnel to a refluxing solution of diethyl malonate (1.52 mL, 10 mmol) and NaH (80% by weight, 0.30 g, 10 mmol) in 100 mL of EtOH. Reflux was continued for 3 h, at which point an aliquot was removed, concentrated by rotary evaporation at aspirator pressure, and dried on a vacuum line at 0.1 Torr. The desired diethyl 2,2,2-trifluoroethylmalonate had been formed, as determined by ^{1}H NMR spectroscopy and comparison to literature chemical shifts.[17] Refluxing was continued for another 2 h, after which ethyl iodide (1.2 mL, 15 mmol) and powdered anhydrous K_2CO_3 (1.66 g, 12 mmol) were added to the mixture. Reflux was continued for 3 days. The reaction mixture was cooled to room temperature and solids were removed by filtration at aspirator pressure. Solvent and excess ethyl iodide were removed from the filtrate by rotary evaporation at aspirator pressure. The resulting colorless oil was judged by ^{1}H NMR spectroscopy to be sufficiently pure diethyl ethyl(2,2,2-trifluoroethyl)malonate to proceed to the next step.

A solution of the malonate (1.5 g, 5.6 mmol) in 20 mL of dry EtOH was added in one portion to a gently refluxing homogeneous solution of urea (0.53 g, 8.8 mmol) and sodium (0.37 g, 16 mmol) in 100 mL of dry EtOH in a round-bottomed flask in an oil bath. The temperature of the bath was increased to 105 °C, and reflux was continued overnight. The reaction was then cooled to room temperature and solvent was removed by rotary evaporation at aspirator pressure. The yellow residue thus obtained was dissolved in 50 mL of H_2O and washed with Et_2O (3 × 50 mL). The aqueous layer was neutralized by dropwise addition of concentrated HCl. The resulting white precipitate was collected by vacuum filtration at aspirator pressure and was recrystallized from hot water, giving 0.73 g (55%) of the barbituric acid. Chemical shifts of the ^{1}H NMR spectrum (300 MHz, acetone-d_6) agreed with literature values.[17]

Preparation of Complexes. Equimolar amounts of **Mel(^{t}Bu)$_2$** and the barbiturate were dissolved together (in one flask) in THF. The solvent was removed by rotary evaporation at aspirator pressure, and the composition of the complex was checked by ^{1}H NMR spectroscopy. If integration of peaks indicated that one component was present in excess, the other component was added to bring their ratio to 1:1. The melting points of the complexes were the following: **Mel(^{t}Bu)$_2$·Bar(Et)$_2$**, 236–8 °C; **Mel(^{t}Bu)$_2$·Bar(Et)(CH$_2$CF$_3$)**, 245–7 °C; **Mel(^{t}Bu)$_2$·Bar(CH$_3$)$_2$**, 248–50 °C; **Mel(^{t}Bu)$_2$·Bar(Ph)$_2$**, 264–6 °C dec.

Crystallization of Complexes. Mel(^{t}Bu)$_2$·Bar(Et)$_2$ and **Mel(^{t}Bu)$_2$·Bar(Ph)$_2$**: Crystals were grown by room-temperature evaporation of a solution of the complex in MeOH in a 5-mL screw-top vial with the lid resting loosely on top of the vial.

Mel(^{t}Bu)$_2$·Bar(Et)(CH$_2$CF$_3$) and **Mel(^{t}Bu)$_2$·Bar(CH$_3$)$_2$**: Crystals were grown by allowing a solution of the complex in boiling EtOH or MeOH, respectively, to cool to room temperature by enclosing a round-bottomed flask containing the solution in a corked Dewar flask. The Dewar flask was allowed to rest undisturbed for 24 h before opening it to check on the progress of crystal growth.

X-ray Crystallography. For details of X-ray data collection, structure solution, and refinement, see the supplementary material. Data were collected on **Mel(^{t}Bu)$_2$·Bar(CH$_3$)$_2$**, **Mel(^{t}Bu)$_2$·Bar(Et)(CH$_2$CF$_3$)**, and **Mel(^{t}Bu)$_2$·Bar(Ph)$_2$** by Molecular Structure Corp., The Woodlands, TX, on a Rigaku AFC5R diffractometer equipped with a rotating anode generator. These structures were solved and refined at Harvard using the Siemens SHELXTL-PLUS package of programs. Data collection, structure solution, and refinement for **Mel(^{t}Bu)$_2$·Bar(Et)$_2$** were performed by Crystalytics Co., Lincoln, NE.

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Supplementary Material Available: Crystallographic details including tables of atomic positional parameters and bond lengths and angles (65 pages); tables of observed and calculated structure factors (44 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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