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Design of Organic Structures in the Solid State: Hydrogen-Bonded Molecular "Tapes"¹

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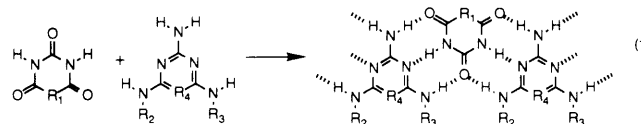
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We have begun a program whose objective is to develop methods to predict the packing of organic molecules in crystalline and noncrystalline solids, starting from the atomic structures of these molecules.² The ability to relate molecular and crystalline structure for organic solids will clarify the interactions that underlie molecular recognition and self-assembly, simplify the preparation of optically or electronically active organic solids, and help to rationalize the macroscopic properties of organic materials in terms of microscopic, molecular structures.

One problem that has frustrated efforts to relate molecular and crystalline structures is the very large number of orientations the molecules can, in principle, adopt: calculating relative energies of all possible packing structures is currently impractical. To limit the scope of the problem, we wish to constrain the possible orientations of the molecules in the solid state. We are developing systems in which strong, directional hydrogen bonds provide the required constraint.

Using the network proposed for melamine/cyanuric acid as a model,^{3,4} we are examining the structures of 1:1 cocrystals of derivatives of melamine (M) and barbituric acid (B), functionalized in patterns that break up the sheet structure but permit

the formation of hydrogen bonds that yield "tapes" (eq 1). Tapes are likely to pack with their axes parallel. This enforced parallelism will, we believe, significantly simplify the computational analysis of these solid-state structures.



Here we summarize evidence that this strategy is successful in generating a family of closely related solid-state structures and that these structures can be classified according to a hierarchy of elementary structural features (Figure 1). The two components, M and B, form tapes with an alternating sequence, ...M·B·M·B...; the tapes pack into sheets with their long axes parallel; the sheets stack and form three-dimensional solids. Table I summarizes crystallographic data for the structures we have examined; complete data will follow in a full paper. We believe that this system has sufficient simplicity to be the object of a systematic study of the influence of molecular structure on crystal structure.

(1) Supported by the National Science Foundation, Grant CHE-88-12709 to G.M.W. and Grant DMR-89-20490 to the Harvard University Materials Research Laboratory.

(2) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: New York, 1989. Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. Hagler, A. T.; Dauber, P. *Acc. Chem. Res.* **1980**, *13*, 105.

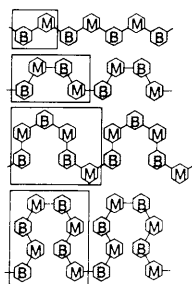
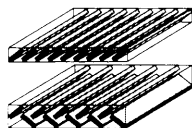
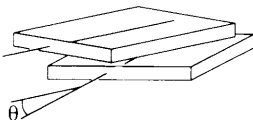
(3) Seto, C.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *112*, 6409.

(4) We have not yet been able to obtain diffraction-quality single crystals from cocrystallizations of derivatives of melamine and cyanuric acid.

Table I. Summary of Structures of Cocrystals of Derivatives of Barbituric Acid and Melamine (Eq 1, $R_4 = N$)

R_1	$R_2 = R_3$	T	S	θ , deg	data ^a	temp. ^b °C	space group	R factor, %	goodness of fit
CEt ₂	C ₆ H ₅	1	2	0	a	-80	<i>Pnma</i>	6.5	1.21
	<i>p</i> -ClC ₆ H ₄	1	2	0	b	23	$P\bar{1}$	9.9	1.44
	<i>p</i> -BrC ₆ H ₄	1	1	0	b	23	$P\bar{1}$	7.2	1.91
	<i>p</i> -IC ₆ H ₄	1	1	0	b	23	$P2_1/n$	4.5	1.39
	<i>p</i> -MeC ₆ H ₄	1	1	0	a	-10	$P2_1/n$	10.3 ^c	1.50
	<i>m</i> -MeC ₆ H ₄	1	1	0	b	23	$P\bar{1}$	5.5	1.54
	<i>tert</i> -butyl	2	2	0	d	20	<i>Pna</i> 2 ₁	3.7	1.19
	<i>m</i> -ClC ₆ H ₄	2	1	0	a	0	<i>C2/c</i>	4.9	0.80
C(CH ₂ C ₆ H ₄ - <i>p</i> -Br) ₂	1-naphthyl	1	2	0	c	23	$P2_1/n$	6.8	2.09
	<i>p</i> -MeOC ₆ H ₄	1	2	0	c	-120	$P2_1/n$	8.6	2.39
CBr ₂	H	1	1	0	a	0	<i>Ccm</i> 2 ₁	4.0	1.05
CH ₂		1	1	90	a	-10	<i>Ccc</i> 2	4.1	2.79

^aData code: a = data collected and structure solved by us; b = data collected by Molecular Structure Corporation (MSC) and solved by us; c = the complete structure determination was performed by MSC; d = the complete structure determination was performed by Crystallitics, Inc. ^bAll temperatures correct to ± 1 °C. ^cFurther refinement is in progress.

TapesI
1
2
3
4**Sheets**S
1
2**Solid**

theta

Figure 1. Classification of features characterizing solid-state structures of 1:1 cocrystals of derivatives of melamine (M) and barbituric acid (B). T = the number of B-M units that constitute a translational repeat unit along a tape (boxed); S = the number of tapes that constitute a translational repeat unit in a sheet. This figure shows representative examples of possible geometries, not an exhaustive list.

We offer two general observations concerning these structures. First, all follow some variant on the motif: tape; sheet; solid. Second, although 1:1 compound formation seems to be general, this system is not yet ideally convenient for studying the physical-organic chemistry of the solid state, because the crystals that grow are often too small for single-crystal X-ray structure determination. Figure 2 shows one representative structure.⁵ Most (10 of 12) of the tapes follow the simple motif shown in this structure ($T = 1$), although we have observed two "crinkled" tapes ($T = 2$). We have not encountered structures in which $T = 3$ or 4.

Others have described hydrogen-bonded chains in the solid state.⁶⁻⁹ In particular, Leiserowitz and co-workers⁷ have examined

(5) Crystal data for *N,N'*-diphenylmelamine/5,5-diethylbarbituric acid: (C₁₅H₁₄N₆)(C₈H₁₂N₂O₃); $a = 12.940$ (3) Å, $b = 9.982$ (5) Å, $c = 17.377$ (3) Å, $V = 2245$ (1) Å³, D_{calc} = 1.37 g/cm³, $Z = 4$ (four M-B pairs).

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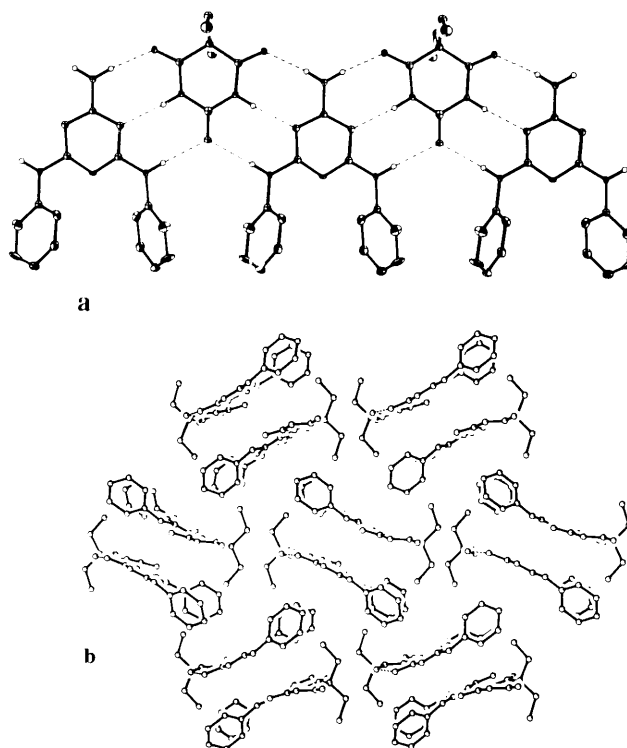


Figure 2. Plots of the packing patterns of *N,N'*-diphenylmelamine/5,5-diethylbarbituric acid complex. (a) Individual tape, ORTEP plot along the [001] direction showing 30% ellipsoids. Non-hydrogen-bonding hydrogen atoms have been omitted for clarity. (b) End-on packing view down the long tape axis, [010] direction. All hydrogen atoms have been omitted for clarity.

patterns in amides in detail. While many of these structures consisted of hydrogen-bonded tapes, a variety of other structural motifs were also identified. Shimizu⁸ and Lehn⁹ have studied structures related to those reported here. We believe that the 1:1 compounds based on the barbituric acid/melamine structure offer predictable stoichiometry and simplicity in packing, while still affording (through variation in R_{1-4}) ample opportunity to vary details of tape-tape and sheet-sheet interactions.

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Supplementary Material Available: Brief synthetic outline, details of X-ray data collection, tables of crystal data and atomic positional parameters and an ORTEP drawing for *N,N'*-diphenylmelamine/5,5-diethylbarbituric acid, and table of lattice parameters for all structures (9 pages). Ordering information is given on any current masthead page.