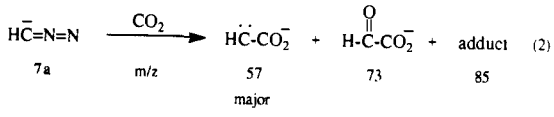
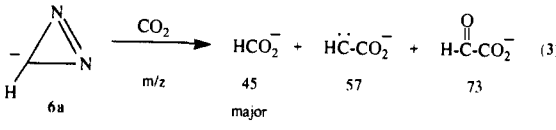
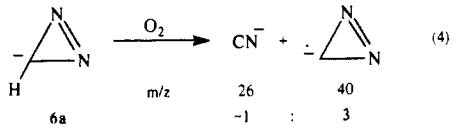
orbital calculations,[13] we conclude that the product is indeed the diazirinyl anion (**6a**).

Consistent with this assignment is the observation that **6a** exchanges one hydrogen for deuterium upon reaction with ND_3. Likewise one might expect the diazirinyl anion to react similarly to the diazomethyl anion, and this is the case with CO_2 (eqs 2 and 3).[10] Both ions lead to the formation of a carbene (m/z 57)

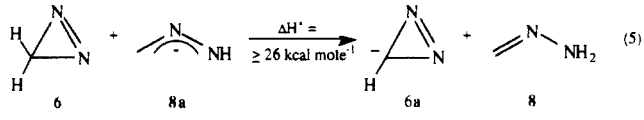




and a glyoxylate ion (m/z 73), but the latter also leads to the formation of a small amount of an adduct (15%)[10] while the former gives rise to a formal hydride ion transfer product (~80%). Given the greater basicity of the diazirinyl anion, one might also expect it to be more reactive than **7a**. Indeed, the diazomethyl anion is inert to O_2, whereas **6a** undergoes a rapid reaction affording two product ions (eq 4). The structure of the m/z 40 ion (P − 2, $CN_2^{\bullet-}$) is intriguing. Three possibilities, cyclic, C–N–N, and N–C–N, exist, and an independent preparation of the two acyclic ions via the reaction of $O^{\bullet-}$ with cyanamide and diazomethane has enabled us to conclude that the reaction product is cyclic. This assignment is based on the different reactivities of the P − 2 ions and indicates that the C–H bond in **6a** is quite weak (≤49 kcal mol^{-1}).[14]



Having established the structure of the diazirinyl anion, we are in a position to address the question of its stability. In this regard, it is of interest to compare **6a** to its acyclic analogue (**8a**, eq 5). The reaction enthalpy is the difference in acidity between **6** and **8**. The latter quantity has not been measured, but the proton affinity of 3-methyl-1-azaallyl anion, 375 ± 3 kcal mol^{-1},[15] can be taken as an upper limit. The acyclic ion is clearly the more stable isomer. This is consistent with the notion of antiaromaticity, but can also be accounted for by the charge repulsion in a constrained allylic system.[16]



Recently Zhou and Parr[17] described the use of relative and absolute hardness in determining the stability and reactivity of cyclic conjugated systems. Their model predicts that the diazirinyl anion should be nonaromatic.[18] This is consistent with more detailed ab initio molecular orbital calculations[13] and suggests that **6a** will be a viable species in solution. Investigations to test this hypothesis are currently underway and will be reported in due course.

(14) We thank one of the referees for pointing this out to us. The bond dissociation energy of O_2-H (49 kcal mol^{-1}) is taken from ref 9.

(15) Dahlke, G. D.; Kass, S. R., unpublished results.

(16) Streitwieser et al. have shown that as the central bond angle of an allylic anion is reduced, the energy rapidly increases. Boerth, D. W.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 750.

(17) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371.

(18) Absolute hardness (η) is given by $\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2$, where the dividing line between aromatic ($\eta > -0.25\beta$) and antiaromatic ($\eta < -0.15\beta$) compounds is about -0.2β. For the diazirinyl anion, $\eta = -0.21\beta$ (HOMO α -0.46β; LUMO α -0.89β).

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

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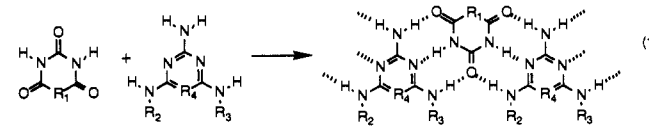
We have begun a program whose objective is to develop methods to predict the packing of organic molecules in crystalline and noncrystalline solids, starting from the atomic structures of these molecules.[2] The ability to relate molecular and crystalline structure for organic solids will clarify the 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.

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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_6H_5	1	2	0	a	−80	*Pnma*	6.5	1.21
	p-ClC_6H_4	1	2	0	b	23	$P\bar{1}$	9.9	1.44
	p-BrC_6H_4	1	1	0	b	23	$P\bar{1}$	7.2	1.91
	p-IC_6H_4	1	1	0	b	23	$P2_1/n$	4.5	1.39
	p-MeC_6H_4	1	1	0	a	−10	$P2_1/n$	10.3[c]	1.50
	m-MeC_6H_4	1	1	0	b	23	$P\bar{1}$	5.5	1.54
	tert-butyl	2	2	0	d	20	$Pna2_1$	3.7	1.19
	m-ClC_6H_4	2	1	0	a	0	$C2/c$	4.9	0.80
$C(CH_2C_6H_4$-*p*-$Br)_2$	1-naphthyl	1	2	0	c	23	$P2_1/n$	6.8	2.09
	p-$MeOC_6H_4$	1	2	0	c	−120	$P2_1/n$	8.6	2.39
CBr_2	H	1	1	0	a	0	$Ccm2_1$	4.0	1.05
CH_2		1	1	90	a	−10	$Ccc2$	4.1	2.79

[a] Data 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 Crystalytics, Inc. [b] All temperatures correct to ±1 °C. [c] Further refinement is in progress.

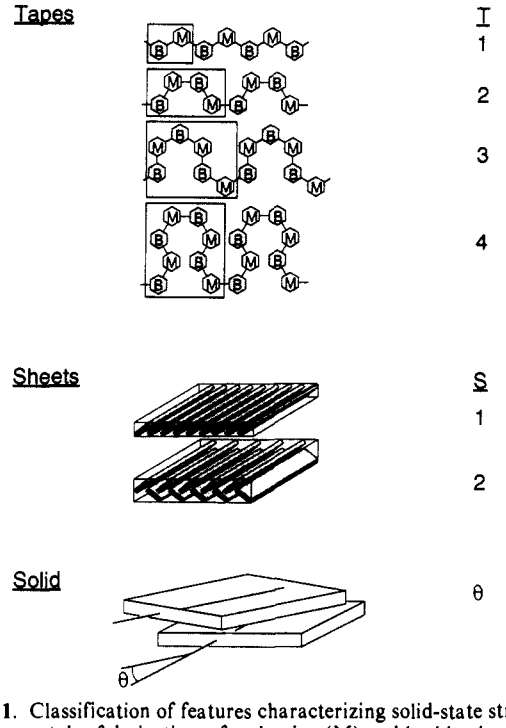

Figure 1. Classification of features characterizing solid-state structures of 1:1 cocrystals of derivatives of melamine (M) and barbituric acid (B). T = the number of B·M units that constitute a translational repeat unit along a tape (boxed); S = the number of tapes that constitute a translational repeat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

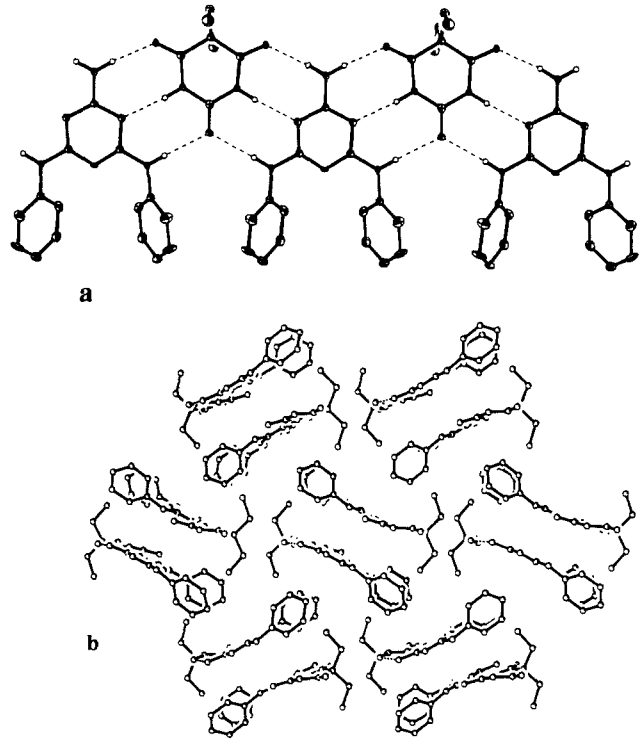

Figure 2. Plots of the packing patterns of *N,N'*-diphenylmelamine/5,5-diethylbarbituric acid complex. (a) Individual tape, ORTEP plot along the [001] direction showing 30% ellipsoids. Non-hydrogen-bonding hydrogen atoms have been omitted for clarity. (b) End-on packing view down the long tape axes,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

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-workers[7] have examined patterns in amides in detail. While many of these structures consisted of hydrogen-bonded tapes, a variety of other structural motifs were also identified. Shimizu[8] and Lehn[9] 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.

Acknowledgment. We acknowledge the support of the National Science Foundation through Grant CHE 80-00670 for the purchase of the Siemens X-ray diffractometer.

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.

(5) Crystal data for *N,N'*-diphenylmelamine/5,5-diethylbarbituric acid: $(C_{15}H_{14}N_6)(C_8H_{12}N_2O_3)$; a = 12.940 (3) Å, b = 9.982 (5) Å, c = 17.377 (3) Å, V = 2245 (1) Å^3, D_{calcd} = 1.37 g/cm^3, Z = 4 (four M·B pairs).

(6) O'Brien, E. J. *J. Mol. Biol.* **1966**, *22*, 377. Voet, D. *J. Am. Chem. Soc.* **1972**, *94*, 8213.
(7) Leiserowitz, L.; Hagler, A. T. *Proc. R. Soc. London* **1983**, *A388*, 133.
(8) Shimizu, N.; Nishigaki, S.; Osaki, K. *Acta Crystallogr.* **1982**, *B38*, 2309.
(9) Lehn, J.-M.; Mascal, M.; DeCian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1990**, 479.