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The Dark Side of Crystal Engineering: Creating Glasses from Small Symmetric Molecules that Form Multiple Hydrogen Bonds

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Amorphous molecular materials (molecular glasses) are a prime source of isotropic thin films for use in optoelectronic devices.[2,3] At present, molecular glasses are most commonly derived from polymers, but compounds of low molecular weight can also exist in amorphous forms with high glass transition temperatures ($T_g >$ 25 °C).[2,3] Because such glasses are derived from small molecules, they offer the advantage of working with materials of precise mass, well-defined composition, high purity, and good processability. However, materials made from small molecules tend to reach thermodynamic equilibrium quickly, thereby converting amorphous forms into ordered crystalline phases. Few low-molecular-weight glasses can forestall this process indefinitely, especially at temperatures above T_g.

Regrettably, there are few reliable guidelines for identifying new small molecules that will form long-lived glasses. Current efforts to design such glasses are based on relatively crude principles, such as inhibiting crystallization by incorporating long alkyl chains and bulky substituents, lowering symmetry, avoiding planarity, increasing molecular size, selecting awkward globular shapes, reducing intermolecular cohesion, and favoring multiple conformations.[4] Recent research in crystal engineering has provided deeper understanding of how molecular crystals can be created by design, thereby raising the possibility of using this understanding not to favor crystallization but to thwart it. For example, crystal engineers have established that hydrogen bonding provides strong directional cohesion that can favor crystallization according to established patterns; at the same time, however, hydrogen bonding creates an opportunity to inhibit crystallization (1) by inducing molecules to aggregate unproductively in ways that preclude effective packing and disfavor crystallization, and (2) by slowing diffusion and reorientation in the amorphous state. At present, high-temperature long-lived glasses made from small molecules that engage in hydrogen bonding are rare, and the role of hydrogen bonding in these materials is not clear.[5] In this paper, we report the results of an initial exploration of the "dark side" of crystal engineering, in which structural features and directional interactions that normally favor crystallization are subverted to work against it.

In exploring the supramolecular chemistry of biguanides and aminotriazines,[6,7] we noted that both 1,5-bis(3,5-dimethylphenyl)-biguanide (**1** = 1,5-dimexylbiguanide)[6,8] and methyl 4,6-bis-(mexylamino)-1,3,5-triazine-2-carboxylate (**2a**)[7] form glasses with high T_g (37 and 75 °C, respectively), as measured by modulated differential scanning calorimetry (mDSC).[9] These glasses result even when melts are cooled slowly, and they do not show a propensity to crystallize, despite the small size of the molecules, their high symmetry, their low degree of flexibility, and their conspicuous ability to form hydrogen bonds.[10] To identify the structural elements that underlie this surprising behavior, we examined the properties of aminotriazine **2a** and related compounds in detail.
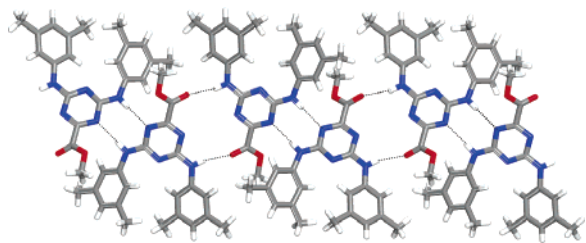
Neither simple bis(phenylamino)triazine **3a**[7] nor its methyl-substituted derivatives **3b–d**[7] formed glasses when melted and
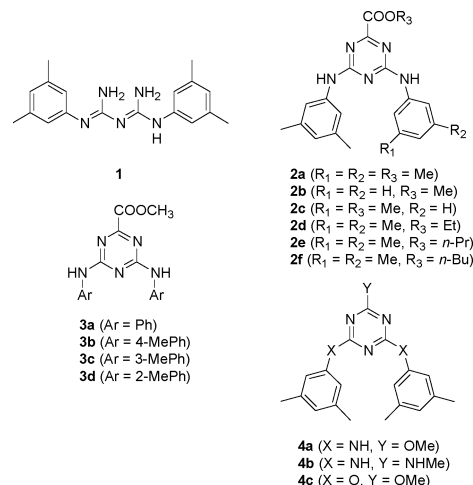

cooled under similar conditions, so the mexyl group appears to play a crucial role in inhibiting crystallization. Monomexyl derivatives **2b,c**, prepared from mexyldicyandiamide by standard methods,[6,7,11] yielded glasses with T_g = 51 and 38 °C, respectively, establishing that a single mexyl group suffices to block crystallization. Not surprisingly, the lower symmetry of derivatives **2b,c** leads to lower values of T_g. Esters **2d–f**, prepared from dimexyl compound **2a** by transesterification,[11] also yielded glasses, and their values of T_g (62, 58, and 54 °C, respectively) decreased as expected as the length of the alkyl chain increased.

In addition, we examined the behavior of derivatives **4a,b**, in which the carbomethoxy group of bis(mexylamino)triazine **2a** has been replaced by other substituents of similar size. Compounds **4a,b**, which were prepared from cyanuric chloride by classic methods,[11,12] both formed glasses (T_g = 54 and 94 °C, respectively). In sharp contrast, very close analogue **4c**, which cannot self-associate by hydrogen bonding, did not produce a glass under similar conditions. Together, these observations suggest that the mexyl group and hydrogen bonding are both essential and act in concert to forestall crystallization, even though strong directional association in small, symmetric, and relatively inflexible molecules normally promotes crystallization.

To probe this unusual behavior, we crystallized bis(mexylamino)-triazine **2a** from CHCl$_3$ and solved its structure by X-ray crystallography. The crystals were found to belong to the monoclinic space group $C2/c$ and to correspond to an inclusion compound of composition **2a**·1CHCl$_3$·xH$_2$O.[13] Approximately 39% of the volume of the crystals is accessible to guests, as measured by standard methods.[14] We suggest that the failure of compound **2a** to yield a normal close-packed structure without included guests helps provide the free volume typically associated with molecular glasses.[2,3] Moreover, it is a sign that structural features in compound **2a** may make efficient crystallization inherently difficult. Like related diarylbiguanides and bis(arylamino)triazines,[6,7] compound **2a** crys-

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Figure 1. View of the structure of crystals of methyl 4,6-bis(mexylamino)-1,3,5-triazine-2-carboxylate (**2a**) grown from CHCl$_3$. The view shows how molecules of compound **2a** adopt an amphiphilic conformation and form hydrogen bonds with two neighbors to define tapes that lie along the *ac* diagonal. Hydrogen bonds are represented by dotted lines. Carbon atoms are shown in gray, hydrogen atoms in white, nitrogen atoms in blue, and oxygen atoms in red.
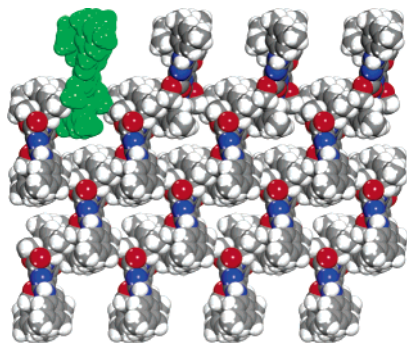
Figure 2. View along the *ac* diagonal showing a truncated 2 × 4 × 1 array of unit cells in the structure of bis(mexylamino)triazine **2a**. The view shows how the characteristic hydrogen-bonded tapes that lie along the *ac* diagonal (Figure 1) are packed along the *b* axis. For clarification, the cross section of one tape is depicted in green, and guest molecules are omitted. Carbon atoms are shown in gray, hydrogen atoms in white, nitrogen atoms in blue, and oxygen atoms in red.

tallizes in an amphiphilic conformation with a lipophilic aryl region and a polar triazinecarboxylate headgroup that forms multiple hydrogen bonds (Figure 1). Association of the headgroups creates tapes with figure-8-shaped cross sections, which then pack with interdigitation of the aryl groups (Figure 2). Related bilayered structures are a common feature of diarylbiguanides and bis-(arylamino)triazines.[6,7] In the case of compound **2a**, however, the mexyl groups can be seen to interfere by preventing efficient packing. In particular, no aromatic interactions are present, and the closest distance between the centers of aromatic rings is 4.84(1) Å.

FT-IR spectra of solutions of bis(mexylamino)triazine **2a** (CH$_2$-Cl$_2$) showed an N–H stretch at 3403 cm^{-1}, which shifted to 3346 cm^{-1} in the glassy state and to 3359 cm^{-1} in crystals, thereby confirming that compound **2a** forms hydrogen-bonded aggregates in the glass. This aggregation does not appear to involve the carbonyl group, which gives rise to similar bands in solution (1747 cm^{-1}) and in the glassy state (1751 cm^{-1}), whereas stretching occurs at 1738 cm^{-1} in crystals. We conclude that hydrogen bonding plays

a crucial role in thwarting crystallization, presumably by causing aminotriazine units to self-associate and to form aggregates with reduced mobility and particular structural features that cannot readily be accommodated in closely packed periodic structures.

Our observations are noteworthy because they demonstrate that long-lived glasses can be made from families of small molecules with properties that normally promote rapid crystallization, including high symmetry, low flexibility, and strong intermolecular cohesion. New molecular glasses can be produced in a rational way by turning to the "dark side" of crystal engineering and making small but carefully selected structural modifications specifically designed to thwart established patterns of crystallization.

Supporting Information Available: Experimental procedures for making compounds **2b**–**f** and **4a**–**c** and characterization of these compounds; representative mDSC traces, additional crystallographic details, and FT-IR spectra for compound **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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