

Host–Guest Mesomorphism: Cooperative Stabilization of a Bowlic Columnar Phase

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It is not generally observed that combinations of two nonmesomorphic substances yield a stable thermotropic liquid crystalline state or that the addition of a guest dramatically transforms a liquid crystal's superstructure. Exceptions are those systems in which a high aspect ratio mesogen is generated by assembly of complementary fragments through hydrogen bonding,¹ systems which incorporate charge-transfer interactions,² and mesophases organized by ion-mediated associations.³ In addition, it has recently been demonstrated that packing disorder in mixtures of homologous compounds can produce stable mesomorphism.⁴ There is growing interest in multicomponent mesomorphic substances based upon molecular recognition and complementary associations since this approach provides a new dimension of diversity for the tailoring of a material's properties. We demonstrate herein how specific host–guest associations can be used to stabilize a bowlic⁵ hexagonal columnar phase (B_h). This new receptor-based liquid crystalline system has the novel feature that only a fractional amount of guest is required to produce persistent mesomorphism.

We have previously reported bowlic liquid crystals based upon calix[4]arene structures in which complexation with a tungsten–oxo group produces a rigid cone conformation.^{5h} In those studies we concluded that a cone conformation is critical to the formation of a columnar bowlic phase and that the molecules organize with a head-to-tail arrangement.⁶ We also found the uncomplexed conformationally flexible calix[4]arene, **1** to display an unusual transient mesophase which is only observed in the first heating. In our continuing studies, we investigated this behavior with X-ray diffraction (XRD), which suggested that the transient phase is a B_h phase ($[100] = 26.35 \text{ \AA}$). Further heating of **1** to $163 \text{ }^\circ\text{C}$ produces an isotropic phase, and subsequent cooling yields a nonbirefringent solid material. XRD of the solid phase indicates that it has isotropic and ordered components. The ordered phase can be indexed to a cubic lattice⁷ $a = 77.6 \text{ \AA}$ ($[200] = 38.8 \text{ \AA}$, $[220] = 28.2 \text{ \AA}$, $[311] = 23.1 \text{ \AA}$), which is consistent with the lack of birefringence. To account for this behavior, we propose that the initial crystal phase (formed by recrystallization from MeOH/THF) organizes **1** in a bowl conformation. Melting this crystal phase allows the bowlic-like molecules to organize into a B_h phase with a

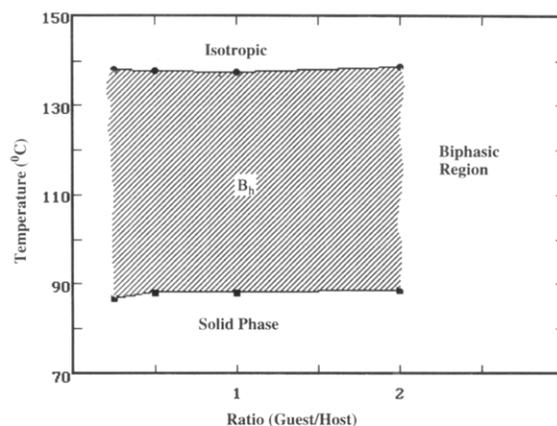
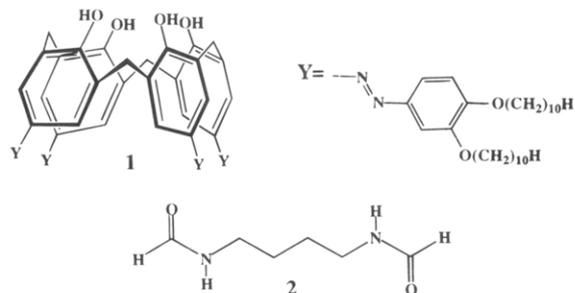


Figure 1. Phase diagram indicating the region of stability of the B_h phase as a function of temperature and the ratio of **1** to **2**. The transition temperatures were measured on the second heating cycle after samples had been heated into their isotropic phases.

head-to-tail order and with favorable dipole interactions. In **1**'s isotropic phase, a mixture of conformations^{8,9} and hydrogen-bonding aggregations is produced, which prevents a return to the B_h phase (Scheme 1).

During our investigations of **1**, we sometimes observed small birefringent liquid crystalline regions which appeared upon cooling the isotropic phase. We also found that **1** only displayed this behavior when it was slightly impure, suggesting that specific impurities (guests) may stabilize this mesophase. Conformationally flexible bowlic phases are of interest for the formation of novel ferroelectric materials,¹⁰ and as a result we endeavored to develop an appropriate guest to stabilize this mesophase. On the basis of our previous studies^{5h} we considered that the guest should be chosen to enforce a cone conformation and to break up head-to-head associations which may result from intermolecular hydrogen bonding. This criterion suggested formamides as likely candidates due to their high affinity for the calix[4]arene cavity, which will promote a cone conformation,¹¹ and their hydrogen-bonding ability, which should interfere with intermolecular H-bonds.



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Initial experiments with simple formamides (e.g., DMF, *N*-n-butylformamide) showed no induction of mesomorphism, indicating that greater care in the design of the guest is required. Recognizing the bifunctional requirements of the guest, we investigated **2** as a guest which has two formamides linked by a flexible butyl spacer. Our results indicate that **2** is especially effective for the formation of a host–guest mesophase with **1**. Contact preparations, subsequent to heating **1** into its isotropic

(8) Calix[4]arenes can adopt different conformations. For general reviews, see: (a) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, 1989. (b) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J., Klewer, V. B., Eds.; Academic Publishers: Dordrecht, 1991.

(9) ¹H NMR indicates that **1** is conformationally dynamic in solution.

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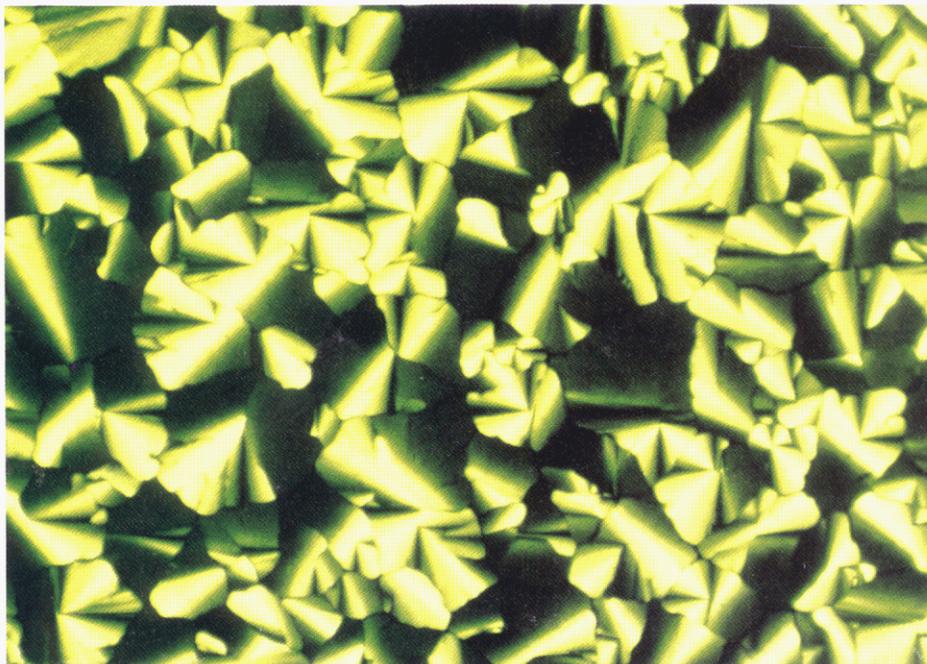
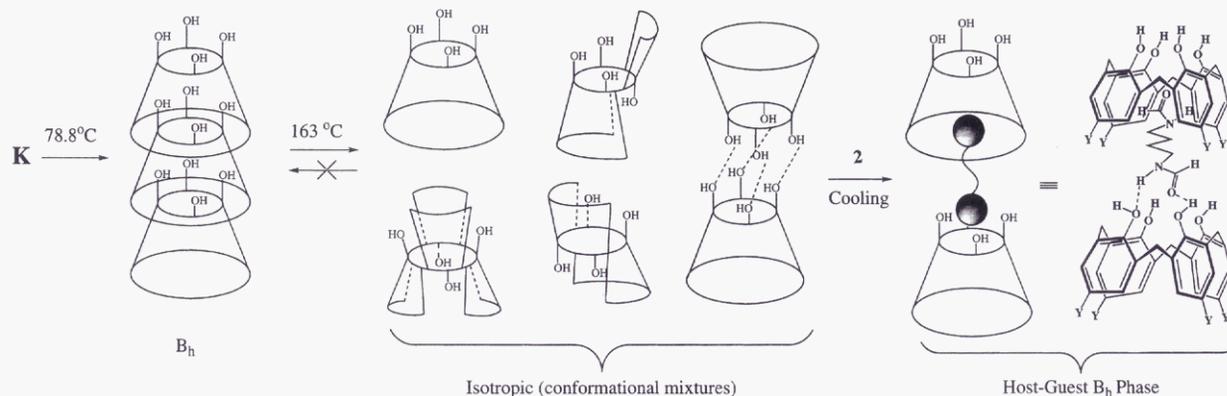


Figure 2. Optical texture of host-guest B_h phase (ratio of **1** to **2** is 2:1) viewed with a polarizing microscope at 103 °C.

Scheme 1. Schematic Representation of **1**'s Phase Behavior with and without **2** (See Text for Details)



phase, showed formation of a mesophase at the interface with **2**. We propose that the function of **2** is as shown in Scheme 1, where one amide binds in the cavity and enforces the cone conformation while the other forms hydrogen bonds with the nearest neighbor, thereby inducing head-to-tail organizations.

The host-guest mesophase displayed high fluidity and thermodynamic stability over a 40 °C range (Figure 1). The clearing enthalpies are small and ranged from 0.89 to 0.25 J/g for guest:host ratios of 0.25 and 1.0, respectively, thereby indicating a disordered phase with short (liquid-like) correlations between molecules. The pure diformamide **2** melts at 90.4 °C ($\Delta H = 45.1$ kcal/mol), and this transition was absent over compositions with guest:host ratios less than 2.0. When more than 2 equiv of **2** was present, biphasic behavior was observed, and the additional melting transition was observed upon heating. The structure of the host-guest liquid crystal phase was determined with an optical microscope, and the optical texture displays both linear birefringent defects and regions of uniform extinction (Figure 2), which indicates a B_h phase.

Striking aspects of this host-guest mesomorphism are that only a small amount of **2** is required to stabilize the B_h phase and that the stability is independent of the host:guest ratio. The former indicates that forcing only a fraction of the molecules into cone conformations and head-to-tail linkages is necessary for mesophase stabilization. As a result, the guest-induced transition to the mesophase is cooperative in nature. The latter suggests, on the basis of thermodynamic considerations, that the phase diagram in Figure 1 may be oversimplified. This

issue has prompted us to perform XRD studies, and consistent with the optical textures we observe the B_h phase ($[100] = 41$ Å) throughout the range indicated in Figure 1. At a guest:host ratio of 2.0 the B_h phase is the only phase; however, at ratios of 1.0 and 0.25 numerous low-intensity peaks are observed between 2.5° and 4.5° (2θ , Cu $K\alpha$), indicating that small amounts of additional unidentifiable phases are present.¹²

In summary, we have demonstrated how host-guest principles can be used to stabilize a B_h phase of a conformationally flexible calix[4]arene. This new and potentially general approach to mesomorphic materials offers greater versatility than single-component systems. For example, noncentrosymmetric (ferroelectric) phases may be obtained by incorporation of chiral guests with achiral hosts. Furthermore, systems which display large organizational changes with only fractional amounts of a guest may find applications in sensory or memory devices. In these cases, perturbations by specific guests may produce large changes in a material's physical properties (i.e., birefringence, optical absorbance, dielectric constant, etc.). Our future investigations will be directed at realizing these novel opportunities afforded by host-guest mesomorphism.

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(12) More than one mesophase can coexist in multiple-component mesomorphic systems. Since each conformation of **1** is an additional component, a number of phases may coexist.