

Liquid Crystalline Calixarenes^{*}

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Abstract. Bowl-shaped (bowl-like) liquid crystals are reviewed and new bowl-like materials containing rigid tungsten-oxo calix[4]arene based cores are discussed. Tungsten-oxo calix[4]arenes with 8 and 12 dodecyloxy sidechains have been investigated and exhibit bowl-like columnar phases which are stable over approximately a 200° temperature range. The uncomplexed tetra-phenol ligands display only a transient liquid crystallinity on the first heating, and the conformational rigidity provided through tungsten-oxo complexation is necessary for well behaved mesomorphism. For the 8 sidechain analog the clearing point is at 320°C and the addition of four more sidechains results in a lower clearing point at 267°C. Polarized optical microscopy and DSC indicate that the 12 sidechain analog displays a phase with the columns packed in a hexagonal lattice which is conducive to the formation of polar phases. Both complexes exhibit a pronounced tendency to bind Lewis base guests in their cavities, and DMF forms very strong complexes which were spectroscopically characterized. The DMF guest produces large effects on the phase behavior by suppressing mesomorphism and lowering the isotropic points by 115°C and 84°C for the 8 and 12 sidechain compounds respectively. This extreme sensitivity to the DMF guest is conclusive proof that bowl-like tungsten-oxo calix[4]arene liquid crystals organize in head-to-tail structures.

Key words: Mesomorphism, calixarenes, bowl-like liquid crystals, nonlinear optics, ferroelectricity

1. Introduction

Much of the interest in calix[4]arenes has arisen from their ability to form bowl (cone) shapes. Bowl-shaped compounds have been key materials in the development of the field of molecular recognition since they exhibit cavities with high degrees of preorganization necessary for strong binding of guest molecules. The majority of the research in this vast effort has been fueled by those wishing to mimic catalysis and signaling processes in nature. As a result, less attention has been given to the application of these types of compounds in the design of new materials. Nevertheless there is growing interest in the integration of host-guest design principles to create novel materials [1]. While this area of research is still young, it is clear that bowl-shaped compounds present unique opportunities in the design of novel new materials. Notable studies include the demonstration that incorporating nonlinear optical (NLO) chromophores into calix[4]arenes can produce materials with greater transparency without loss of hyperpolarizability [2]. Hence calix[4]arenes offer an approach to a long-standing goal of the NLO com-

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munity. Another notable example is the use of calix[6]arenes for the formation of porous materials for separation technologies [3]. The focus of this article will be on the use of calixarene-based liquid crystals for the formation of bowl-shaped (bowllic) liquid crystals [4].

2. Liquid Crystallinity and Bowllic Compounds

The liquid crystalline (mesomorphic) state is produced by a combination of dispersive and attractive forces [5]. In this state of matter, intermolecular interactions are sufficiently weakened to force a substance into a liquid state but attractive dipolar interaction hold the 'molten molecules' into a low dimensional lattice which lacks long range positional order. The weakening of the intermolecular interactions can be accomplished by heating the material which creates molecular motions or by the addition of a liquid component which partially solvates the material. Liquid crystalline phases formed by heating and solvation are termed thermotropics and lyotropics respectively and the remainder of our discussion will focus on thermotropic materials.

Molecular shape plays a large role in determining the structure of a liquid crystalline phase (mesophase). Typical liquid crystals contain a rigid polarizable core (mesogen) to which flexible sidechains are attached. The critical shape is a composite of the mesogen and the sidechains. Molecules with a rod-like (calamitic) shape generally display nematic and/or smectic phases. Nematics are the least ordered liquid crystal phases and the molecules have only directional order. In smectics the molecules have directional order but they also organize into two dimensional or lamellar superstructures [6]. Molecules which present a circular or disc (discotic) shape most often organize into phases in which the molecules stack in columns [7]. While there is only liquid-like order between molecules in the columns, the columns pack in a two dimensional superstructure which may have very long ($> 10^3$ Å) correlation lengths (Figure 1).

The bowllic liquid crystals investigated to date (Figure 2) are related to discotic materials since a projection of their mesogenic cores into the plane parallel to their greatest aspect ratio results in a circular shape. This circular shape is responsible for the fact that they all exhibit columnar structures in their liquid crystalline phases. There are however important differences since bowllic molecules lack the mirror symmetry through the mesogenic core common to most discotic molecules. In other words, the bowllic mesogen has inequivalent faces which are concave and convex. The first examples of bowllic crystals were based on the cyclotrimeratrylene mesogen **1** [8] and these compounds have received the most extensive study [9]. A crystal structure on one derivative showed the bowls have head-to-tail or ferroelectric order within the column [8a]. However, this is not proof of head-to-tail order in the mesophase since the organization in the liquid crystal phase is not necessarily the same as that in the crystal phase. NMR investigations of the dynamic processes in these materials suggest that the motion of these compounds in the liquid crystal

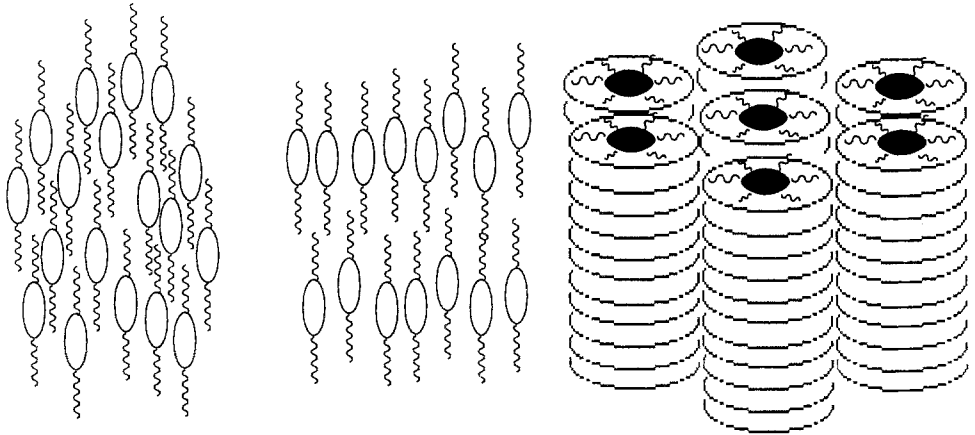


Fig. 1. Calamitic liquid crystals in nematic (left) and smectic (center) phases. Discotic liquid crystals in a columnar phase (right).

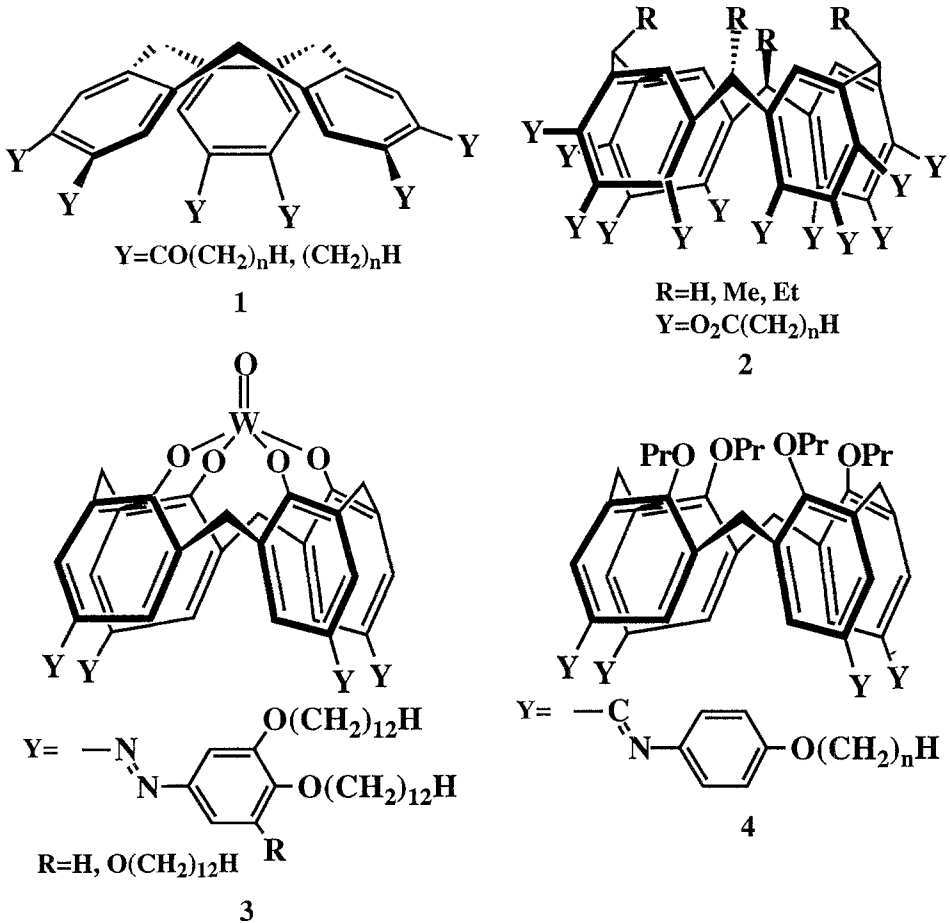


Fig. 2. Bowlic liquid crystals.

phase may be more restricted than most liquid crystals [9e]. Based upon these results Zimmerman suggested that these materials “are very similar to soft solids” [9e]. Indeed the entropy changes associated with the liquid crystal to isotropic phase transitions of these bowls are higher than those observed for most discotics and indicate that the liquid crystal phase is more highly organized. However it is clear that dynamic processes are present in these materials, since by isolating chiral analogs of **1** and monitoring the racemization, it has been determined that the cores undergo inversion in the mesophase [9c]. There have also been a number of studies on pyrogallol based calixarenes **2** [10]. In this case single crystal X-ray studies and structural investigations of the mesophases reveal that there is head-to-head or antiferroelectric order between neighboring cores within the columns. We have investigated liquid crystals containing rigid tungsten-oxo calix[4]arene cores **3** [11]. These materials are the only metal containing bowllic liquid crystals and will be discussed in more detail in the following sections. More recently another class of bowllic calix[4]arenes **4** were reported to display a columnar mesophase [12]. The same group had previously reported that related calix[8]arene compounds are liquid crystalline [13].

3. Polar Order in Bowllic Liquid Crystals

Our interest in bowllic liquid crystals has arisen from the proposal that bowl shaped molecules may exhibit polar (noncentrosymmetric) organization in the liquid crystalline phases [4, 8, 9]. Indeed bowllic liquid crystals are natural noncentrosymmetric building blocks since a head-to-tail organization maximizes the interactions between bowllic cores. New methodologies for the creation of noncentrosymmetric structures in molecular solids and liquids are critical to the development of new materials with ferroelectric and second order nonlinear optical (NLO) properties [14, 15]. Liquid crystalline methods are particularly attractive since liquid crystalline materials are easily deposited for device construction and are readily aligned.

While the bowllic structure is conducive to the formation of columns with head-to-tail or ferroelectric order, the presence of polar columns does not necessarily generate a bulk polar structure. Indeed it is generally difficult to generate thermodynamically stable polar assemblies due to the tendency of materials to avoid internal electric fields and adopt antiferroelectric structures. To overcome this obstacle and find an optimal balance of interactions which will generate a ferroelectric liquid crystalline state, we have been interested in hexagonal columnar superstructures with axial polarity [16]. The importance of this structure is illustrated for polar bowllic mesogens in Figure 3 and as shown the triangular symmetry of a hexagonal lattice cannot accommodate bulk antiferroelectric order.

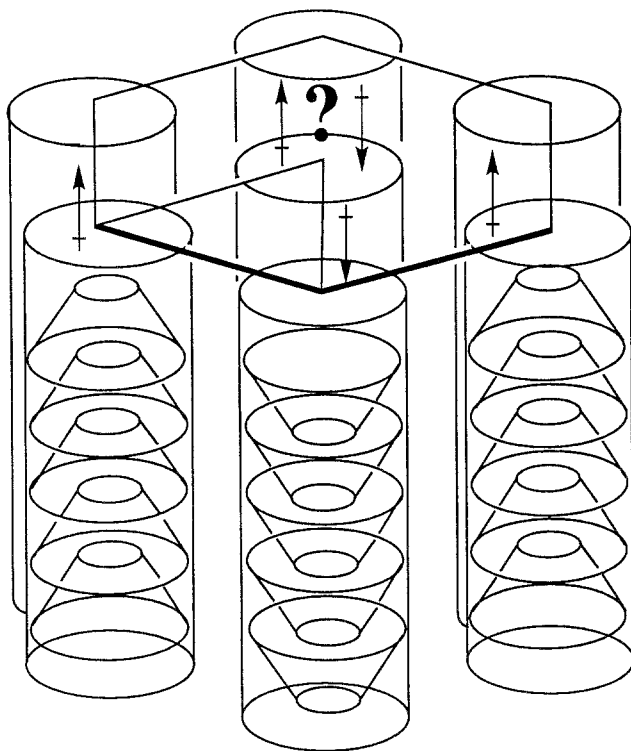


Fig. 3. Demonstration of frustration in a hexagonal columnar structure in which bowl-like mesogens have a head-to-tail arrangement and thereby create dipoles within each column. The triangular symmetry of the lattice will not allow the dipoles to organize into an antiferroelectric state and forces either a paraelectric or a ferroelectric state.

4. Liquid Crystallinity in Tungsten-Oxo Calix[4]arenes

Our attention was drawn to calix[4]arenes due to the propensity for bowl-like conformations and the extensive reaction chemistry of this class of macrocycles. In the synthesis of liquid crystalline materials we generally find that reactions subsequent to attaching the sidechains must be high yielding to easily obtain pure materials. We have been able to satisfy this requirement using diazonium addition reactions to calix[4]arene [17] which we have found to proceed in nearly quantitative yields. Hence we have synthesized azo-substituted calix[4]arene derivatives **5** with dodecycloxy sidechains as shown in Figure 4. Subsequent complexation with tungsten was performed under conditions similar to those reported for the parent *t*-butylcalix[4]arene and also proceeded in excellent yield [18].

$^1\text{H-NMR}$ of the uncomplexed calix[4]arene **5** shows it to exhibit a bowl conformation in solution. However the bridging methylenes are broadened indicating dynamic behavior. As a result it is likely that recrystallization from solution produces a crystal phase which exhibits a bowl conformation. When heated the virgin crystals melt to give a fluid phase which is birefringent when viewed with a polar-

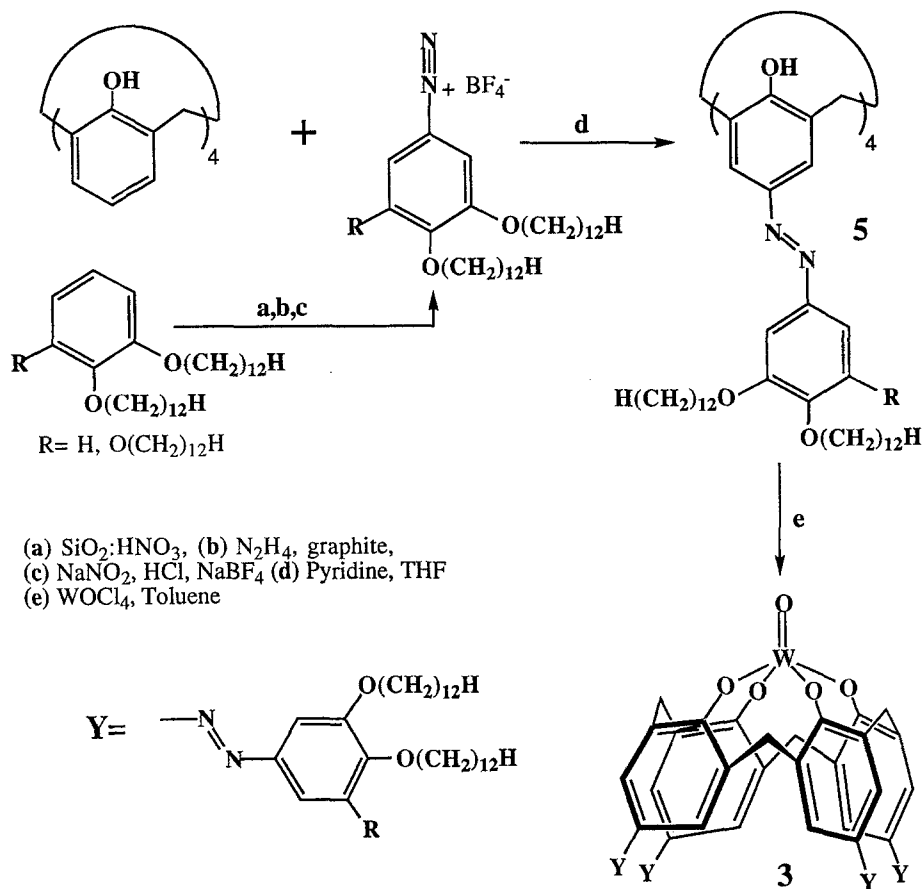


Fig. 4. Synthesis of liquid crystalline tungsten-oxo based calixarenes.

ized microscope. The fluidity and the birefringence of this phase suggest that it is liquid crystalline. However, this mesophase is transient since it is only observed on first heating. Once heated into the isotropic phase, these compounds lose their mesomorphism and cooling produces only nonbirefringent glasses. As illustrated in Figure 5 an explanation of this phenomena is that the initial crystal phase exhibits a bowl conformation which is compatible with liquid crystalline behavior, but when heated into the isotropic phase a mixture of conformations are produced which prevent a return to the liquid crystalline phase.

Capping **5** with a tungsten-oxo group to form **3** produces a mesogen with a rigid bowl conformation. These compounds exhibit well-behaved liquid crystallinity which is regained after heating into the isotropic phase. These results are also consistent with the assumption that the bowl conformation is necessary for liquid crystalline behavior. We note that others have also arrived at similar conclusions, since in the case of **4** the bulky groups on the lower rim were necessary to preserve the cone conformation and the liquid crystalline behavior [12].

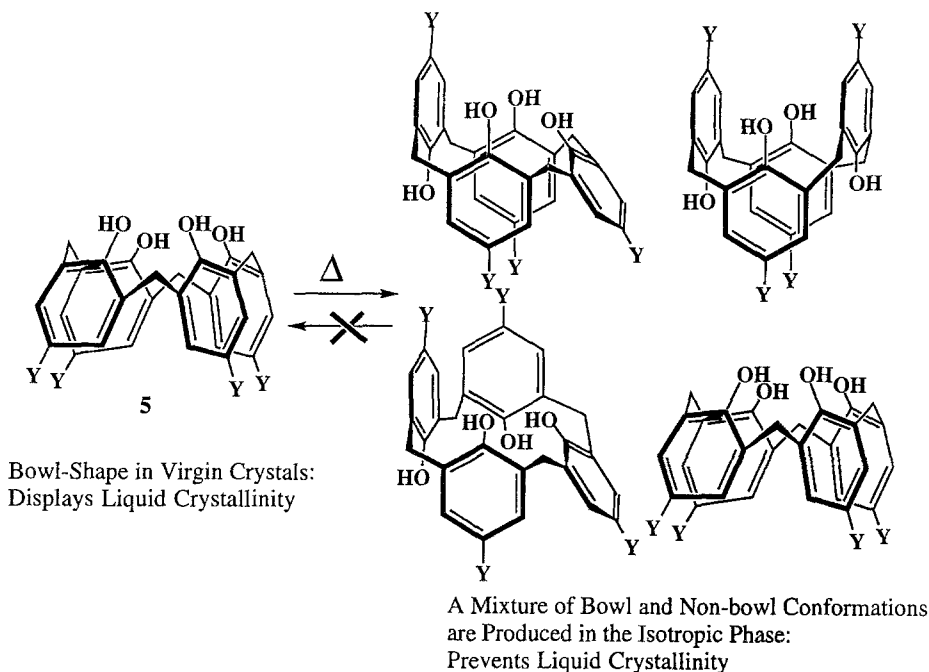


Fig. 5. Explanation of the transient liquid crystalline behavior of **5**.

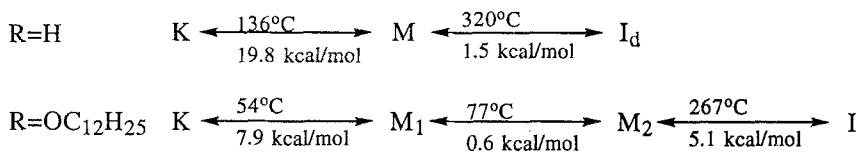


Fig. 6. Transition temperatures and enthalpies of **3**.

Both derivatives of **3** display columnar mesophases which are stable over a very wide temperature range as shown in Figure 6. The nature of the mesophases has been investigated by DSC and optical textures were viewed with a polarizing microscope. The mesophase to isotropic transition enthalpies are fairly small (1.5 kcal/mol and 5.1 kcal/mol for the 8 and 12 sidechain analogs respectively) indicating that these mesophases are likely disordered phases with liquid-like correlation between mesogens. The structure of the mesophase of **3** (R=H), M could not be determined conclusively by an optical microscope, however the textures were indicative of a columnar structure. The R=OC₁₂H₂₅ derivative displays two columnar phases M₁ and M₂, and the additional four sidechains lowers the melting and isotropic transitions by 82° and 53° respectively. Miscibility studies determined that M₁ and M₂ have different structures. By slow cooling of the isotropic phase an optical texture of the M₂ phase developed which displays digitized contours, leaf patterns, and large regions of uniform extinction. The large areas of extinc-

tion are suggestive of a uniaxial structure, and the observation of digitized stars with six-fold symmetry and 120° facets confirms a hexagonal arrangement of the columns in M_2 . We therefore characterize M_2 as a hexagonal bowlic phase B_h .

The combination of the rigid cavity and the Lewis acidic nature of the square pyramidal tungsten produces a pronounced tendency for **3** to display host-guest interactions with Lewis bases. Although a number of compounds may serve as guests, we have focused on DMF complexes due to their strong association and 1 : 1 complexes are obtained by recrystallization from anhydrous DMF. Infrared spectroscopy confirms that DMF forms a Lewis base complex. The W=O band undergoes a characteristic shift from 1074 cm^{-1} (^{18}O 1019 cm^{-1}) to 990 cm^{-1} (^{18}O 938 cm^{-1}) with DMF complexation. Likewise, the C=O band of the DMF of the host-guest complex in CH_2Cl_2 solution occurs at 1645 cm^{-1} which is 25 cm^{-1} lower in energy than uncomplexed DMF in CH_2Cl_2 . NOESY NMR experiments conclusively show the DMF to occupy the cavity and all of the DMF protons experience a large up-field shift consistent with the shielding environment provided by the cavity.

The most dramatic consequence of host-guest complexation is its effect upon the mesomorphic behavior of the complexes. While the R=H analog exhibits a discotic mesophase from 135° to 330°C , its DMF complex melts directly to an isotropic phase at 115°C ($\Delta H = 12.3\text{ kcal/mol}$). Likewise, the R= $\text{OC}_{12}\text{H}_{25}$ DMF complex melts to form an isotropic phase at 84°C . Complexes with pyridine guests were found to exhibit isotropic transitions at the same temperatures, indicating that a filled cavity is more important than the nature of the guest. With further heating (200°C to 250°C), the DMF complex slowly dissociates to form the liquid crystalline phase.

The deleterious effect of a DMF or pyridine guest on the mesophase stability indicates that occupation of the cavity is critical. This fact, combined with the columnar structure of the mesophases, is proof that the bowlic cores exhibit a head-to-tail arrangement whereby tungsten-oxo groups protrude into the cavity of the neighboring mesogen (Figure 7). Hence, in **3** with R= $\text{OC}_{12}\text{H}_{25}$ we have an example of a material which exhibits ferroelectric order within the columns and a hexagonal lattice. As discussed earlier these features preclude bulk antiferroelectric order and most likely force the material into a frustrated paraelectric state. Bulk ferroelectric order may be introduced by formation of the mesophase in the presence of an electric field.

5. Conclusion

Calixarenes are attractive materials for the design of new materials. The established synthetic procedures for their functionalization, their bowl shapes, and their host-guest chemistry offers a wealth of opportunities for the design of novel materials. In this report we have focused upon the use of the bowlic shape to generate materials with polar order. However, there are many other aspects of these materials

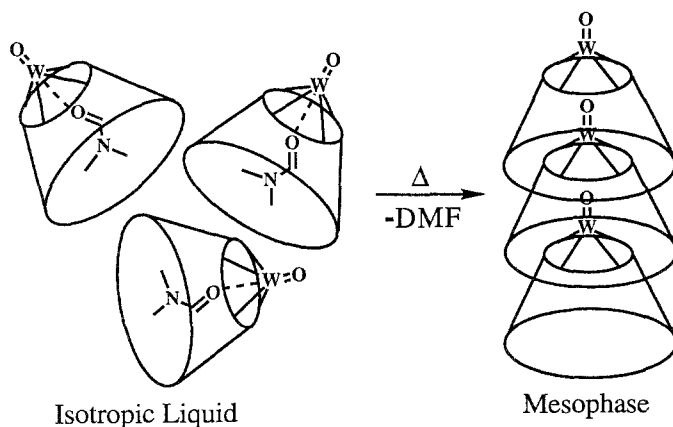


Fig. 7. Illustration of how blocking of the cavity by the DMF guest prevents mesophase formation. Heating to temperatures greater than 200°C liberates DMF and allows mesophase formation.

which may impart useful effects in materials design. For example, we found that the isotropic point of **3** is depressed dramatically through host-guest complexation. This type of process may be useful in processing materials, since it provides a route to a low viscosity state at reduced temperatures. As a result host-guest complexes of very high melting bowl-like complexes may be poled at lower temperatures as host-guest melts and subsequent dissociation of the guest will produce noncentrosymmetric materials with high temporal stability.

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References

1. H.-J. Schneider and H. Dürr (Eds.): *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, VCH (1991).
2. E. Kelderman, L. Derhaeg, G. J. T. Heesink, W. Verboom, J. R. J. Engbersen, N. R. van Hulst, A. Persoons, and D. N. Reinhoudt: *Angew. Chem. Int. Ed. Engl.* **31**, 1075 (1992).
3. M. D. Conner, V. Janout, I. Kudelka, P. Dedek, J. Zhu, and S. L. Regen: *Langmuir* **9**, 2389 (1993).
4. L. Lei: *Mol. Cryst. Liq. Cryst.* **146**, 41 (1987).
5. G. W. Gray (Ed.): *Thermotropic Liquid Crystals: Critical Reports on Applied Chemistry Vol. 22*, Society of Chemical Industry (1987).
6. G. W. Gray and J. W. G. Goodby: *Smectic Liquid Crystals: Textures and Structures*, Leonard Hill Pub., Glasgow (1984).
7. S. Chandrasekhar and G. S. Ranganath: *Rep. Prog. Phys.* **53**, 57 (1990).
8. These materials were reported nearly simultaneously by two groups. (a) J. Malthete and A. Collet: *Nouv. J. Chim.* **9**, 151 (1985). (b) H. Zimmerman, R. Poupko, Z. Luz, and J. Billard: *Z. Naturforsch., A: Phys., Phys. Chem. Kosmophys.* **40A**, 149 (1985).
9. (a) H. Zimmerman, R. Poupko, Z. Luz, and J. Billard: *Z. Naturforsch., A: Phys., Phys. Chem. Kosmophys.* **41A**, 1137 (1986). (b) A.-M. Levelut, J. Malthete, and A. Collet: *J. Physique* **47**,

- 351 (1986). (c) J. Malthete and A. Collet: *J. Am. Chem. Soc.* **109**, 7544 (1987). (d) J. M. Buisine, H. Zimmermann, R. Poupko, Z. Luz, and J. Billard: *Mol. Cryst. Liq. Cryst.* **151**, 391 (1987). (e) R. Poupko, Z. Luz, N. Spielberg, and H. Zimmermann: *J. Am. Chem. Soc.* **111**, 6094 (1989). (f) W. Kranig, H. W. Spiess, and H. Zimmermann: *Liq. Cryst.* **7**, 123 (1990). (g) L. Wang, Z. Sun, X. Pei, and Y. Zhu: *Chem. Phys.* **142**, 335 (1990).
10. (a) G. Cometti, E. Dalcanale, A. Du vosel, and A.-M. Levelut: *Chem. Commun.* 163 (1990). (b) S. Bonsignore, G. Commetti, E. Dalcanale, and A. Du vosel: *Liq. Cryst.* **8**, 639 (1990). (c) E. Dalcanale, A. Du vosel, A.-M. Levelut, and J. Malthete: *Liq. Cryst.* **10**, 185 (1991). (d) G. Cometti, E. Dalcanale, A. Du vosel, and A.-M. Levelut: *Liq. Cryst.* **11**, 93 (1992). (e) S. Bonsignore, A. Du vosel, G. Guglielmetti, E. Dalcanale, and F. Uguzzoli: *Liq. Cryst.* **13**, 471 (1993).
11. B. Xu and T. M. Swager: *J. Am. Chem. Soc.* **115**, 1159 (1993).
12. T. Komori and S. Shinkai: *Chem. Lett.* 1455 (1993).
13. T. Komori and S. Shinkai: *Chem. Lett.* 901 (1992).
14. J. W. Goodby, R. Blinc, N. A. Clark, S. T. Lagerwall, M. A. Osipov, S. A. Pikin, T. Sakurai, Y. Koshino, and B. Zeks: *Ferroelectric Liquid Crystals: Principles, Properties, and Applications*, Gordon and Breach Science Publishers, Amsterdam (1991).
15. S. R. Marder, J. E. Sohn, and G. D. Stucky (Eds.): *Materials for Nonlinear Optics: Chemical Perspectives*, ACS Symposium Series 455, Washington (1991).
16. (a) H. Zheng, P. J. Carroll, and T. M. Swager: *Liq. Cryst.* **14**, 1421 (1993). (b) A. G. Serrette and T. M. Swager: *J. Am. Chem. Soc.* **115**, 8879 (1993).
17. S. Shinkai, K. Araki, J. Shibata, D. Tsugawa, and O. Manabe: *J. Chem. Soc., Perkin Trans.* 3333 (1990).
18. F. Corazza, C. Floriani, A. Chiesi-Villa, and C. Rizzoli: *Inorg. Chem.* **30**, 4465 (1991).