Communication

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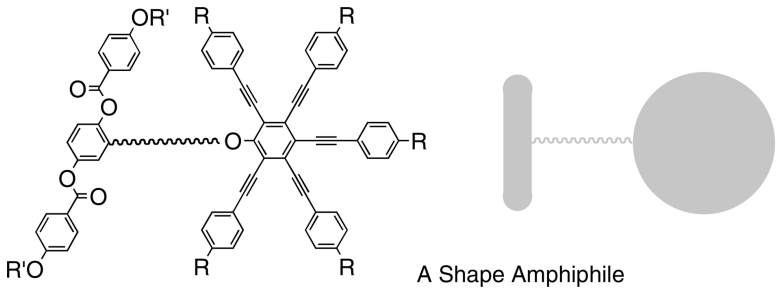

A Shape Amphiphile

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Shape Amphiphiles: Mixing Rods and Disks in Liquid Crystals

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The idea that some liquids do not mix is familiar, and, for example, water and hexane are immiscible due to the very different polarity of the two solvents. However, it is possible to cause two immiscible components to mix if an amphiphile is used. Indeed, amphiphiles can stabilize oil−water emulsions and are used frequently as phase-transfer agents in synthesis and catalysis. Similarly, hydrocarbons and perfluorocarbons can be persuaded to mix if a different type of amphiphile is used, one which contains a hydrocarbon and a fluorocarbon fragment bound together covalently. Thus, the amphiphile can either act as a surfactant leading to the formation of a dispersion or act as a cosolvent leading to statistical mixing of the components.

In the study of liquid crystals, the biaxial nematic phase is of great interest. It was predicted theoretically by Freiser[1] in 1970, and, since that time, there has been considerable interest in the demonstration of the phase as a physical reality, and extensive debate in the literature concerning the validity, or otherwise, of putative examples,[2] perhaps the one, unequivocal example being that in a ternary lyotropic system.[3] In the uniaxial nematic phase (N_u) of liquid crystals, there is no positional order, and the unique axis of the molecules is oriented about a director, **n**. In the biaxial nematic phase (N_b), there is, additionally, a correlation of the molecules in a direction perpendicular to **n**, and so, whereas in the N_u phase the physical properties in the plane perpendicular to **n** are angle-independent, in the N_b phase this is not the case. A simple schematic representation of the N_b phase composed of lozenge-shaped molecules is shown as Chart 1.

In mean-field calculations,[4] the biaxial nematic phase is obtained by changing a shape biaxiality parameter (η) between a rod at one extreme ($\eta = 0$) and a disk ($\eta = 1$) at the other. The N_b phase exists over ranges such as $0.2 \leq \eta \leq 0.8$, but is most stable at $\eta = 0.4$. Such a structure is then properly intermediate between a rod and a disk, and this led to proposals that the N_b phase might be realized in rod/disk mixtures. This idea was investigated in theoretical approaches to the biaxial nematic phase formed from binary mixtures of rod- and disklike molecules.[5] The situation with respect to physical mixtures is not so straightforward because a mixture of rods and disks should,[6] and indeed does,[7] separate into two uniaxial nematic phases, one rich in rods and the other rich in disks. However, theoretical work by Sharma et al.[8] and by Vanakaras et al.[9] has shown that rod/disk mixtures can lead to N_b phases if the rod and the disk are attracted more to one another than to each other.

We had tackled this problem by linking the rod and the disk together covalently (**1**) so that they could not phase separate, and we reported that such molecules align biaxially in a rodlike liquid crystal solvent.[10] The symmetry of the nematic phase of **1** remains under investigation.

If rods and disks phase separate, then in a simplistic interpretation they represent two effectively immiscible liquids. Compound **1** could then be regarded as an amphiphile, possessing features of a rod and features of a disk − a shape amphiphile. If this is true, then it should be possible to use **1** to stabilize mixtures of rods and disks and suppress phase separation.

Chart 1. Representation of a Biaxial Nematic Phase

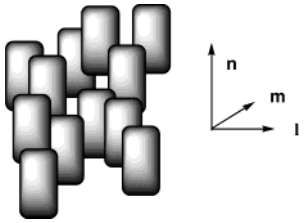
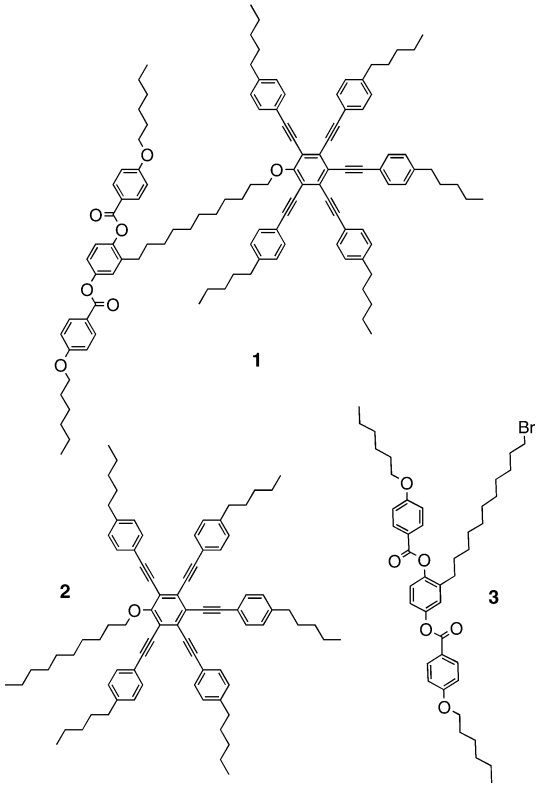


Chart 2. Compounds Used in This Study



To test these assumptions, we made related disk- and rodlike molecules **2** and **3**, respectively, and proceeded to evaluate their mesomorphism and then investigate their miscibility in binary mixtures with each other and with **1** (Chart 2). The syntheses of **1** and **3** are described in ref 10, while **2** is obtained by literature methods.[11] The mixtures were made by dissolving both components in dichloromethane at the required ratio and then evaporating the solvent. The mixture so produced was then annealed before being studied in detail by polarized optical microscopy and DSC.

As reported previously,[10] **1** has a monotropic nematic phase Cr (28.5 N) 74 I, and it was found that the nematic phase of **3** is similarly monotropic, while that of **2** is enantiotropic: **2** Cr 82 N

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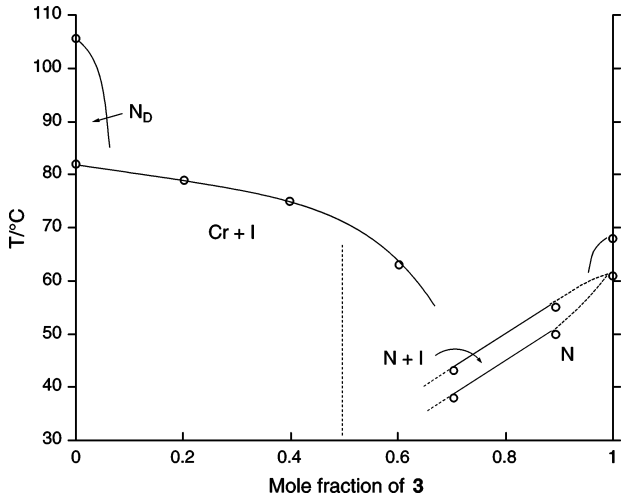

Figure 1. Binary phase diagram between **2** and **3**.

105.5 I; **3** Cr (61 N) 68 I. The monotropic nature of the phases in **1** and **3** made the mixture experiments demanding, especially when it was found that, in most cases, nematic glasses were formed on cooling rather than crystalline states.

Figure 1 shows the binary phase diagram obtained for mixtures of **2** and **3**, obtained to investigate the predicted phase separation between the nematic phases of the rod- and disklike materials. The phase diagram shows that, when moderate amounts of **2** are added to **3** (up to about 30%), then the two materials appear to be miscible as evidenced by the observation of a nematic phase, albeit with a wide, biphasic region to isotropic. However, such mixtures are clearly not ideal as **2** evidently destabilizes the nematic phase of **3**. At higher concentrations of **2**, the behavior changes significantly, and the nematic phase is no longer observed, showing that **3** is extremely effective in destabilizing the nematic phase of **2**. Further, the immiscibility is indicated by the fact that **2** readily crystallizes to give a biphasic Cr + I regime at all measured concentrations of **3** up to 60%.

To test the idea of amphiphilicity in **1**, we then chose to examine ternary mixtures between a 50:50 mixture of **2** and **3** which shows total phase separation, and **1**. The binary phase diagram is shown as Figure 2 in which the temperatures shown at 0% of **1** represent the behavior of the 50:50 mixture. At 10% of **1** in the mixture, it is only possible to observe destabilization of the melting points of the mixture, but at mole fractions of **1** $\geq$ 20%, a nematic phase is seen all the way to 80% of **1** and below a rather narrow, biphasic N + I region. Clearly then, the rod−disk dimer, **1**, has acted to cosolubilize **2** and **3** to allow a nematic phase to be observed and, as such, has acted as an amphiphile as the rod part of **1** must have solubilized **3**, while the disk part has solubilized **2**.

There is, of course, a legitimate question surrounding the nature of the homogeneous phase of **1** mixed with **2** and **3**. It could be that each component is distributed statistically throughout the

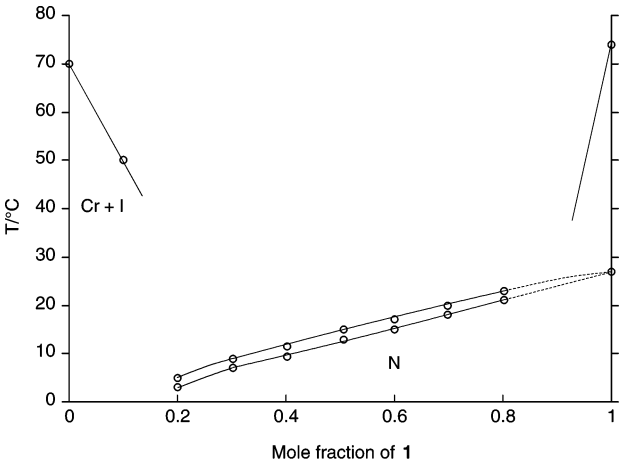

Figure 2. Binary phase diagram between **1** and a 1:1 mixture of **2** and **3**.

medium, or it is possible that there are rod-rich and disk-rich regions and, therefore, interfaces. However, to answer this question requires detailed studies by, for example, small-angle neutron scattering using selectively deuterated materials. In due course, such experiments will be undertaken, but the answer will not change the result reported here that rods and disks can be mixed using a shape amphiphile − a concept which we believe to be novel. Further given that biaxial nematic phases are predicted in rod/disk mixtures and that we have shown that stabilization of such mixtures is now possible through the use of this kind of amphiphile, then it is expected that this will prove a productive strategy in the design of N_b materials.

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