IN SEARCH OF THE BIAXIAL NEMATIC PHASE

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The biaxial nematic phase of low molar mass thermotropic liquid crystals remains elusive and
despite the substantial efforts that have gone into synthesising carefully identified candidate
molecules, there are no unequivocal demonstrations of the existence of the phase. Indeed, the
only undisputed example of a biaxial nematic exists in lyotropic systems,1 although an example
in thermotropic polymeric systems2 appears relatively uncontroversial.

For a single component nematic, the requirement for the formation of a
biaxial phase is that different axes in the molecule tend to be aligned
parallel to two orthogonal directors (Figure 1). Praefcke has maintained
for some time that a productive avenue for exploitation is to marry in
one molecule the features of both rods and disks.3 This suggestion has
some intuitive attractions and it is important to pay close attention to the
reasons why such a suggestion was made at all. In fact, the idea comes
from theoretical approaches to the biaxial nematic phase formed from
binary mixtures of rod-like and disk-like molecules.4 Since the characteristic axes of rods and
disks tend to align orthogonal to each other, an equimolar mixture might be expected to build a
nematic with two orthogonal directors. However, the situation with respect to physical mixtures
is not so straightforward because in practise, a mixture of rods and disks should5 and indeed does6
separate into two uniaxial nematic phases, one rich in rods and the other in disks.

The important idea contained in these results is that, however the rods and disks are combined,
the aim is simply to arrive at a situation where there are directors in two perpendicular directions.
Such a situation might be realised in a variety of different ways based upon a general concept of
molecular biaxiality which is expressed, in its simplest form, as a shape biaxiality, but which
could also find expression in terms of, for example, attractive interactions. Theoretical work by
Sharma et al.7 and by Photinos and colleagues8 has shown that rod/disk mixtures can lead to
biaxial nematic phases if the rod and the disk are attracted more to one another than to each other.
We have been working on several approaches to the biaxial nematic phase and these will be
reviewed in the presentation with the idea of seeing what lessons can be learnt.

**Porphyrin Systems:** In this approach, we followed the idea that rod and disk could be combined into a single molecule and so, following the idea that the porphyrin is our disk, we looked at its modification to endow it with rod-like features, accomplished by selective functionalisation at the 5- and 15- positions. This generated a range of materials, all with nematic phases and some rather close to room temperature. This design idea is explored.

![Porphyrin System](image)

**Non-covalently Attached Rods and Disks:** This work is based on the theoretical idea advanced by Photinos and demonstrated in simulations, that if rods and disks can be attached non-covalently, then phase separation is suppressed and biaxial phases can result. In Photinos' original work, the interaction he used was a hydrogen bond, but we have chosen to use Lewis acid/base interactions in series of metal complexes based on the salicylaldimato ligand. Thus, we build a rod-like mesogen with a nematic phase containing a Lewis acidic metal centre and we mix it with a more disk-like mesogen containing a Lewis basic metal fragment, or vice versa.

**Mesogens with Enhanced Lateral Interactions:** In this approach, we reasoned that we would appeal to the idea of a biaxial system where the biaxiality arose not from shape, but from biaxiality of interaction. Thus, we wished to choose a nematic system and then develop it chemically so that we could promote lateral interactions. Interestingly, this work now finds a basis in simulation following work by Berardi and Zannoni. We selected palladium complexes for this study and have some interesting results from 1H NMR which will be discussed.

![Mesogen with Enhanced Lateral Interactions](image)
Covalently Linked Rods and Disks: This approach is, to a first approximation, a logical extension of the idea concerning non-covalently bound systems as by linking two parts of a molecule with a covalent interaction, phase separation is simply impossible! Here we have developed a rod-disk molecule with a nematic phase around room temperature and, at the time of writing the abstract, we are making our first 2H NMR measurements.

Acknowledgements: We are very grateful to NEDO, the European Union, the EPSRC, the British Council, Merck(UK) and Johnson Matthey for supporting this work.

References: