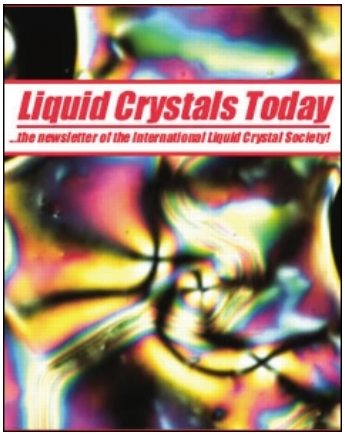

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The dawn in the area of thermotropic biaxial nematics

Symposium on Biaxial Liquid Crystals, Kent, 27–28 October 2008

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Thermotropic biaxial nematic phases of low molar mass mesogens are highly sougth materials not only for liquid crystal display technology. Recent progress in molecular design, synthesis, experimental methods to study biaxiality and theory gave occassion to organise a symposium on biaxial liquid crystals in Kent. The stimulating interdisplinary discussion shows that this challanging field of research is in his dawn.

Keywords: biaxial liquid crystals; biaxial nematics; order parameter; Kent symposium

Almost 40 years ago, M.J. Freiser predicted that nematogens, which were treated as molecules with cylindrical symmetry in uniaxial nematic phases, possess a non-cylindrical shape for the real molecules and should form biaxial nematic phases at an appropriate low temperature (*1*). A biaxial nematic phase was found first in lyotropic mixtures, where the micelar shape can be gradually tuned (*2*). The thermotropic biaxial nematic formed from a low molar mass molecule remained elusive. Therefore topical meetings on biaxial LC, especially ones focused on nematics, have a long tradition, beginning with the Oxford Workshop on Biaxial Liquid Crystals in 1996 (*3*), two topical meetings in Southampton in 2004 and 2006 and a biaxial roundtable in 2005. In this tradition a Symposium on Biaxial Liquid Crystals was initiated last year in Kent, organised by David Allender who gathered many specialists for two days of discussion on the subject.

What is a biaxial nematic and why is it so interesting? Uniaxial and biaxial phases can be best understood by the property from which they derive their names; that is, the behaviour when light propagates in the material. The optical behaviour of a uniaxial phase can be described by two refractive indices spanning a rotational symmetric ellipsoid, also called indicatrix (Figure 1, left side). There is one preferred direction, perpendicular to the circular cross-section of this special ellipsoid, along which the propagating linear polarised light does not change its polarisation. This direction is called the optical axis. In a uniaxial phase there is only one optical axis. However, if the materials have to be optically described with three different refractive indices, the indicatrix is an ellipsoid spanned by three different semi-principal axes and possesses two different circular cross-sections and consequently two optical axes (Figure 1, right side). Examples of uniaxial phases include conventional nematics, SmA or columnar hexagonal phases. Examples of biaxial phases are SmC, columnar rectangular or orthorhombic phases. A uniaxial nematic of calamitic mesogens is a phase in which the molecular long axes are aligned along a director and the molecular centre of gravity is distributed like in a liquid. In a biaxial nematic phase three molecular axes should align along individual directors resulting in a material with three different refractive indices. This material has at the same time a liquid-like distribution of the molecular centres of gravity. The high order should be maintained in spite of the large molecular mobility. These two parameters have to be balanced precisely in order to obtain a thermotropic biaxial nematic with low molar mass molecules (*4*).

In 2004, such a material was found in the series of V-shaped molecules (*5, 6*). Since then several new materials have been designed and reported to be biaxial, among others shape-persistent V-shaped molecules, tetrapodes and banana-shaped oligoesters. Lee *et al.* reported a response time during switching along the director of the short molecular axis which is up to 100 times faster compared with the switching along the director of the long molecular axis (*7*). However, a recent comment of R. Stannarius outlined that some of the interpretations should be carefully reconsidered (*8*). Several patents appeared in the field on biaxial switching or switching of induced biaxial phases (*9, 10*). Finally, in a keynote lecture at the ILCC 2008 in Jeju, Dr. J.J. Souk (Samsung) pointed out that biaxial phases might be one possible way to improve liquid crystal display technologies in the future with respect to their switching times. For this purpose a low viscous, enantiotropic biaxial nematic phase at ambient temperatures is urgently required. Besides the appealing task of proving the consistency of theoretical predictions and experimental results, the design, synthesis and the experimental evidence for biaxiality is extremely

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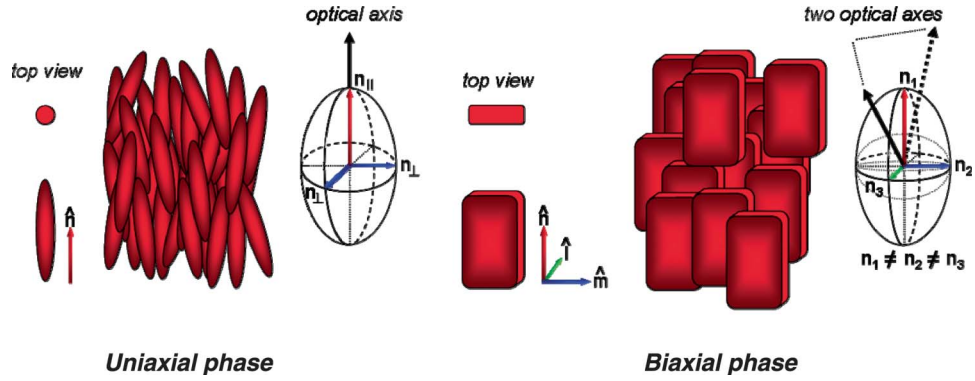

Figure 1. Uniaxial nematic (Left) and biaxial nematic (Right) phases and their corresponding indicatrices.

challenging and therefore very attractive for researchers in the area of liquid crystals. The recent progress on biaxial nematic liquid crystals and necessity of such materials in industry seems to have induced a dawn in the area of thermotropic biaxial nematics. Thus, the place and time for last year's symposium was perfectly selected, gathering specialists in the field, inducing fruitful discussions and creating new collaborations. The symposium was divided into four sections: (i) design and synthesis of new biaxial nematic materials; (ii) new experimental methods to measure biaxiality and the biaxial order parameters; (iii) theory; and (iv) non-nematic biaxial phases.

The rational design and synthesis of new structures is extremely important and has always been accompanied by suggestions arising from theoretical work. Shape-persistent V-shaped nematogens, reported in the first talk by M. Lehmann, are based on the theoretical concept of Masters and Luckhurst (*4, 11*). The formation of crystal or higher ordered liquid crystal phases is prevented by the molecular structures; however, the lack of enantiotropic phases was until recently a major problem (*12*). The development of a series of new oxadiazole and thiadiazole derivatives has resulted in nematic mesophases with low temperature enantiotropic nematic phases for which preliminary studies point to phase biaxiality. V. Prasad presented new work on banana-shaped molecules forming nematic phases (*13*) and new azo derivatives based on the design of Praefke's cinnamic acid nematogens (*14*). X-ray work on the latter compounds presented by S.W. Kang led to the conclusion that the special X-ray patterns can be interpreted by a model of weakly hydrogen-bonded biaxial dimers, supported by FT-IR- and optical studies. Indications for phase biaxiality have been reported. X-ray is one powerful method to get information on the degree of alignment in a biaxial nematic sample (*6, 15*). This was highlighted by B.R. Acharya, who discussed the simulation of the X-ray patterns observed for oxadiazoles in their biaxial nematic phase, for which the molecular form factor plays a predominant role. The X-ray pattern reported in 2004 shows four split diffraction signals interpreted as reflections originating from a biaxial phase of V-shaped molecules. These signals were also discussed with respect to cybotactic clusters. S. Kumar pointed out that a common agreement about the nature and definition of cybotactic clusters is missing. Generally they are regarded as pretransitional phenomena, which should be observed a few degrees above the transition, but not across all the temperature range of the nematic phase (which extends over 30°C for some oxadiazole derivatives). Polarised Raman-scattering is another technique which was only recently used to gather information about biaxial order parameters <P220>, <P420> and <P440>. It was performed by H. Gleeson *et al.* who could clearly confirm a uniaxial to biaxial nematic phase transition for an oxadiazole derivative (*16*). Similar studies by Park *et al.* supported the biaxial nature of the bananas synthesised by the group of V. Prasad. Such a non-symmetric banana molecule with various different dipoles in the scaffold was further investigated by A. Marini by means of ^{13}C Solid-State NMR spectroscopy (*17*).

As outlined earlier, theory stimulates synthetic design and vice versa. Sometimes proposals from theoretical work are translated to molecular representations, as happened in the case of shape-persistent V-shaped mesogens, and theory again explains experimental observations. The latter was exemplified by L. Longa, who studied V-shaped molecules consisting of two and three Gay-Berne particles with or without a dipole along the apex of the mesogens. As recently reported with a simpler model by M.A. Bates (*18*), L. Longa found direct transitions from the isotropic liquid to the biaxial nematics, so-called Landau points. With increasing magnitude of the dipoles the apex angle can vary from the ideal angle of about 100°. Even for three-part mesogens a Landau line emerged. These

results explain for example why the oxadiazole derivatives of Samulski *et al.*, possessing a large dipole along the bisector, form biaxial nematic phases with an apex angle much larger than the one theoretically predicted. Longa also proposed new exotic tetrahedratic phases for V-shaped mesogens with four arms.

Eventually, biaxial materials must not inevitably form a nematic but may instead assemble in SmA_P phases, such as the bent-shaped oligoesters of E.-J. Choi with a 3,4-substituted naphthalene core or banana-shaped oligoesters presented by N.A. Clark. Such phases have also been shown to exhibit a very fast response time. The talks and discussion sessions were complemented by poster sessions (Figure 2) which spanned studies of recently reported thermotropic biaxial nematics – oxadiazoles, shape-persistent V-shaped mesogens, tetrapodes – (S.W. Kim, M. Lehmann, A. Kocot, K. Neupane, B. Senyuk), field-induced biaxial smectic phases (S. Taushanoff, C. Zhu), new bent core BINOL materials (M.R. Korn) and biaxial nematic polymer actuators (M.-H. Lee).

This symposium was a successful meeting which left enough room for discussion. It became obvious that researchers must augment their efforts in collaborations between synthetic chemists, experimental physicists and theoreticians. This may also help to overcome some confusion with the nomenclature of biaxial order

Figure 2. Top: Discussion session – from the left: L. Longa, E. Virga, H. Gleeson, M.S. Park. Middle: Participants of the biaxial symposium. David Allender, the organiser, standing in the middle. Bottom: Poster sessions.

parameters for various methods and the solid definition and understanding of cybotactic clusters. Moreover, the dream of an ambient temperature-stable, fast-switching, biaxial nematic mesophase of low molar mass molecules will become a reality only with stimulating interactions of all the different specialists. This is why the participants decided that a similar meeting will be repeated every second year in Kent. Thus, it only remains to hope that the next symposium will be as successful as the first one, and that it will be attractive for all groups working in the field.

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