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Yves Galerne [a]

[a] Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, 23 rue du Lœss, F-67037, Strasbourg, France

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Characterization of Biaxial Nematic Phases in the Thermotropic Liquid Crystals

YVES GALERNE*

Institut de Physique et Chimie des Matériaux de Strasbourg,
Groupe des Matériaux Organiques, 23 rue du Lœss, F-67037 Strasbourg, France

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In the hopes of helping the discovery of a really biaxial nematic phase in the thermotropic liquid crystal family, we give a brief review on the experimental methods available for proving biaxiality in oriented or disoriented samples. We discuss the relative advantages and problems that arise with the biaxial tests based on the NMR techniques, X-ray and neutron scatterings, dynamic modes analysis, inspection of defects, or the determination of coupling constants as in conoscopy. Among these different methods, two, conoscopy and defects analysis, seem particularly useful since they may be really conclusive without excessive sophistications. They may therefore be recommended as tests for biaxiality. Conoscopy is most probably the safest way to prove biaxiality, but it needs perfectly oriented samples. In order to warrant that the samples are indeed correctly oriented, the conoscopic patterns should be observed with several entire and well-contrasted rings. Conversely, if the rings are incomplete or fading somewhere, the observed biaxiality is only apparent and likely to be produced by orientation gradients. The analysis of the disclination lines may also be used with benefit to prove biaxiality. One should then carefully control the width and contrast of the lines to keep them sharp and regular all along, in order not to confuse them with mirages. To prove biaxiality, at least two types of disclination lines should be observed with typical variations of the zigzag angles, contrasts and relaxation rates as functions of temperature.

Keywords: Thermotropic and lyotropic; liquid crystal; biaxial nematic phase; orientation gradients; conoscopy; defect inspection; NMR; X-ray and neutron scattering

PACS numbers: 61.30. -v; 61.30. Eb; 61.30. Gd; 61.30. Jf; 64.70. Md

INTRODUCTION

Since the discovery of the biaxial nematic phase (N_b) in lyotropic mixtures by Yu and Saupe in 1980 [1], there have been several claims of N_b phases in

*Fax: +33 3 88 10 72 46.

the thermotropic liquid crystals (LC), small molescules [2–4] and polymers [5]. However, these announcements of biaxiality in the thermotropics have been questioned because they failed to be confirmed. For instance, it seems now that 4-[3′,4′,5′-tri(*p-n*-dodecyloxybenzyloxy)]-benzoyloxy, 4″-*p-n*-dodecyloxybenzoyloxybiphenyl does not exhibit the N_b phase announced in Ref. [2], but instead a smectic C phase [6].

It should be noted concerning the N_b phase, that the thermotropics are in marked contrast with the lyotropics where complementary and accurate experiments have confirmed biaxiality [7], although they are more difficult to manipulate. Let us recall that an essential experimental difficulty with the lyotropics is water evaporation which complicates the precise control of the water concentration necessary to obtain the N_b phase. To avoid this problem, the samples have to be sealed, without pollution from the glue, and this is not particularly easy to realize. Other experimental handicaps of the lyotropic LC's may be mentioned also, for instance their large viscosity compared to the thermotropic LC's with small molecules, which gives them relaxation times larger by a factor of 10 to 100. The stabilization times after the samples have been perturbed, are therefore lengthened by the same factor, making their manipulation rather uneasy. Another experimental difficulty of the lyotropic LC's is that their anchoring possibilities onto the substrates are restricted. At present, only one alignment direction can be realized per nematic phase, planar in the calamitic nematic phase and homeotropic in the discotic one. The situation is thus not so rich as in the thermotropics where both orientations may be achieved for a lot of molecules, not including the intermediate angles now currently available. Finally, we may notice that the optical index differences in the lyotropic LC's, *i.e.*, the birefringence and possibly the biaxiality, are much smaller than in thermotropics, and therefore more difficult to detect and to measure. In order to preserve accuracy, the experimentalists have to prepare thick samples ($\sim$ 1 mm or more), which are *a priori* difficult to orient uniformly. In spite of all these drawbacks, the biaxiality in lyotropic mixtures has been clearly demonstrated by different means, and measured reproducibly independently of the experimental conditions, and in particular, independently of sample thickness. The situation in the thermotropics is unfortunately the opposite, and this naturally introduces some doubts upon the reality of the N_b phases claimed up to now in these systems. The current feeling has now become even more confused, and could discourage people from the initially exciting subject of the N_b phases.

In order to help in clarifying the problem of the thermotropic N_b phases, we discuss in this paper on the experimental means available for really

proving the existence of this interesting phase. We then mention a few traps not to fall in when trying to demonstrate biaxiality in a thermotropic LC phase, and a way to avoid them.

EVIDENCE OF THE NEMATIC PHASE

First of all, one must be sure that the phase under study is really nematic. The diagnostic of the nematic phase seems easy; nevertheless mistakes at this stage may arise as probably in Ref. [2] when working with non or badly oriented samples. In order to avoid errors, let us quickly recall here some simple features useful to look at. One may begin with the observation of textures with a polarizing microscope. This is a well-known and immediate way to get information on the typical defects, distortions and fluctuations of the phase. In the nematic phases, one observes disclination lines in the form of curly loops [8] and possibly zigzag lines if the phae is uniaxial [9] or biaxial [10]. One may also qualitatively look at the hydrodynamic behavior of a sample prepared with glass plates between spacers by gently pressing it in the middle. This action produces characteristic 3D-flows in the nematic phases that can easily be observed under microscope. The nematic phase may also be recognized, though this is not a really practical method, through its easy and immediate response to applied fields. The director may thus be observed to orient with the magnetic or the electric fields. It is to be noticed that the surface fields developed by the substrates may yield useful indications too. Thus one can get the homeotropic or the planar anchorings with the nematic phase. If these simple means fail to prove the existence of the nematic phase, one may perform X-ray scatterings and observe the diffuse ring corresponding to the lateral distance between the molecules, and a second one at small angles, due to cybotactic groups in the nematic phase, more or less faint and diffuse.

All these tests must however be performed with enough care to avoid confusions with the smectic C phase, because this phase possesses a **c** director which may be confused under some circumstances with the nematic director **n**. The **c** director, defined by the average projection of the molecules onto the smectic layers, acts on the intensity of the polarized light in a similar manner as the **n** director. The smectic C phase therefore exhibits textures, as is well-known, which often resemble those of the nematic phase with orientational distortions and walls, dynamic light-intensity fluctuations, and even disclinations in some cases. The occurrence of focal conics is in principle a good argument in favor of the smectic phase, but they are sometimes too small to be recognized, or also they may be confused with orientational distortions

in a nematic phase, reminiscent of focal conics in a neighboring smectic phase and anchored onto the substrates. The schlieren textures should be informative too since, the **c** director differing from $-\mathbf{c}$, 4-branches defects only can be observed in the smectic C phase. This makes, in principle, a marked difference with the nematic phase in which **n** is equivalent to $-\mathbf{n}$, and thus the 2-branches defect lines are possible as well, and eventually observed. Unfortunately, the schlieren textures are often too tiny to be correctly resolved and recognized without any doubts. Moreover, one may be confused with the smectic O or smectic C_A phase in which the **c**-director is equivalent to $-\mathbf{c}$, and consequently dispiration defect lines with 2-branches fringes may arise [11], producing nematic-like schlieren textures. The hydrodynamic test also cannot be considered safe since the smectics allow 2D-flows (they have 1D-positional ordering only) which resemble very much the 3D-flows of nematics. As it appears in all these experimental tests essentially based on texture observations in disordered samples, the difference between nematics and smectics is not always obvious. It is to be noticed too that the X-ray diffraction patterns differ quantitatively from those obtained in the nematic phase, with the small angle ring, typical of smectic order, sharper and more intense. This difference may however not be so well-cut and cannot systematically lead to the right answer. So, in some particular cases, it could eventually be impossible to deliver a sure diagnostic with non-oriented samples.

The above tests on the textures can become more certain and even unambiguous if one makes use of uniformly oriented samples. With the planar or bookshelf alignment, for instance, samples in the smectic C phase can eventually be recognized by means of the dislocation lines parallel to the smectic layer direction, close to the glass plates. In the sampe spirit, one may also pay attention to the characteristic effects of external fields applied to the sample. In particular, it is easy to observe the unidirectional flow produced when applying a slight pressure with a spatula upon the cover glass. One may finally perform X-ray diffraction on samples uniformly oriented with a strong magnetic field, and obtain typical patterns with four sharp and intense spots in the smectic C phase. In the nematic phase, these spots also exist due to the cybotactic groups, but fainter and more diffuse.

EVIDENCE OF BIAXIALITY

The different experimental methods available to provide evidence of biaxiality in a nematic sample, are naturally based on the observation of

characteristic properties of biaxiality [12]; they are well-known too. The proofs that they yield, are actually more delicate and misleading than those recalled above for proving the nematic phase. They generally make use of macroscopic averages over all the molecules in a sample. They may therefore be divided into two subclasses according to whether the sample is perfectly oriented as a monocrystal, or just disoriented in a so-called powder.

Uniformly Oriented Samples

Without going too much into the details, let us just recall here that the biaxiality may be evidenced by measuring the coupling constants of the nematic phase to external fields in a uniformly oriented sample. The magnetic susceptibility, the dielectric constant, the conductivity, the diffusivity, *etc*... should thus appear to be tensorial quantities with three different coefficients in a biaxial sample. In fact, such measurements are often not very realistic since they should need perfectly oriented biaxial samples in the three canonical configurations, with alternately the three biaxial directors perpendicular to the sample plates.

The more practical physical constants to be determined experimentally, are the optical indices which couple light to the nematic phase. They are measured with interferometric methods, generally in oblique incidences with experiments essentially equivalent to conoscopy. In conoscopy, the birefringence Δn and the biaxiality δn are determined from distance measurements between the interference fringes, more specifically from the ring radii and the cross splitting, respectively (Fig. 1).

Biaxiality may also be evidenced in uniformly oriented samples by means of NMR. This technique is really rich. It yields direct measurements of the

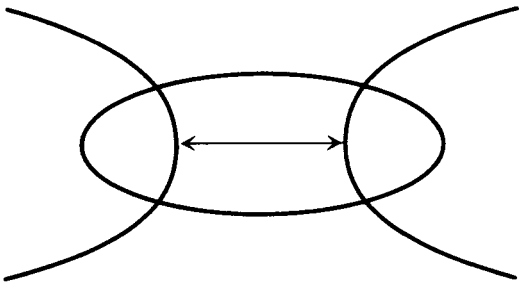


FIGURE 1 Biaxial conoscopic pattern. The diameter of the elliptical rings and the splitting distance marked with the arrow on the figure, respectively yield the two optical index differences, the birefringence Δn and the biaxiality δn.

order parameter from the splitting of the spectral line shapes. Moreover, it allows one to perform other types of measurements like spin echo and spin relaxation [13], which give complementary information on spin diffusion around the biaxial elementary objects, and therefore on their shape. These measurements however, are rather indirect, and they need theoretical models in order that one may extract useful information. They moreover are well-adapted to the lyotropic case only, where the diffusion of the counterions in the water surrounding the micelles may give indirect information on the micellar shape. In the thermotropics, because the spins keep attached to the molecules, a similar mechanism does not work. Let us notice also that the NMR technique in itself, is less accurate for uniformly oriented samples than optical interferometry for instance, due to the relatively large width of the line shapes.

In the same spirit, one may measure the structure factors of the short range order in the nematic phases by means of X-ray or neutron scattering. The same problem of limited accuracy arises here again, because diffraction being essentially sensitive to positional order which is only short range and poorly correlated in the nematic phases, the diffracted line shapes are really broad. Nevertheless, this method may allow for the determination of three different kinds of diffuse spots in uniformly oriented samples, typical of a local positional order with three characteristic lengths, giving evidence of biaxial orientational order at the same time [14].

To finish with the advantages of the uniformly oriented samples for evidencing biaxiality, let us mention the possibility that they yield for looking at the dynamics in the N_b phase without mixing the fluctuation modes. For instance, with light scattering, they allow one to study the characteristic relaxation times and the average amplitudes of the biaxial modes, the soft and the Goldstone modes, individually [15].

Disordered Samples

Though generally less conclusive, experiments which yield macroscopic averages may also be performed in disordered samples, *i.e.*, in powders, for proving biaxiality. X-ray and neutron scatterings should thus exhibit patterns with superimposed rings of three different radii. Unfortunately, as discussed above, the positional correlations in the nematic phases are weak and the corresponding distances poorly defined. The diffracted rings are therefore diffuse and they mix together becoming practically unseparable and useless for drawing conclusions about biaxiality.

With more success, one may study the dynamics of the mode at zero wave-vector by means of dielectric relaxation measurements. Such an experiment is naturally easier to perform than light scattering, since the sample may be disoriented, but of course, less instructive too.

NMR measurements may also be performed in partial powder samples. In this case, the sample is not completely disordered, but spun about an axis perpendicular to the applied magnetic field, at an angular frequency larger than the inverse of the characteristic relaxation time. In this manner, 2D-averagings are performed which yield recordings as shown in Figure 2, and which allow one to reach to real conclusions about biaxiality. This method is considered to be safe because in principle it does not need perfectly oriented samples [13].

Local Probes

To finish with the different experimental methods useful for investigating biaxiality, let us mention the local probes that the defects themselves constitute. The major advantage of the defects is that they do not make any averaging and therefore they are not sensitive at all to orientation gradients. Defect inspection is thus naturally indicated in the case of compounds difficult to orient uniformly. Formally, three kinds of disclination lines should be observed in the N_b phase with the strength 1/2 and one with the strength 1, with particular conditions at their intersections [16]. The real observation of three, or at least two, 1/2-disclination lines should then be sufficient to prove biaxiality since the N_u phase exhibits only one kind of

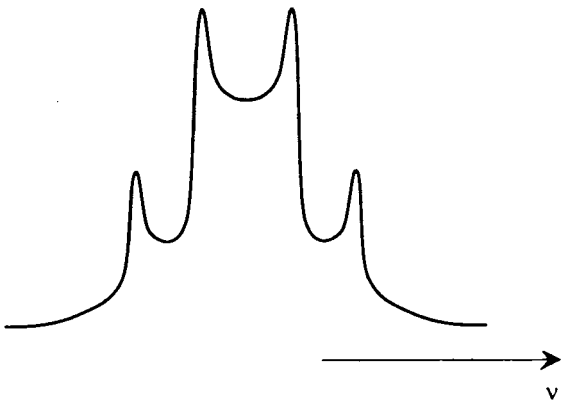


FIGURE 2 NMR-spectrum of a biaxial phase with a two-dimensional powder orientation.

1/2-disclination lines. Other characteristic features of the biaxial disclination lines may also be noticed to diagnostic the N_b phase, as their zigzag shapes with a temperature dependent angle [10], or their crossing rules relative to one another [16].

DIFFICULTIES IN PROVING BIAXIALITY

Let us now look further into the difficulties which have to be overcome when trying to prove biaxiality in a nematic phase. Clearly, the gradient effects make major troubles with the methods which take an average over a macroscopic sample which is supposed to be uniformly oriented, as where coupling constants to an external field are measured. Let us consider, for instance, the case of the dielectric constant ε. This is a uniaxial or biaxial tensor with two or three different eigen-values according to the nature of the nematic phase, uniaxial or biaxial. The measured quantity is in fact, the average of $<\mathbf{R}^{-1}\cdot\boldsymbol{\varepsilon}\cdot\mathbf{R}>$ where $\mathbf{R}$ is the rotation tensor which describes the local orientation of the nematic phase referred to the laboratory frame. In disordered samples, $\mathbf{R}$ depends on the space coordinates, and the average $<\mathbf{R}^{-1}\cdot\boldsymbol{\varepsilon}\cdot\mathbf{R}>$ may be biaxial even if ε is a uniaxial tensor. The uniaxial nematic phase may then look to be a biaxial one. The same consequences arise in particular, in conoscopic experiments and their equivalents. Let us make explicit this effect in the case where the orientation gradients are just vertical (Fig. 3a). To simplify, we may roughly sketch the sample as made of two symmetric parts (Fig. 3b). Each of these elementary samples is uniformly oriented in a tilted direction and would produce an off-centered conoscopy cross (Fig. 3c). Let us focus on the center of the conoscopy pattern. It corresponds to the light ray perpendicular to the sample which is composed of two waves, ordinary and extraordinary. At this point, the path difference between the waves for the elementary samples, δ_0, is non-zero since the corresponding conoscopy cross is off-centered and therefore some light arises from the polarizer. The total path difference at the center of the figure for the whole sample has therefore a non-zero value, $2\delta_0$, making the light reappear, and the conoscopy cross to split as if the sample were biaxial (Fig. 3d). Naturally, such an observation is *a priori* confusing with that performed on a true N_b sample. Fortunately, as we shall recall it in the next chapter, it is not much difficult to avoid this problem.

The problems which arise from the NMR technique are similar. The measured line shape splitting $\Delta\nu \sim S < P_2(\cos\theta) >$ mixes the orientational order parameter of the molecules S, with the statistics of the orientations

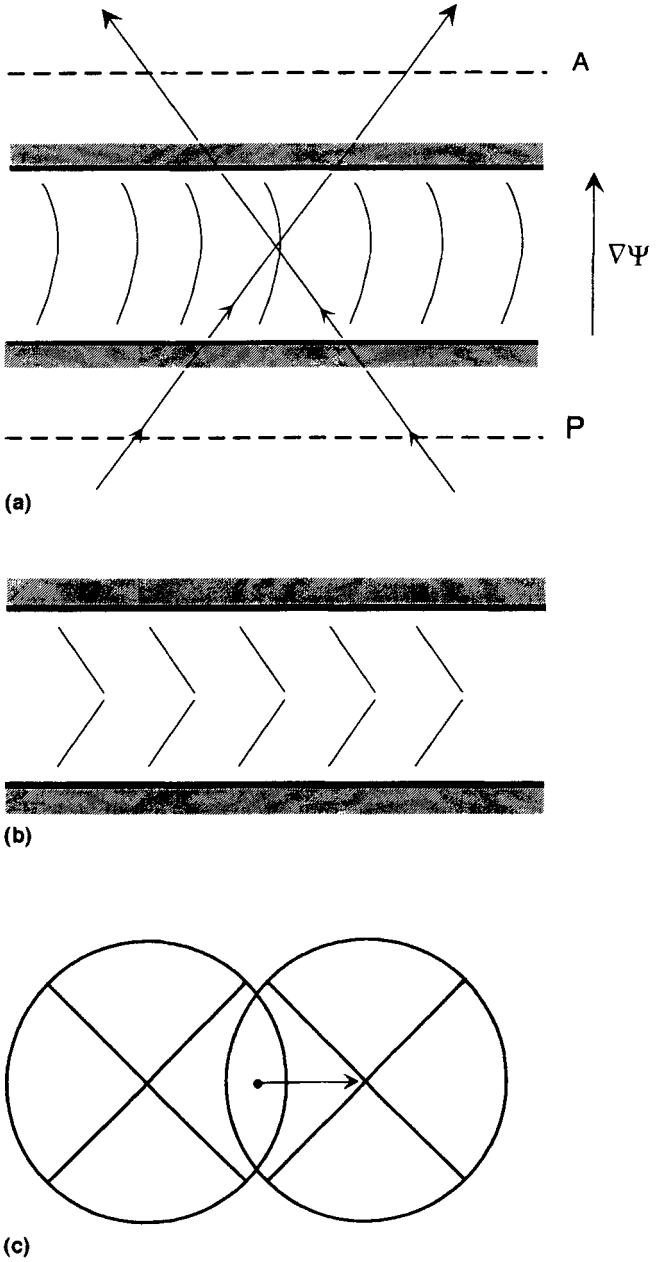
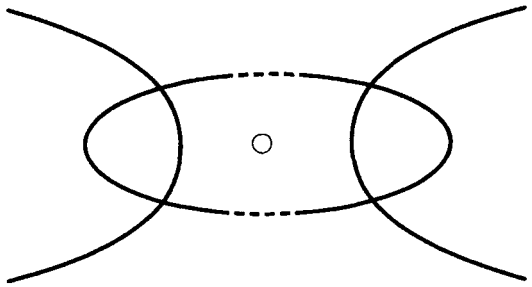


FIGURE 3 Biaxial-like conoscopy pattern in a uniaxial sample containing orientation gradients. a – General schematic of the conoscopy experiment. The sample with vertical orientation gradients ($\nabla\Psi$) is placed between crossed polarizers and shined with a converging light; b – Orientation gradients sketched as uniformly oriented domains; c – Off-centered uniaxial crosses produced by each of the uniform parts of the sample sketched in Figure 3b. The center of the conoscopy pattern which corresponds to the normal ray, is marked by a closed dot; d – Final interference pattern. Some light arises at the center. The cross is therefore split.



(d)

FIGURE 3 (Continued).

into the sample, expressed by the average Legendre polynomial $< P_2(\cos\theta) >$. Orientation gradients may thus give again the illusion of biaxiality. Let us notice that the powder spectra obtained with rotating samples, are not free from orientational problems too. In particular, their statistics should be purely two dimensional, otherwise they could erroneously give a biaxial answer. This condition means that the sample should be perfectly oriented in its rotating frame, which is probably more difficult to realize than in the laboratory frame if one considers the effects of possible hydrodynamic perturbations produced from unavoidable variations in the angular speed of rotation. The other NMR measurements are restricted to lyotropics and more delicate to use since they yield rather indirect informations which need one to chose a specific model to extract. For instance, the spin relaxation data in the lyotropic nematics, may be exploited only if one knows or guesses the shape and the dimensions of the micelles, together with the most probable paths of of the diffusing ions.

More subtle, though fundamental, errors may also occur. Among them, let us mention confusions between the short and long range orders in non-oriented samples. As X-ray or neutron scattering shows in the lyotropic nematics, the short range order in the uniaxial nematic phases, is often of the biaxial type up to a distance of a few elementary units [15]. Biaxial measurements in disordered samples require special attention to be paid to the correlation length of the biaxial order. The same problem may naturally arise with the NMR experiments which also only see the local environment of the molecules, or of the micelles.

Another mistake that currently arises when trying to prove biaxiality originates from an incorrect analysis of the defect lines in the nematic phase.

Let us recall that the observation of zigzag disclination lines under a polarizing microscope does not prove biaxiality in itself since similar zigzag lines do exist in the uniaxial nematic phases too [9]. The existence of two or three different kinds of lines should not be more conclusive. Mirages or light focusing lines, resembling disclination lines in an overlooking inspection [17], may be observed in distorted samples too. As sketched in Figure 4, the director distortions modulate the extraordinary optical index forming converging and diverging lenses from place to place in the sample. Most probably, these lenses are rather cylindrical than spherical, which is a too symmetrical shape to have a real chance to occur spontaneously. The light of the microscope is thus focused along lines parallel to the axes of the cylindrical distortions. Very often, the distortions are produced by hydrodynamic flows. In this case, they may be decomposed in individual vortices, each one with a roughly toric shape coiled around. Their focalisation lines then make closed loops which may easily be confused with disclinations, since they involve the extraordinary index only and thus obey the same polarization rules as the disclinations. So, being optical images produced by index gradients, *i.e.*, mirages, the focal lines rather complicate the defect analysis in the nematic phases. In particular, they make the observation of crossings between disclination lines really problematic [18]. To this particular goal, the nature and the direction of the disclination lines should be both controlled, which is not an easy task, even in the lyotropic case where, to our knowledge, such a crossing between disclination lines has not been observed yet. On the whole, the great advantage of the defect inspection for proving biaxiality, that it is insensitive to the sample alignment quality, is partially compensated by the special care that the analysis needs.

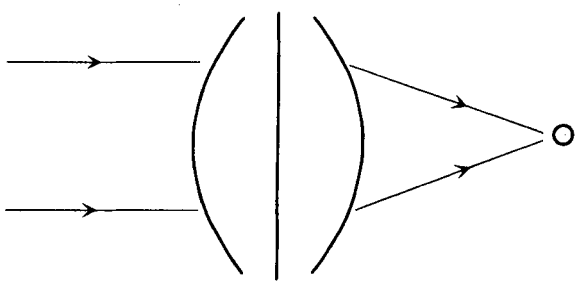


FIGURE 4 Nematic distortion forming a converging lens for the extraordinary rays, and focusing them in a place which looks like a defect.

HOW TO AVOID MISTAKES IN PROVING BIAXIALITY?

Contrary to the general feeling that these remarks may have produced, it is not excessively difficult to really prove biaxiality, and to avoid the experimental traps evoked above. Let us now summarise the situation.

Coupling Constants

The measurements of coupling constants, *e.g.*, magnetic susceptibility, dielectric constant, conductivity, diffusivity,... as first suggested above to evidence biaxiality, indeed contain too restricted information by themselves to be easily treated against the problems arising from the orientation gradients. The only means left then, that should always be performed, consists in testing the reproducibility on repeating the measurements under different experimental conditions, different sample thicknesses and anchoring treatments, and then by comparing them. The measurements should be reproducible only if the sample were really biaxial, not in the case of an apparent biaxiality due to gradient effects, provided that the experimental conditions are effectively changed between the measurements.

Conoscopy

The case of conoscopy as a method for measuring the coupling constants of light, *i.e.*, the optical indices, is special since it is able to yield a lot of information when performed with some care, and in particular, it is able to tell alone if orientation gradients eventually pollute the results or not. If orientation gradients do exist, the sample may be decomposed in uniformly oriented parts that the converging light shines separately. Each of these parts yield a different conoscopic cross that interferes with the others on the screen. Let us for instance, consider the case where the sample is uniaxial and roughly equivalent to two uniformly oriented samples in a side position as shown in Figure 5a. This case is somewhat different from the case discussed in Figure 3, but comes to about the same result. The two conoscopic patterns arising from the two parts aside, are differently tilted uniaxial crosses (Fig. 5b). Since they arise from the same converging beam, they interfere on the screen across their common field around the central region, and they roughly yield the pattern of a split cross with elliptical rings (Fig. 5c). In the interference region, the fringes are destroyed and they recombine differently, making breaks in the conoscopic rings that the true biaxial sample never exhibits. With these

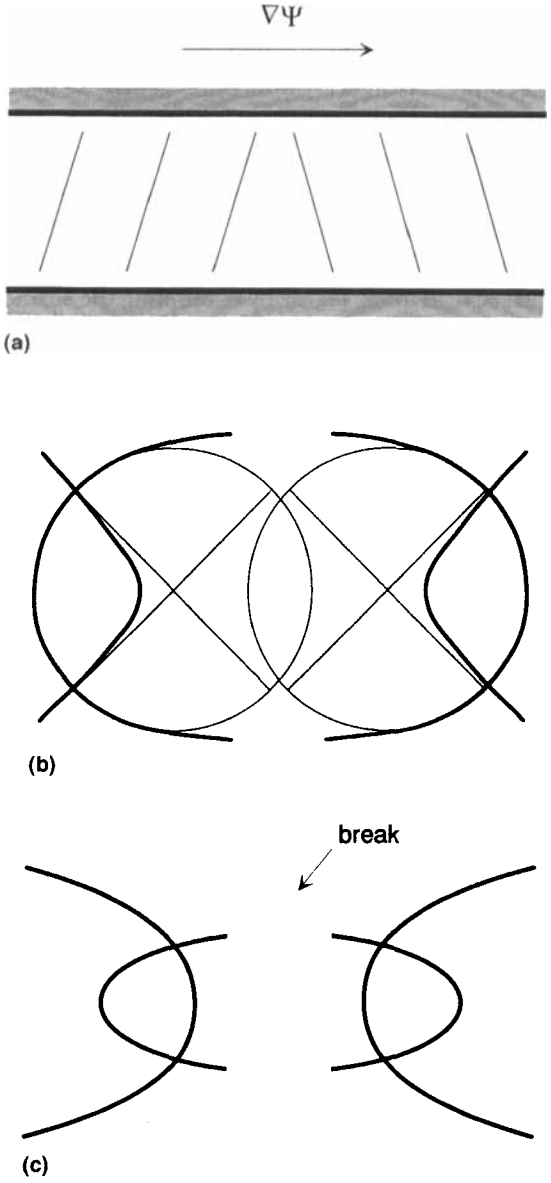


FIGURE 5 Broken conoscopy pattern in a uniaxial sample with orientation gradients. a – Uniaxial sample with an horizontal orientation gradients; b – Shifted uniaxial crosses arising from each uniformly oriented parts of the sample in the case of imperfect light focussing; c – The interference between the two shifted crosses produces some confusion in the mid screen where they overlap (in grey). Conversely, the light on the two sides of the screen arises from uniformly oriented areas, and consequently, produces well-contrasted fringes there. On the whole, the conoscopic pattern eventually resembles very much that of a biaxial sample, but with breaks in the fringes.

remarks, we conclude that conoscopy may be used to prove biaxiality provided that the characteristic biaxial patterns are observed entirely without any breaks in the elliptical fringes [7], or in other words, we deduce that, unless several and complete rings are actually observed with a constant and strong contrast all along, conoscopic measurements cannot be invoked for proving biaxiality. Naturally, the major difficulty with conoscopy, consists in orienting uniformly the two (i.e. three) biaxial directors of the sample at the same time. This condition has been achieved rather simply in the lyotropics by means of the surface field alone [1], or by combining the surface field with an applied magnetic field [7]. In the case of the thermotropics, this alignment problem could be experimentally difficult to solve, when a biaxial nematic really becomes available.

X-ray and Neutron Scatterings

The same problems with the alignment quality also arise in the X-ray and neutron diffraction experiments performed on uniformly oriented samples, with even more difficulties since very thin glass windows are required then. If however, one accepts to work with disoriented samples, let us recall that the three diffracted bands should be very broad, because of the weak positional order in nematic LC's. They could moreover be close to one another and therefore difficult to separate, if the molecular shape anisotropy is weak; and this will probably be the case with the thermotropics since it seems difficult to synthesize liquid crystal compounds with a large molecular anisotropy. Let us incidentally recall that small shape anisotropies ~ 2 as in lyotropics, may be sufficient to induce the N_b phase, although the Onsager's criterion requires shape anisotropies ~ 10, provided that the interactions between the molecules are highly anisotropic and strong enough to add up significantly to the steric interactions [19]. X-ray and neutron scattering therefore seem less promising tools for a first proof of biaxiality in a new compound than conoscopy. If performed on a disoriented sample, they moreover should be complemented with the determination of the correlation length of the biaxial order, for instance by means of light scattering measurements [15], to distinguish from the short range biaxial order in the uniaxial phases as discussed above.

Defects Inspection

It is not so difficult to analyze correctly the disclinations in a nematic phase, and to use them subsequently for proving biaxiality. In particular, it is not

difficult to distinguish them from the focal lines mentioned above. For that, one has to pay attention to the width and contrast of the lines. They should be regular all along if the lines are really disclinations. On the opposite, if they are focal lines or mirages, their optical appearance should continuously vary according to the undetermined geometrical parameters of the quasi-cylindrical lenses that produce them, and which are built up in the sample by the distortions. For instance, an increase of the lens width increases the light intensity collected by the lens, and consequently also increases the contrast of the line from the background, while variations in the focal distance defocus the line, and therefore result in changes in both its width and contrast.

To clarify the observations on the defect lines, let us first recall some typical features that the 1/2-disclinations should exhibit in the N_b phase depending on the director **m**, **n**, or **l**, that, as uniaxial objects, they bear [17], and let us consider the simple case, which seems the most current one in the thermotropic liquid crystals, where biaxiality is small compared to birefringence, *i.e.*, a small biaxial order parameter. The sample is then close to the N_u to N_b phase transition, at a distance formally measured by the temperature difference ΔT. We may then call **n** the uniaxial director, which persists into the N_u phase, and **m** and **l** the two biaxial ones. The disclinations of the **m** and **l** types, which respectively bear the biaxial director **m** or **l**, exhibit pretransitional behaviors. For instance, the angle of the zigzags that they make in a quasi-uniformly oriented sample, decreases to zero as ΔT [10]. However, most of their physical properties keep about constant across the N_u to N_b phase transition, with negligible pretransitional behaviors. More specifically, because the **m** and **l** disclination lines destroy the **n** director as the disclination lines do in the N_u phase, they produce similar breaks in the amplitudes of the optical indices in both the phases. The optical contrast and the visibility of the **m** and **l** disclinations therefore keep roughly the same in the N_b and N_u phases. Also related to the **n** destruction, their free energy and their line tension keep roughly independent of temperature across the N_u to N_b phase transition. The viscosity coefficients behaving smoothly also around the transition, we deduce that the relaxation rate of the free disclination lines of the **m** and **l** types is as fast in the N_b phase as in the N_u phase too.

The **m** and **l** lines have rather high energies since they both break the **n** director. The most energetic one, the **l** line in the lyotropics of Ref. [17], should therefore be unstable and should decompose into the two other 1/2-disclinations, namely the **m** and the **n** lines, according to the addition rules of the quaternions [16]. Only two of the three 1/2-disclinations should thus be observed at the same time in the same sample, the **m** and **n** lines.

The **n** lines are clearly different from the two other types of lines. Bearing the **n** director, they break the two biaxial **m** and **l** directors, *i.e.*, they break biaxiality. Close to the biaxial transition, their contrast decreases therefore as the square of the biaxiality, *i.e.*, $\sim\Delta T^2$, and they finally vanish at the transition, justifying the appellation of vanishing lines proposed in Ref. [17]. Their total line tension, which again includes the core energy and the elastic energy relative to the distortions of the biaxial directors, is proportional to the biaxial elastic constants, *i.e.*, $\sim\Delta T$. It results that the relaxation time of the vanishing or **n** lines, proportional to the average viscosity divided by the line tension, diverges as ΔT^{-1} close to the N_u to N_b phase transition. They therefore shrink extremely slowly when approaching to the biaxial transition, very differently from the **m** and **l** lines. In principle, the **n** lines make cusps and zigzags as the other 1/2-disclinations in the N_b phase, but because they are only weakly coupled to the **n** field, the cusps remain negligible and unobservable, just making so-called ghost point defects on the **n** lines [17]. Naturally, farther from the biaxial transition, breaks reappear along the line, producing observable zigzags as on the other disclinations. As they may anchor onto the solid surfaces of the sample, and since they have an extremely low line tension, these **n** lines may often keep zigzagging when coming back close to the biaxial transition until they completely disappear. Such a non-equilibrium observation is nevertheless not really confusing since it may be avoided on passing the transition in the other way, from the N_u to N_b phase.

To finish with the characteristic features of the biaxial defects, let us recall that the disclinations of strength 1 are topologically stable in the N_b phase contrarily to the N_u case where they actually escape in the third dimension. Nevertheless, as far as we know, they have not been observed yet in a confirmed N_b phase. This probably means that they are energetically unstable and that they immediately decompose into two 1/2-disclinations. Incidentally, the point defects stuck onto the sample plates should not be confused with 1-disclinations perpendicular to the sample, though they could both appear as decorated with four fringes between crossed polarizers. A simple test is to observe the 1-disclinations as real lines running across the sample at least in some parts of it. Though this situation should occur naturally, since the lines cannot always be perpendicular to the sample, one may eventually help them to appear on exerting a small shear onto the sample in order to tilt them substantially in the bulk of the sample. If the lines definitely refuse to appear, one may then surely conclude that point defects are actually observed indeed. The four branches defects are therefore not a proof of biaxiality, nor conversely a proof of uniaxiality.

On the whole, the typical features of the biaxial defects appear relatively easy to handle with. The behavior of the contrast, relaxation rates, and zigzag angles of the lines, should not be missed, even in the haste to discover the first thermotropic N_b phase. Combined together, they may yield a clear and sure diagnostic of the N_b phase.

Variations of Physical Parameters

Although certain conclusions about biaxiality in a nematic sample may directly be reached by considering its biaxial behavior, it is also of benefit to study the dependence of its physical properties on parameters such as temperature or external fields. Such analyses are generally easy to perform. They should therfore be recommended as key-controls for the biaxiality in addition to the reproducibility test suggested at the beginning of this chapter. Temperature is the easiest external parameter to vary. It allows one to readily perform an order parameter analysis on plotting the invariants of the biaxial order parameter as functions of temperature. As shown in the lyotropics [7], the invariants of the order parameter behave linearly in the classical regime, *i.e.*, farther from the biaxial transition than $\sim$0.01 K [20]. Such a behavior is easily evidenced in the case of a real N_b phase. In particular, this analysis shows that the biaxial order parameter cannot both keep constant and small close to the N_u to N_b phase transition. Conversely, far from transition, the order parameter should be observed to be steady, but large. Such a criterion may even be used in the case of row conoscopic patterns where estimates of the biaxial order parameter are just available from the ratio of biaxiality over birefringence. It should at least avoid contradictory assertions. In this manner, one should also be able to distinguish from anchoring transitions or temperature dependent elastic constant effects which under some circumstances, could simulate the N_u to N_b phase transition.

Other typical temperature variations of the N_b physical properties may serve to prove biaxiality, as those concerning the defects, namely the zigzag angles, contrast and relaxation rates according to the disclination type. Varying the aligning fields may also be an indirect but efficient way to prove biaxiality, on showing that the orientational gradients are negligible, and thus that the observed biaxiality is a real one. With their coupling to sample alignment, the fields provide a practical means to evaluate the gradients' amplitude, and eventually therefore, to really prove that the samples are well-oriented. One may, for instance, proceed by comparing the reduction in gradients that the fields produce, with the calculated one. Among these field parameters, the sample thickness should naturally not be forgotten since it

governs the relative importance of the surface to the whole sample volume for the anchoring fields. The usual electric and magnetic fields may be used too, and although it may not be necessary to estimate the orientational gradients as suggested above, one should at least pay attention that the biaxiality variations that they induce are negligible, just by varying the magnitude of the applied fields. In the opposite case, field-dependent orientational gradients should most probably arise and produce some apparent biaxiality. If nevertheless, only real biaxiality is induced by the field, it should be ascertained that its variations with both the field amplitude and the temperature obey the classical laws, especially close to the N_u to N_b phase transition. Let us finish with the advantages of varying the physical parameters in the experiment, by noting that it is a practical way for performing measurements in different conditions, and therefore for testing reproducibility, as always necessary in physics, particularly when trying to evidence controversial physical properties.

CONCLUSIONS

So, though it is not a straightforward task to really prove biaxiality in a thermotropic LC sample, different means are actually available for one to avoid the traps mentioned above. Two of them seem to stand out, which are conoscopy and defects inspection. Conoscopy is probably easier to perform, but with the major drawback that it needs perfectly oriented samples. To justify this crucial point, one should therefore demand the observation of conoscopic patterns with several entire and contrasted rings, and verify that the measured biaxiality behaves normally under the control parameters such as the temperature and the applied fields. In particular, the biaxiality should not be observed to decrease with the applied fields. This effect would most probably be the signature of orientation gradients which naturally decrease with the applied fields. Conversely, a truly induced biaxiality, if not negligible, would increase under the fields action. At least, one may simply test that the measured biaxiality is reproducible, and independent of the applied fields, of the sample thickness, and of the other preparation conditions. The inspection of defects may be a sure manner for proving biaxiality too, provided that some caution is taken. In particular, the disclination lines should not be confused with mirages. To be sure, the width and contrast should be constant all along the lines. Several types of disclination lines should then be observed with characteristic variations of the zigzag angles, contrasts and relaxation rates as functions of temperature.

To conclude, it is to be hoped that the experimental methods for proving biaxiality recalled here, will be received constructively, and that they will eventually help to reduce the actual confusion about the thermotropic N_b phase, and perhaps to restore the interest of the scientific community upon biaxiality in liquid crystals. Also hopefully the real discovery of a thermotropic N_b phase will occur soon, and will at the same time definitely close the polemics about this fascinating phase in the thermotropic liquid crystals.

References

[1] L. J. Yu and A. Saupe, *Phys. Rev. Lett.*, **45**, 1000 (1980).
[2] J. Malthête, L. Liébert, A.-M. Levelut and Y. Galerne, *Compte R. Ac. Sciences*, **303**, 1073 (1986).
[3] S. Chandrasekhar, B. K. Sadashiva, B. R. Ratna and V. N. Raja, Pramana, *J. Phys.*, **30**, L 491 (1988).
[4] K. Praefcke, B. Kohne, B. Gündogan, D. Demus, S. Diele and G. Pelzl, *Mol. Cryst. Liq. Cryst. Lett.*, **7**, 27 (1990).
[5] F. Hessel and H. Finkelmann, *Polymer Bulletin*, **15**, 349 (1986).
[6] A. Saupe, Workshop on "Order in Fluids", TUB and Wissenschaftskolleg zu Berlin, Germany (1990).
[7] Y. Galerne and J.-P. Marcerou, *Phys. Rev. Lett.*, **51**, 2109 (1983); *J. Physique*, **46**, 589 (1985).
[8] P.-G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, Clarendon (Oxford) 1993.
[9] Y. Galerne, J. Itoua and L. Liébert, *J. Physique*, **49**, 681 (1988); M. Mihaïlovic and P. Oswald, *J. Physique*, **49**, 1467 (1988).
[10] Y. Galerne and L. Liébert, *Phys. Rev. Lett.*, **55**, 2449 (1985).
[11] Y. Takanishi, H. Takezoe, A. Fukuda, H. Komuara and J. Watanabe, *J. Mater. Chem.*, **2**, 71 (1992).
[12] Y. Galerne, *Mol. Cryst. Liq. Cryst.*, **165**, 131 (1988); and references therein.
[13] B. Halle, P.-O. Quist and I. Furo, *Liq. Cryst.*, **14**, 227 (1993); and references therein.
[14] Y. Galerne, A. M. Figueiredo Neto and L. Liébert, *J. Chem. Phys.*, **87**, 1851 (1987).
[15] M. B. Lacerda Santos, Y. Galerne and G. Durand, *Phys. Rev. Lett.*, **53**, 787 (1984).
[16] G. Toulouse, *J. Physique Lett.*, **38**, L-67 (1977).
[17] Y. Galerne, *Mol. Cryst. Liq. Cryst.*, **292**, 103 (1997).
[18] T. De'Neve, M. Kléman and P. Navard, *J. Physique II*, **2**, 187 (1992).
[19] Y. Galerne, A. M. Figueiredo Neto and L. Liébert, *J. Chem. Phys.*, **87**, 1851 (1987).
[20] P. Boonbrahm and A. Saupe, *J. Chem. Phys.*, **81**, 2076 (1984).