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ELECTRIC FIELD INDUCED BIAXIALITY IN THE NEMATIC PHASE

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Resumé. — Les techniques de résonance magnétique nucléaire ont été employées pour démontrer l'existence de l'ordre biaxiale induit par champs électriques dans la phase nématique.

Abstract. — Nuclear magnetic resonance techniques were used to determine the presence of electric field induced biaxiality in the nematic phase of MBBA.

Electric fields have been observed to produce optical rotations in thin nematic films ascribable to induced biaxiality [1]. In the present paper we report a direct observation of electric field induced biaxiality in a bulk nematic sample using NMR techniques. These preliminary measurements demonstrate that these techniques may provide a powerful tool for elucidating biaxial order parameters in a variety of liquid crystal phases.

1. Molecular order in the nematic phase. — The simplest picture of the molecular order present in the nematic phase views the molecules as tumbling about some locally preferred direction defined by the director \( N_0 \). Taking the molecules to have cylindrical symmetry and making an appropriate statistical average of these tumbling motions then leads to a single order parameter

\[
S_{zz} = \frac{1}{2} (3 \cos^2 \theta_0 - 1)
\]

where \( \theta_0 \) is the average polar angle of the molecular axis \( M \) with respect to \( N_0 \). This order parameter is one which is easily measured directly, as the spin interactions observed in an NMR experiment transform in this way. In particular, the second moment \( M_2 \) of an NMR absorption line with a dipolar interaction is proportional to \( S_{zz}^2 \).

Most molecules forming liquid crystalline phases depart from this simple cylindrical symmetry. In order to satisfactorily account for the observed experimental data and to be able to discriminate between various theoretical treatments, it is necessary to consider more complex order parameters.

In the following discussion considerable use has been made of the lucid treatment of order parameters and the calculational aides in reference [2]. It should be stressed that this approach differs from that generally used, particularly in aligned solvent studies [3]. In solvent studies, well defined axes on the molecule are taken as a reference, and all angles are referred to these axes. This approach for a nematic phase leads to the Saupe order matrix [4] whose elements contain five order parameters. In the approach used by Doane [2] a different description results. In his treatment the basic coordinate system is taken to be the principal axis system of the interaction of interest. This interaction basis is the natural system, in that it is the major axis of this coordinate frame which aligns with the director. Because of the symmetry of the interaction frame, the number of order parameters required is reduced. In particular, for a uniaxial apolar nematic phase only two order parameters are required.

While both of these formulations are in principle equivalent, the latter has certain advantages for our purposes. For example, although the interaction coordinates are not exactly known, this approach yields physical descriptions which are diagonal in the order matrix elements. A physical measurement of a parameter such as a quadrupole splitting yields a direct measure of these diagonal elements and is thus easily interpretable. In contrast, using well defined basis coordinates requires that certain assumptions be made in order to render the results in a diagonal form. In the example case of quadrupole splittings one would need to have accurate values for the magnitudes of the various quadrupolar interactions in order to perform this diagonalization.

The nematic phase is normally uniaxial, that is, only a single director is required to describe the molecular order. If one considers the dipole interaction of pairs of identical spin one-half particles, such as protons, on molecules ordered in a nematic phase,
then one obtains the following expression for the second moment of the NMR absorption line:

$$\begin{align*}
M_2 &= \frac{9}{4} \left( \frac{\gamma^2 h^2}{2 \pi} \right)^2 \left( \frac{3}{2} \cos^2 \theta_0 - \frac{1}{2} \right)^2 \times \\
& \quad \times \sum_{p \neq q} \frac{1}{r_{pq}^6} \left\{ S_{zz} \left( \frac{3}{2} \cos^2 \beta_{pq} - \frac{1}{2} \right) \\
& \quad + \frac{1}{2} \left( S_{xx} - S_{yy} \right) \left( \sin^2 \beta_{pq} \cos^2 \sigma_{pq} \right) \\
& \quad + \frac{1}{2} \left\langle \sin 2 \theta \sin \psi \right\rangle \left( \sin 2 \beta_{pq} \right) \right\}^2,
\end{align*}$$

(1)

where the summation is taken to be only over spins on the same molecules and where $\theta_0$ is the angle between the magnetic field and the time averaged principal $z$-axis of the interaction, $\alpha$ and $\beta$ are the angles of the principle instantaneous interaction axes in the frame of the molecules, and $\theta$, $\psi$ and $\zeta$ are the angles describing the orientation of the molecular axes in the frame of the time averaged interaction.

The order parameter terms are defined by:

$$S_{zz} = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle,$$

$$\left( S_{xx} - S_{yy} \right) = \left\langle \frac{3}{2} \sin^2 \theta \cos 2 \psi \right\rangle,$$

and

$$\left\langle \sin 2 \theta \sin \psi \right\rangle,$$

which is zero for apolar molecules.

The expression above is rather general, and the time average on the terms involving molecular conformation have been deliberately retained because of the possibility of changes in molecular conformation with temperature as might occur at a phase transition. This is an extremely important point as the question of changes in molecular conformation may be raised as an alternative way of treating some of these data. Recent experiments by Doane [5] indicate that the molecular conformation does not change in the measurements that he reports. This may be seen from the fact that he is able to fit the temperature dependences of each of the quadrupolar splittings which he observes as a linear combination of other splittings. That is, if there are $n$ order parameters necessary to fit the observed data, then the temperature dependence of any splitting may be expressed as the linear combination of $n$ other splittings. If conformational changes were to occur, this would, in general, not be possible.

Writing eq. (1) in a simpler form taking the geometric terms to be constants, one obtains

$$\begin{align*}
M_2 &= \left( \frac{3}{2} \cos^2 \theta_0 - \frac{1}{2} \right)^2 \sum_{p \neq q} \frac{1}{r_{pq}^6} \left\{ A_1^{pq} S_{zz} + \\
& \quad + \frac{1}{2} A_2^{pq} \left( S_{xx} - S_{yy} \right) + \frac{1}{2} A_3^{pq} \left\langle \sin 2 \theta \sin \psi \right\rangle \right\}^2.
\end{align*}$$

(2)

If a second director is required to describe the molecular order then a phase is by definition biaxial. In such a phase additional order parameters are present. In particular, it can be shown that the analog of eq. (2) is of the form:

$$\begin{align*}
M_2 &= \sum_{p \neq q} \left\{ [C_1^{pq} S_{zz} + C_2^{pq} (S_{xx} - S_{yy})] \times \\
& \quad \times \left( \frac{3}{2} \cos^2 \theta_0 - \frac{1}{2} \right) + C_3^{pq} B_1 \sin 2 \theta_0 \\
& \quad + C_4^{pq} B_2 \sin^2 \theta_0 \right\}^2
\end{align*}$$

(3)

where the biaxial order parameters $B_1$ and $B_2$ are given by:

$$B_1 = \left\langle \cos \zeta \right\rangle,$$

and

$$B_2 = \left\langle \cos 2 \zeta \right\rangle,$$

and where the complexity of eq. (3) has been reduced by assuming a well ordered sample ($S_{zz} \approx 1$) and by judicious choice of axes.

2. Experiment. — Let us consider how it might be possible experimentally to induce and to observe biaxial order in a normally uniaxial phase. To understand the former we shall first consider the ordering effects of magnetic and electric fields on a nematogen exhibiting positive diamagnetic anisotropy ($\chi_{\parallel} > \chi_{\perp}$) and negative dielectric anisotropy ($\varepsilon_{\parallel} > \varepsilon_{\perp}$). In such a material the molecules will align with their long axes preferring a director parallel to a magnetic field. If there were no electric field applied then the phase would have uniaxial cylindrical symmetry. If an electric field were simultaneously applied then the phase would have uniaxial cylindrical symmetry. If an electric field were simultaneously applied a very different situation would obtain.

Consider, for example, the simplistic model shown in figure 1. There the principal values of the dielectric tensor are superimposed upon a molecule with the broken cylindrical symmetry of a flattened cigar. In the absence of an electric field, the molecules would rotate rapidly about the director (i.e., the direction of an applied magnetic field), and the resulting time averaged symmetry would appear cylindrical and uniaxial on the time scale of an NMR experiment.

![Fig. 1. — Pictorial representation of the principal values of dielectric tensor on an asymmetric molecule.](image-url)
If, in addition to a magnetic field, an electric field were applied in a direction perpendicular to the director, the director would remain parallel to the magnetic field. If, however, the electric field intensity were sufficiently high then the free rotation of the molecules about their long axes would be hindered, and a second director parallel to the electric field would be required to specify the order in the phase. It is important to note that it is not possible to induce biaxiality in this manner for molecules with a positive dielectric anisotropy.

In order to observe induced biaxiality using nuclear magnetic resonance one must do more than simply apply an intense electric field perpendicular to the magnetic field. In particular, one sees from eq. (3) that the biaxial terms vanish for \( \theta_0 = 0 \). Thus it is necessary to perform an experiment in which \( \theta_0 \) is varied in order to observe the effects of the induced biaxiality.

We have made measurements of the orientational dependence of the proton second moment \( M_2 \) in MBBA (p-methoxy-p-n-butylanaline) which has a large negative dielectric anisotropy. These measurements were made at a frequency of 30 MHz which corresponds to a magnetic field of \( \sim 7 \) kG. The measurements were made with a 5 kHz electric field with an intensity of 6 kV/cm. The frequency of this field was well above the critical field for conductivity alignment. All of the measurements reported were made using quadrature phase detection Fourier transform spectroscopy. Typical spectra are shown in figure 2 for various angles \( \theta_{IN} \) between the director and the magnetic field.

In order to insure that the director was oriented as postulated, the principal dipolar splitting of the phenyl protons was also measured. This dipolar interaction is on the para-axis (and hence nearly parallel to the long molecular axis) and, thus, should not be influenced by hindering of rotational motions about the long axis. The results are shown in figure 3. We note that the phenyl splitting follows \( P_2(\cos \theta_0) \) as predicted, while \( M_2 \) deviates strongly from the \( (P_2(\cos \theta_0))^2 \) dependences which would hold if there were only uniaxial order present.

**FIG. 3.**—Second moment of the proton resonance in fully protonated MBBA and the major dipolar splitting of the phenyl protons in MBBA versus the angle \( \theta_{IN} \) between the nematic director and the magnetic field. All data are normalized to their values at \( \theta_{IN} = 0^\circ \).

3. **Conclusion.**—The orientational dependence of the proton second moment of MBBA aligned in competing magnetic and electric fields indicate the presence of biaxial order. It is clear that second moment measurements do not provide a particularly sensitive tool for making quantitative measurements of biaxial order. Analogous measurements employing electric fields to study the orientational dependence of deuteron quadrupole splittings are currently underway in our laboratory. The quadrupole splittings are well resolved and should provide a very sensitive measure of biaxial order parameters. Finally, we note that the orientational data provide information not attainable from temperature dependence measurements alone.

**References**