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Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Version of record first published: 17 Sep 2007.

To cite this article: A. M. Thayer , M. Luzar & A. Pines (1987): Zero-field N.M.R. study of the biaxial smectic E phase, Liquid Crystals, 2:2, 241-244

To link to this article: http://dx.doi.org/10.1080/02678298708086296

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LIQUID CRYSTALS, 1987, VOL. 2, NO. 2, 241–244

Zero-field N.M.R. study of the biaxial smectic E phase

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(*Received 17 November 1986; accepted 20 January 1987*)

Preliminary results on the measurement of smectic liquid crystal phases by zero-field N.M.R. methods are presented. The non-axial symmetry of the smectic E phase is immediately apparent in the zero-field N.M.R. dipolar spectrum of a methylene dichloride probe molecule.

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Recently, we have conducted a number of zero-field N.M.R. experiments on liquid-crystalline systems. Initial experiments on aligned nematics sought to measure the order parameters in the absence of an applied magnetic field [1, 2]. The usefulness of the zero-field N.M.R. experiment lies in the ability to obtain sharp well-resolved spectra for disordered materials [3]. Whereas in an applied field the orientational anisotropy of the nuclear spin interactions produces a broadened dipolar or quadrupolar spectrum, in zero field the isotropy of space makes all interactions identical in the molecular frame. Thus even for a powder distribution of orientations, the zero-field N.M.R. spectrum consists of discrete frequencies corresponding to the nuclear spin interactions.

Many of the more interesting liquid-crystalline mesophases are the smectic phases which do not necessarily order in a magnetic field [4] unless prepared from a preceding nematic or isotropic phase. These more complex phases show a more diverse arrangement of the molecules of which it would be desirable to gain a direct measure. For example, as shown schematically for two smectic phases each with a hexagonal packing in figure 1, the molecules arrange themselves not only in layers but also in more complicated intralayer structures. The smectic B phase in figure 1 shows the rotational freedom of the molecules in the layers which leads to an axially symmetric phase. In contrast, phases such as the smectic E, have restricted rotational freedom of the molecules about the long molecular axes which is expected to lead to a biaxiality of the phase [5–7]. This biaxiality has been observed in the high-field deuterium spectra of aligned samples [6], and in the motional effects on the deuterium asymmetry parameters in a selectively deuteriated smectic E phase [7]. These studies required the use of aligned samples measured at many different orientations with respect to the applied field, to derive complete information on the system. The effect of the biaxiality is often subtle and may not be observable in the high field powder spectra of unaligned samples.

Zero-field N.M.R. spectra are very sensitive to the perturbations of small amplitude motions and the motionally induced asymmetry in dipolar coupling tensors

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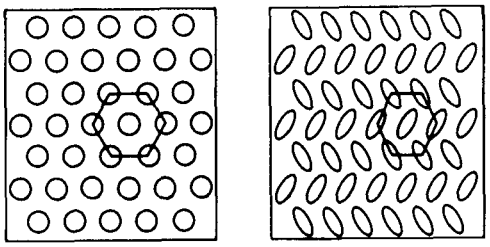

Figure 1. Schematic drawing of the molecular ordering within a layer of two different smectic liquid-crystalline phases. In the smectic B phase, the molecules are free to rotate about their long molecular axes (as indicated by the circles) and there is positional order within the plane. The smectic E phase shows a molecular packing in which the molecules can oscillate between two positions (represented by ellipses) within the layers. There no longer is the freedom of rotation about the long molecular axes which leads to a biaxiality to the phase. The methylene dichloride probe molecules are expected to reside between the molecules exhibiting the local symmetry.

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[8]. The dipolar coupling of two protons is inherently an axially symmetric nuclear spin interaction in its principal axis system. In a uniaxial liquid crystalline phase, the partially averaged dipolar tensor interaction retains this symmetry and a coupling scaled by the order parameter of the H–H internuclear vector is measured. In zero field, the state of such a nuclear spin system consists of two degenerate energy levels and a third level with energies given by,

$$\left.\begin{aligned} E_1 = E_2 &= -\frac{S\omega_D}{2}, \\ E_3 &= S\omega_D, \end{aligned}\right\} \tag{1}$$

where $\omega_D = \gamma^2 h/2\pi r^3$ and S is the order parameter of the H–H vector in the uniaxial phase. This produces three lines in the zero-field spectrum at $\pm 3S\omega_D/2$ and at zero frequency. If the dipolar coupling is observed in a biaxial phase, then the restricted reorientational freedom of the molecules induces an asymmetry, η, in the averaged dipolar tensor in the director frame [5, 6]. The asymmetry lifts the degeneracy of the two lowest energy levels to give

$$\left.\begin{aligned} E_1 &= -\frac{S\omega_D}{2}(1+\eta), \\ E_2 &= -\frac{S\omega_D}{2}(1-\eta), \\ E_3 &= S\omega_D, \end{aligned}\right\} \tag{2}$$

thereby introducing six possible transition frequencies. This situation is analogous to that of a non-axially symmetric quadrupolar interaction for a spin $I = 1$ nucleus. From a measure of the zero-field spectral frequencies, values of S and η can be determined.

We have recently obtained the zero-field N.M.R. spectra of several liquid-crystalline smectic phases and report here a direct observation of the symmetry of the phase. The zero-field N.M.R. spectrum of a methylene dichloride (CH_2Cl_2) probe

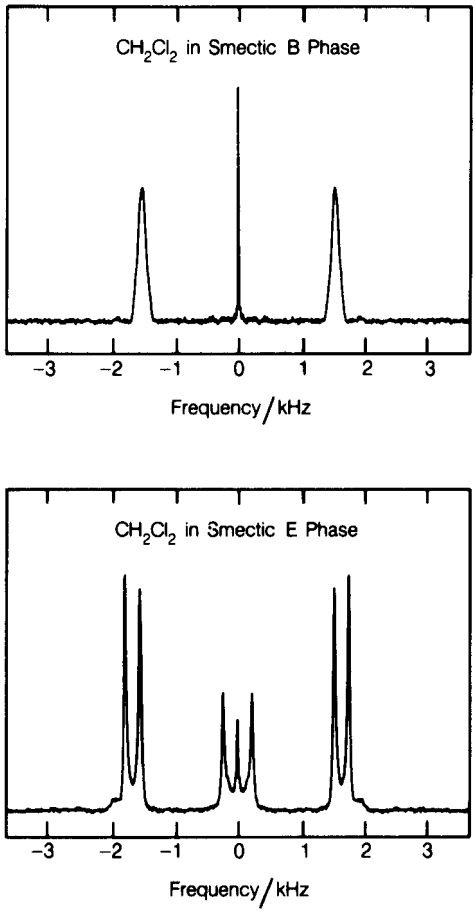

Figure 2. Zero-field N.M.R. spectra of the two protons in a methylene dichloride (CH_2Cl_2) probe molecule in smectic B and E phases. The unaligned smectic B sample produces the usual dipolar triplet in zero field from which an order parameter of the probe can be measured. The differing linewidths can be attributed to residual field effects and are not a function of the symmetry of the phase. The spectrum of the smectic E phase shows a more complicated pattern of six lines (plus one at zero frequency due to the residual field effects). The asymmetry parameter induced in the dipolar coupling by the biaxiality of the phase can be calculated directly from the spectrum.

molecule in an unaligned smectic B sample [9] (5 wt % CH_2Cl_2 in a binary mixture of 60 per cent 4-*n*-butyloxybenzylidene-4′-*n*-octylaniline (40·8) and 40 per cent 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB)) appears in figure 2. In the uniaxial smectic B phase, the resulting spectrum is a triplet of lines [2] corresponding to the axially symmetric dipolar coupling of the two protons scaled by the order parameter of the inter proton vector. The separation in frequency from zero is given by

$$\nu = S3\gamma^2 h/8\pi r^3$$

and is then a direct measure of this order parameter. The zero-field N.M.R. spectrum of the disordered smectic E phase is also shown in figure 2. This sample consists of ~ 5–10 wt % CH_2Cl_2 in a 50–50 per cent binary mixture of the same components as the smectic B phase and forms a very stable room temperature smectic E phase [9].

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The zero-field N.M.R. spectrum shows the pattern of six lines (and one at zero frequency due to residual field effects [10]); the additional lines are directly attributable to the non-axial symmetry in the dipolar coupling as induced by the symmetry of the phase. An asymmetry parameter of $\eta = 0{\cdot}208 \pm 0{\cdot}002$ and a value of $S = 0{\cdot}045 \pm 0{\cdot}001$ can be calculated for the methylene dichloride probe molecule from the spectrum.

These experiments demonstrate the further applicability of the zero-field N.M.R. experiment to the study of unaligned liquid-crystalline phases. The spectra provide direct observation of subtle features of the phases by measuring nuclear spin interactions on a molecular scale. A more detailed report of this work and its applications to other phases will appear in the near future.

We thank Professor J. W. Doane for valuable discussions concerning the smectic E samples. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. A.M.T. was supported by a General Motors Industrial Fellowship during the course of this work.

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