Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electric Field-Induced Alignment of the Directors in the Smectic A Phase of 4-Octyl-4′-Cyanobiphenyl. A Deuterium NMR Study

Geoffrey R. Luckhurst [a], Tetsuo Miyamoto [b], Akihiko Sugimura [c] & Bakir A. Timimi [a]

[a] Department of Chemistry and Southampton Liquid, Crystal Institute, University of Southampton, Southampton, SO17 1BJ, UK

[b] Department of Electronics and Physics, Osaka Prefecture University, Guken-cho, Sakai, Osaka, 599-8531, Japan

[c] Department of Information Systems Engineering, Osaka Sangyo University, 3-1-1 Nakagaito, Daito-Shi, Osaka, 574-8530, Japan

Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 347, pp. 147-156
Reprints available directly from the publisher
Photocopying permitted by license only

Electric Field-Induced Alignment of the Directors in the Smectic A Phase of 4-Octyl-4′-Cyanobiphenyl. A Deuterium NMR Study

GEOFFREY R. LUCKHURST[a], TETSUO MIYAMOTO[b], AKIHIKO SUGIMURA[c] and BAKIR A. TIMIMI[a]

[a]*Department of Chemistry and Southampton Liquid Crystal Institute, University of Southampton, Southampton SO17 1BJ, UK,* [b]*Department of Electronics and Physics, Osaka Prefecture University, Guken-cho, Sakai, Osaka 599–8531, Japan and* [c]*Department of Information Systems Engineering, Osaka Sangyo University, 3–1–1 Nakagaito, Daito-Shi, Osaka 574–8530, Japan*

Deuterium nuclear magnetic resonance (NMR) spectroscopy has been used to investigate the electric field-induced alignment of the director of the smectic A phase of the liquid crystal, 4-α,α-d_2-octyl-4′-cyanobiphenyl (8CB-d_2), at 303.3K. The electric field is arranged to be orthogonal to the magnetic field. The alignment process has been investigated at different electric field strengths and the rate of director alignment was monitored by recording the deuterium NMR spectra as a function of time after the electric field was switched on. The results reveal a complex pattern of electric field-induced director alignment. At high electric field strengths a rapid process is observed in which the director switches from an orientation parallel to the magnetic field to one in which it is parallel to the electric field. An induction period is also observed in which no apparent change in director orientation occurs. This induction period becomes longer (hours in magnitude) as the electric field strength is lowered. Other, intermediate, director orientations are observed as the electric field strength is lowered further. The role of defects is invoked in trying to interpret some of the observed processes underlying the mechanism of the director alignment in the smectic A phase.

Keywords: deuterium nuclear magnetic resonance; smectic A director alignment; induction period; electric field-induced alignment

INTRODUCTION

The defining characteristic of the smectic A phase is its layer structure with the director parallel to the layer normal. When the alignment of a monodomain SmA sample is changed by applying an aligning field, the orientation of the director, **n**, will be changed and the layered structure will have to be re-established orthogonal to the new direction. This is clearly a more complex process than the alignment of the director in a nematic phase and the following questions arise. Do the smectic layers align as a monodomain or does the mechanism of alignment involve the disruption of the original layers and their reforming around the new direction? Are there other factors such as the boundary conditions involved in this process? Is there a threshold value for the aligning field?

In an attempt to learn more about the processes involved in the alignment of the SmA phase we have used an electric field to induce the alignment of the director in the presence of the magnetic field of the NMR spectrometer. Recently, the magnetic field-induced alignment of the SmA directors has been investigated [1]. This was carried out at a fixed magnetic field of 4.7 T provided by the NMR spectrometer. One of the advantages of using the electric field in the alignment experiment is that we could vary the electric field strength and hence the torque exerted on the director. This provides us with a way to vary the rate of the alignment processes at constant temperature. We present here the results of a study of the effect on a SmA phase of applying an electric field of varying strength to align the mesophase director, $\mathbf{n}(\mathbf{r})$. The alignment process has been monitored by deuterium NMR spectroscopy which is a particularly useful method for determining the director orientation because it also allows the director distribution to be determined. A group of equivalent deuterium nuclei in a molecule which is in a uniformly aligned uniaxial liquid crystalline phase, that is one described by a single director, **n**, gives a quadrupolar doublet in the NMR spectrum whose separation is $\Delta\nu(\theta)$. This quadrupolar splitting depends on the angle, θ, between **n** and **B**, the direction of the magnetic field of the spectrometer, according to

$$\Delta\nu(\theta) = \Delta\nu(0^0)(3\cos^2\theta - 1)/2\,, \qquad (1)$$

where $\Delta\nu(0^0)$ is the splitting when the director is parallel to the field. As the director distribution broadens so new spectral features appear corresponding to specific director orientations. In particular, if the spread of the director orientations is small, then a broadening of the doublet is produced. In the limit of a random distribution the spectrum has a broad characteristic shape with an intense pair of lines coming from the director perpendicular to the field and two weak shoulders originating from the director parallel to the field. The spectra, therefore, are able to reveal how the sample is aligned in the magnetic field at various stages in an experiment provided that they can be recorded in a time which is short compared with the time scale of the alignment process.

In this study we use a slab of specifically deuteriated 4-octyl-4'-cyanobiphenyl (8CB-d_2), which has a nematic and a smectic A phase (T_{NI} = 313.8K and T_{SmAN} = 306.8K) and is deuteriated in the chain α position. Because of the positive anisotropy, $\Delta\chi$, in the diamagnetic susceptibility, the directors can be uniformly aligned in the nematic phase parallel to the magnetic field, $\mathbf{B}_0$, in the spectrometer. Cooling into the SmA phase preserves this alignment, so that a monodomain SmA is produced. As the liquid crystal sample is a slab of material confined between two glass plates that are placed parallel to the magnetic field, this SmA alignment produces a monodomain sample in a book-shelf geometry, that is with the layers orthogonal to the glass plates. This initial alignment is then changed by switching on an electric field of **E** in a direction normal to the glass plate and hence also normal to the magnetic field direction and the original director. If the electric field of **E** is sufficiently strong to overcome the torque exerted on the director by the magnetic field, by the constraining effect of the SmA structure and by the surface forces then provided the material has positive anisotropy in the dielectric permittivity, $\Delta\varepsilon$, as in 8CB, this will cause the director to align along the electric field direction. In other words, when the electric field of **E** is greater than a certain threshold value [2], the director will align along the electric field direction. The deuterium spectrum is then used to monitor how the smectic phase director aligns towards the electric field direction.

EXPERIMENTAL

The preparation of 8CB deuteriated in the α position in the alkyl chain has been described before [1]; the transition temperatures were found to agree with literature values [3].

The sample of 8CB-d_2 was contained in a flat cell made up of two glass plates and a spacer. The indium/tin oxide coated glass surface is rubbed parallel to the short side with a wire soldered to the surface. The cell is held together by a special glue which is stable in the presence of the cyanobiphenyls and can be cured using UV radiation for a few minutes. An amplifier and a function generator are used to provide a 1 kHz sinusoidal ac electric field to the cell. This frequency is sufficient to overcome the effects of ionic impurities without essentially affecting the value of $\Delta\varepsilon$. The cell is held in the NMR probe head so that the glass plates and the rubbing direction are aligned parallel to the magnetic field. The final adjustment of the cell alignment is carried out by switching the electric field on while the sample is in the nematic phase and rotating the cell using the spectrometer goniometer until a doublet splitting is obtained which is ½ (to within ± 0.2 kHz) of the splitting without the electric field (this condition means that the electric field is orthogonal to the magnetic field to within $\pm 3^0$). Samples contained in cells with thickness of approximately 50 and 100μm were examined at different temperatures and using different electric field strengths. Here we present the results for

measurements at 303.3K and for two cells by one 55.8μm thick (at 65, 60 and 55V_{rms}) and the other 100μm thick (at 100, 95 and 90 V_{rms}). The exact thickness of the nominal 100μm cell is uncertain as we do not have a method of accurately measuring the thickness and its variation over the entire cell; we are, therefore, using the nominal value of the spacer given by the supplier. The electric field strength for these two cells varies from 1.17 MV/m to 0.99 MV/m for the 55.8 μm cell and from 1.00 to 0.90 MV/m for the nominal 100 μm cell.

The spectra were recorded using a JEOL Lambda 300 spectrometer which has a magnetic field of 7.05 T. The spectra were obtained using a quadrupolar echo sequence, with a 90^0 pulse of 7 μs and interpulse delay of 40 μs. The number of free induction decays(FID), each of ~ 85 ms duration, used to produce spectra with good signal to noise varied from 4000 to 10000 depending on sample thickness and the rate of change of the director orientation. This leads, unavoidably, to a long acquisition time varying from 5 to a maximum of 15 min.

In a typical experiment, a director monodomain is obtained by heating the sample into the nematic phase. This director monodomain is found to be preserved in the smectic A phase by cooling the sample slowly from the nematic phase. To ensure a good SmA monodomain, the sample is then allowed to anneal for at least one hour before the electric field is switched on and the director alignment measurement started.

RESULTS AND DISCUSSION

A typical deuterium NMR spectrum for 8CB-d_2 in the SmA phase at 303.3K consists of a doublet with a quadrupolar splitting of 62.35±0.1 kHz and a linewidth at half height of ~ 1.7 kHz. We start with Figures 1 to 3 which summarise the results at 303.3K for the 55.8 μm cell at 65V [1.17 MV/m], 60 V [1.08 MV/m] and 55 V [0.99 MV/m], respectively. The spectra marked 0^- are taken before the electric field is switched on. The spectra marked 0^+ are taken starting immediately after the electric field is switched on. The start of the time at which the rest of the spectra are collected is marked on each spectrum.

The results in Figure 1 show the fastest rate of alignment of the SmA director observed in this work. After 15 min the alignment of the director is complete (the final angle the director makes with the magnetic field is 87^0), that is, the director has essentially been aligned parallel to **E** and no further change in alignment is observed after that. The most interesting spectrum in Figure 1 is that marked 0^+ which shows just two sets of doublets with apparently nothing in between: the low intensity (~ 10% of the total) doublet with the larger splitting corresponds to the initial director orientation prior to the electric field being switched on (at $\theta = 0^0$) and the other doublet with the much higher intensity and smaller splitting corresponds to the final director alignment (at $\theta = 87^0$). The total time taken to acquire this spectrum is 11 min 19 s.

That we only see two director orientations under this fast condition could mean one of the following.

(a) That the director is not aligning as a monodomain (the NMR lines would have been then smeared out over the acquisition time which would have resulted in a broad spectrum).

(b) That there was an induction period during which no apparent change in the director alignment would have occurred followed by the fast realignment process in order to produce this ~10% intensity at $\theta = 0^0$. This point will become clear when we consider the rest of the results.

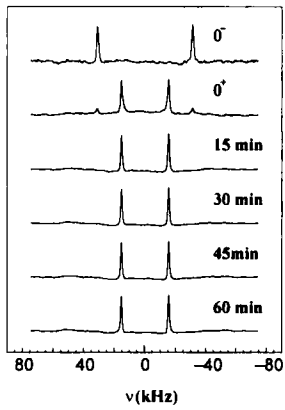

FIGURE 1 Spectra recorded as a function of time for the 55.8 μm cell at 303.3K and E = 1.17 MV/m (V = 65 V)

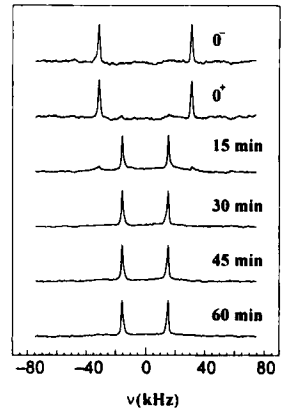

FIGURE 2 Spectra recorded as a function of time for the 55.8 μm cell at 303.3K and E = 1.08 MV/m (V = 60 V)

(c) That the director realignment process between $\theta = 0^0$ and 90^0 is faster than the time required to record a single FID (85 ms). For this reason we are unable to observe the presence of the intermediate orientations in the alignment process. Only when we slow down the realignment process sufficiently will we be able to see these intermediate orientations. This point will be made clear later.

By reducing the voltage from 65V to 60V [1.08 MV/m], we slow down the alignment process (see Figure 2, where the acquisition time is 11 min and 19 s). Now in contrast to Figure 1, the 0^+ spectrum is almost identical to 0^- except for a very small intensity corresponding to $\theta = 87^0$. This shows that the director is essentially parallel to **B** but that only a very small part is parallel to **E** and with nothing in between. The spectrum taken 15 min after the electric field was switched on looks almost identical with the 0^- spectrum of Figure 1, in other words it contains a pair of lines associated with $\mathbf{n} \parallel \mathbf{E}$ and a weak pair associated with **n** parallel to **B**. The alignment process now looks complete at 30 min

in contrast to 15 min for the higher voltage. Here again, we do not detect any intensity between the outer and inner doublets, i.e. no intermediate director orientations are detected.

Slowing down the director alignment still further by reducing the voltage to 55V [0.99 MV/m], we are able to see some intermediate director orientations as shown in the spectra given in Figure 3. The 0^+ and 0^- spectra are identical and clearly show the presence of an induction period (the total acquisition time here is also 11min 19s). The spectra at 15 and 30 min show just the two sets of doublets. The inner splitting corresponds to $\theta \approx 87$ to 85^0 while the outer doublet corresponds to $\theta = 0^0$; again there is no observable spectral intensity in between these two extreme orientations.

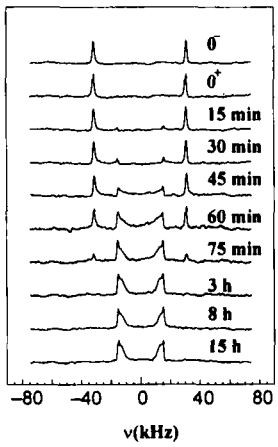

FIGURE 3 Spectra recorded as a function of time for the 55.8 μm cell at 303.3K and E = 0.99 MV/m (V = 55 V)

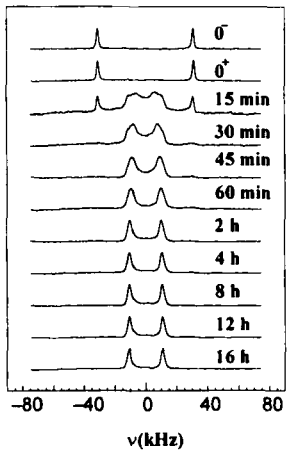

FIGURE 4 Spectra recorded as a function of time for the nominal 100 μm cell at 303.3K E = 1.00 MV/m (V = 100 V)

The spectra at 45, 60 and 75 min are, however, different and extremely interesting for they show very clearly the presence of intermediate director orientations. In addition to the doublets associated with director orientations $\theta = 85^0$ and around $\theta = 0^0$ there is clear NMR intensity in the region between the inner doublet. These intermediate director orientations correspond, according to Eq (1), to a restricted distribution from either a value of $\theta = 36^0$ (if the sign of $\Delta\nu(\theta)$ is the same as $\Delta\nu(0^0)$) or a value of $\theta = 85^0$ (if the sign of $\Delta\nu(\theta)$ is opposite to $\Delta\nu(0^0)$) to the magic angle of 54.5^0. Why this restricted director distribution occurs as it aligns in this slower regime is not clear. Furthermore, at 75 min and up to 15 h, the director distribution appears to be locked in two orientations corresponding, perhaps, to two different domains; one at $\theta \approx 85^0$ and the

other at $\theta \approx 78^0$. A similar situation was observed in the magnetic field-induced alignment of the smectic phase of certain non-symmetric liquid crystal dimers [4].

In a recent study of the magnetic field-induced alignment of 8CB-d_2 contained in a 5mm NMR tube from an initial monodomain director at $\theta = 88^0$ to a final orientation at $\theta = 0^0$ (i.e. from orthogonal to the magnetic field to parallel to the field, which is the reverse of our case) a pattern of alignment at two director orientations of $\theta = 88^0$ and $\theta = 0^0$, similar to the results described here, was also observed as well as an induction period [1]. To explain the induction period, it was suggested that the SmA sample cannot rotate as a monodomain because of anchoring of the layers at the glass surface. The layers must first break down into domains having a range of translational correlation lengths while still on the whole preserving the initial director alignment. As the correlation length for a domain decreases and decoupling from neighbouring layers occurs, a point is reached when it begins to rotate in the field. The sample in these domains is thought to be more nematic than smectic-like. Computer simulation studies of magnetic field-induced alignment of the director in the SmA phase appear to support this model [5].The final stage is a slow process when the domains with their directors more or less parallel to the aligning field unite to form a monodomain smectic A structure. The induction period is thus associated with the initial disruption of the layer structure. This disruption is facilitated by the presence of defects in the spatial ordering [2,6-8]. Such defects in the smectic layers will always be present in monodomain samples and their concentration will depend on the history of the sample as it is cooled into the smectic phase. The concentration, rate of diffusion and propagation of these defects have all been suggested to play a major role in the mechanism of alignment of the smectic phase [2,6-8]. In this context it would clearly be of some interest to observe the optical texture of the sample during the alignment process in the presence of both fields. We are, therefore, attempting to construct an optical system necessary to do this.

We now look at the results for the alignment of the smectic A phase at 303.3K using a cell of 100 μm nominal thickness. We expect to obtain analogous results with this cell as with the previous one at the same value of the electric field strength. The results for measurements using the nominal 100 μm cell are given in Figures 4, 5 and 6.

To begin with, the 0^+ spectrum in Figure 4 (which takes 15 min to acquire) is identical with the 0^- spectrum which shows an induction period for the alignment process. The spectrum collected 15 min after the electric field was switched on exhibits essentially two sets of quadrupolar doublets: one has a splitting close to that for the initial director (in fact it corresponds to $\theta \approx 3^0$) and the second is a pair of broad lines with the outer edges corresponding to $\theta \approx 41.5^0$ and the inner most broad peaks to $\theta \approx 63.5^0$. The spectrum collected after 30 min shows the intensity of the splitting corresponding to $\theta \approx 3^0$ has almost completely disappeared and only the broad peaks in the centre of the spectrum

remained. These broad central peaks sharpen up continuously with time, implying a narrowing of the director distribution around the angle corresponding to the central peaks. After 60 min, the director orientation peaks at $\theta=69^0$. The director orientation, however, does not change much after that and reaches only $\theta=71^0$ after 16 h.

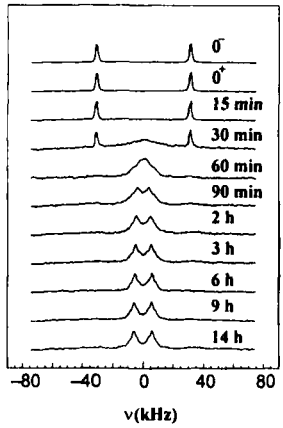

FIGURE 5 Spectra recorded as a function of time for the nominal 100 μm cell at 303.3K E = 0.95 MV/m (V = 95 V)

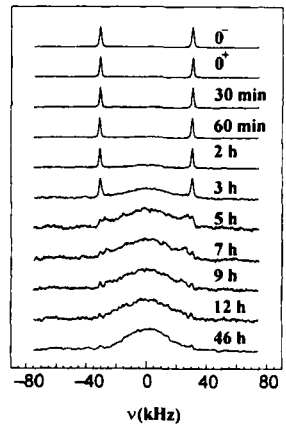

FIGURE 6 Spectra recorded as a function of time for the nominal 100 μm cell at 303.3K E = 0.90 MV/m (V = 90 V)

The pattern of alignment observed in this 100 μm cell at this field strength [1.00 MV/m] is quite different from that observed for the 55.8 μm cell at 55V [.99 MV/m] where a narrower director distribution was found during the alignment process in which the director reached $\theta=85^0$ within 15 min. It is not clear to us why this is so, i.e. why there is this thickness dependence of the alignment process, although the two cells are more or less at the same electric field intensity of ~ 1 MV/m. We suspect that a possible reason is that the actual thickness of the nominal 100 μm cell could very well be larger than 100 μm by as much as possibly 10% or more [9].

Slowing down the process of alignment further (see Figure 5, where the acquisition time is 5 min), by reducing the voltage to 95V [0.95 MV/m], produces a pattern of alignment consistent with that at the higher voltage. We see a longer induction period followed, 30 min after switching the electric field on, by the appearance of a low intensity, very broad peak (corresponding to a broad director distribution around $\theta \approx 54.5^0$) which sharpens up to some extent to give after 14 h a (still relatively broad) director distribution centred on $\theta \approx 63^0$.

In Figure 6 (where the acquisition time is 11 min 19 s) the alignment measurement was run for nearly two days at a reduced voltage of 90V [0.90 MV/m]. It is clear from a comparison of the spectra in Figure 6 with those in Figures 4 and 5 that:

(a) The induction period is much longer than before (nearly 2 h now).

(b) The director distribution during the alignment is much broader than before.

(c) Furthermore, we can now see intermediate director orientations from $\theta = 0^0$ continuously to higher alignment angles. This is clearly seen in the spectra marked 3, 5, 7 h etc.

(d) After 46 h we could still see some intensity remaining around $\theta \approx 0^0$. The broad component in the middle has very weak shoulders corresponding to $\theta \approx 90^0$. The increase in intensity in the middle of this broad component (compared with earlier spectra) indicates a substantial fraction of the director domains aligned at approximately the magic angle of 54.5^0.

CONCLUSIONS

One of the main conclusions is that deuterium NMR can reveal many facets of the alignment process of a SmA phase induced by an electric field. The results show that the electric-field induced alignment of the SmA directors of 8CB-d_2 is more complex and qualitatively different from that observed in nematic samples. The main features of this complex process may be summarised as follows:

• The existence of an induction period. This induction period is short (~minutes) at relatively high electric fields but becomes of the order of hours at relatively low electric fields ($\leq$ 0.90 MV/m).

* The smectic directors do not align as a monodomain. The mechanism of alignment clearly involves an initial disruption of the smectic layers and their reformation later on as the alignment process proceeds towards completion.

* At the highest value of the electric field strength used in this work (1.17 MV/m in the 55.8 μm cell) the fastest alignment process is observed as a switch from the initial director orientation (parallel to the magnetic field) to the final director orientation (essentially parallel to the electric field) without apparently any intermediate director orientations.

* At intermediate values of the electric field, intermediate orientations of the director are observed with a curious cut out from ~ 40^0 to 90^0. The final director orientation is not a monodomain but appears to be locked at two orientations: one essentially parallel to the electric field and the other short of this by about 10^0.

* By contrast, at the lowest value of the electric field strength used in this work (nominally 0.90 MV/m) a continuous distribution of director orientations from 0^0 to 90^0 is observed.

* Some of these features have been observed in work on the magnetic field-induced realignment of the director in the smectic phase of 8CB-d_2 [1], liquid crystal dimers [4] and electric field alignment of 8CB [2].

Acknowledgment

We are grateful to the Royal Society for the award of a British-Japanese Joint Research Grant which has facilitated the collaboration between the Southampton and Osaka Laboratories.

References

[1] J. W. Emsley, J. E. Long, G. R. Luckhurst and P. Pedrielli, *Phys. Rev. E,* **60,** 1831(1999).
[2] D. A. Dunmur and T. W. Walton, *Mol. Cryst. Liq. Cryst. Letters,* **2,** 7 (1985).
[3] M. L. Magnuson and B. M. Fung, *J. Chem. Phys.,* **100,** 1470 (1994).
[4] P. J. Le Masurier and G. R. Luckhurst, *Chem. Phys. Lett,* **287,** 435 (1998).
[5] C. Bacchiocchi, G. R. Luckhurst and G. Saielli, in preparation.
[6] O. Parodi, *Sol. St. Comm.,* **11,** 1503 (1972).
[7] D. Coates, W. A. Crossland, J. H. Morrissy and B. Needham, *J. Phys. D: Appl Phys.,* **11,** 2025 (1978).
[8] M. Hareng, S. Le Berre and J. J. Metzger, *Appl. Phys. Lett.,* **27,** 575 (1975).
[9] N. Kunimatsu, Displays, Hitachi Ltd, private communication.