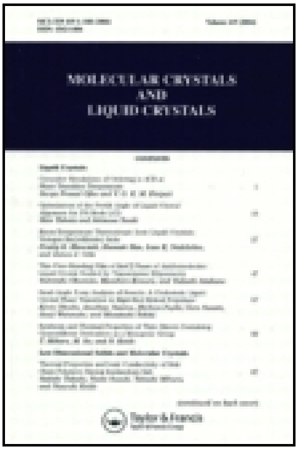

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Chemically-Induced Discotic Liquid Crystals. Structural Studies with Nmr Spectroscopy

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CHEMICALLY-INDUCED DISCOTIC LIQUID CRYSTALS. STRUCTURAL STUDIES WITH NMR SPECTROSCOPY

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Deuterium NMR spectroscopy provides an especially important technique with which to investigate a wide range of liquid crystal behaviour. Here, we describe its use in the structural study of liquid crystals formed from discotic or disc-like molecules and, to illustrate the breadth and power of the NMR method, we have selected two systems in which the liquid crystal phases are chemically induced. The binary mixtures are similar in that one component is a radial multiyne but differ significantly in the nature of the chemical inductor. In one case the inductor is a nitrated fluorenone which has a similar anisotropy to the radial multiyne while for the second system the inductor, a substituted o-xylene is considerably smaller and far less anisotropic. By measuring the deuterium NMR spectra of suitably deuteriated versions of the components we show how it is possible to investigate the orientational order of the components in the various induced phases, their effective molecular symmetry, the molecular geometry, the chain flexibility and orientational order together with the phase symmetry. The results of these investigations are described and explained.

Keywords: discotic liquid crystals; chemically-induced phases; deuterium NMR spectroscopy

1. INTRODUCTION

The defining characteristic of a liquid crystal is its long range orientational order; that is one or more axes set in the constituent molecules tend to be highly correlated, even when separated by many millions of molecules. It follows, therefore, that a prime requirement for the formation of a liquid crystal is an anisotropy in the molecular shape. Of course, attractive forces are also important in influencing the formation of a liquid crystal, but for the moment we shall concentrate on the shape. Following the observation by Reinitzer [1] that cholesteryl benzoate formed a chiral nematic phase, the materials which were subsequently found to exhibit liquid crystal phases were made of essentially rod-like molecules. It was the long axes or near symmetry axes which tended to be orientationally correlated over large distances. There is, however, no apparent reason why molecules with different shape anisotropies should not form liquid crystal phases. One of the most obvious shapes is that which is at the opposite extreme of a rod, namely a disc, molecules with such a shape are commonly referred to as discotic. However, it was not until the seminal work by Chandrasekhar and his colleagues [2] that a liquid crystal mesophase exhibited by discotic molecules was first observed for a hexasubstituted benzene. Since then numerous other materials with discotic molecules have been shown to form liquid crystal phases [3]. It seems as if once it had been demonstrated that liquid crystals are indeed formed by discotic molecules then chemists were given the confidence to hunt for, and find, many more examples. As additional discotic materials were prepared, so the range of liquid crystal phases formed by such disc-like molecules grew. It is now clear that there is a rich polymorphism with nematic and a significant number of columnar phases having been characterised [4].

NMR spectroscopy in general, and deuterium NMR spectroscopy in particular, has been shown to be a very powerful technique for the study of liquid crystals composed of rod-like molecules [5]. There was every reason to believe that the technique would be as valuable for the study of mesophases formed from discotic molecules and this has certainly proved to be the case. Indeed, just a few years after their discovery, the first NMR investigation of a discotic liquid crystal appeared [6], and since then many other studies have been undertaken [7]. Here we illustrate the power of the NMR technique for discotic systems by considering two particular examples for which the orientational order, molecular geometry chain flexibility and phase symmetry have been determined. However, before we come to such studies we shall first consider, in the following section, the basic features of deuterium NMR spectroscopy and its use in the investigation of liquid crystals. In sections 3 and 4 we describe our results for the structure of two quite different discotic liquid crystals formed by chemical induction, but with very different molecules inducing the mesophases. Our conclusions are given in section 5 and the syntheses of the deuteriated materials, essential for such NMR investigations, are described in section 7.

2. DEUTERIUM NMR SPECTROSCOPY: THE BASICS

Although there are several magnetic nuclei whose NMR spectra could be used to investigate the liquid crystal phase, we shall only be concerned with deuterium primarily because the spectra are relatively simple, straightforward to analyse and extremely informative [5]. We begin by considering a molecule containing a single deuteron. In the isotropic phase the spectrum consists of a single line made up of a pair of degenerate transitions, since the spin quantum number of deuterium is one. In a liquid crystal phase the degeneracy of the transitions is lifted and the NMR spectrum contains two lines. The degeneracy is removed because of the quadrupolar interaction experienced by the deuteron which, unlike the isotropic phase, is not averaged to zero by the rapid tumbling of the molecule because of the long range orientational order of the liquid crystal phase. The observation of just two spectral lines requires a further condition, namely that the director of the phase, assuming that it is uniaxial, is uniformly aligned with respect to the magnetic field inherent in the NMR spectrometer. This is usually easy to achieve, at least for a nematic since the director will be aligned either parallel to the field ($\Delta\tilde{\chi} > 0$) or perpendicular to it ($\Delta\tilde{\chi} < 0$). For discotic materials the diamagnetic anisotropy, $\Delta\tilde{\chi}$, is usually negative and so the director is aligned perpendicular to the magnetic field. We shall discuss shortly what form the spectrum takes if the director is not uniformly aligned.

The magnitude of the quadrupolar splitting depends on the orientational order and when the director is orthogonal to the field is given by

$$\Delta\tilde{v} = -(3/4)q_{CD}S_{CD}. \tag{1}$$

This simple expression results because the magnetic quadrupolar interaction for a deuteron attached to a carbon atom approximates closely to being cylindrically symmetric. Here q_{CD} is the quadrupolar coupling constant and if the magnetic field of the spectrometer was applied along the C-D bond direction, the observed quadrupolar splitting would be $(3/2)q_{CD}$. The magnitude of q_{CD} varies slightly with the chemical structure; it is about 183 kHz for an aromatic deuteron and 168 kHz for an aliphatic deuteron. The orientational order parameter, S_{CD}, is defined as

$$S_{CD} = (3\overline{\cos^2\beta_{CD}} - 1)/2, \tag{2}$$

where the bar indicates an average over all molecular orientations and β_{CD} is the angle between the C-D bond and the director. When the molecule has cylindrical symmetry, its orientational order at the second rank level is defined by the Tsvetkov order parameter [8]

$$S = (3\overline{\cos^2\beta} - 1)/2, \tag{3}$$

where β is the angle between the molecular symmetry axis and the director. The two order parameters are related by

$$S_{CD} = S(3\cos^2\gamma - 1)/2, \tag{4}$$

where γ is the angle between the C-D bond and the molecular symmetry axis. This angle is often 90° as we shall see and so S is just minus twice the order parameter S_{CD} available from the quadrupolar splitting.

Real discotic molecules are rarely cylindrically symmetric [3] and so their orientational order cannot be described with a single order parameter. What is needed is a matrix of order parameters which was introduced by Saupe [8]. For a rigid molecule an element of the ordering matrix is given by

$$S_{ab} = (3\overline{\cos\beta_a\cos\beta_b} - \delta_{ab})/2, \tag{5}$$

where a denotes a molecular axis, β_a is the angle between this axis and the director while δ_{ab} is the Kroenecker delta. In the principal axis system, only the diagonal elements of **S** are non-zero and because the matrix is traceless there are just two independent order parameters [8]. These are generally taken to be S_{zz}, the major order parameter, and $(S_{xx} - S_{yy})$, the biaxial order parameter, where the axis labels are chosen so that $(S_{xx} - S_{yy})$ is positive and smaller than $|S_{zz}|$. It is important to recognise that $(S_{\mathrm{xx}} - S_{\mathrm{yy}})$ refers to the biaxial ordering of the molecule with respect to the director and does not reflect the symmetry of the phase. The C-D bond order parameter is related to the elements of the Saupe ordering matrix and in the principal axis system for **S**

$$S_{CD} = \{(3\cos^2\gamma_z - 1)/2\}S_{zz} + (\cos^2\gamma_x - \cos^2\gamma_y)(S_{xx} - S_{yy}), \qquad (6)$$

where, for example, γ_{z} is the angle between the C-D bond and the z axis. Clearly, at least two quadrupolar splittings together with a knowledge of the molecular geometry and the location of the principal axes are needed to determine the major and biaxial order parameters.

So far we have been concerned with a monodomain sample of the liquid crystal, that is one in which the director is uniformly oriented. When the director adopts a range of orientations with respect to the magnetic field, the observed spectrum is a sum of spectra from the various director orientations. The quadrupolar splitting varies with the director orientation according to

$$\Delta\tilde{\nu}(\theta) = \Delta\tilde{\nu}_0(3\cos^2\theta - 1)/2, \qquad (7)$$

where θ is the angle made by the director with the magnetic field and $\Delta\tilde{\nu}_0$ is the splitting when the director is parallel to the field. It is then the largest splitting and as the angle, θ, increases, so the splitting decreases, passes through zero at the magic angle ($\theta = \cos^{-1} 1/\sqrt{3} = 54.74°$) and increases to half the original value when the director is orthogonal to the magnetic field. Strictly the quadrupolar splitting is $-\Delta\tilde{\nu}_0/2$ although its sign is not readily available from the NMR experiment. The powder pattern obtained by adding spectra from all director orientations with a totally random distribution is shown in Figure 1(a). It has two distinct features, firstly the horns in the centre of the spectrum which are associated with those regions of the sample where the director is perpendicular to the magnetic field. Secondly, there are weaker shoulders at the extremes of the spectrum which come from the director being parallel to the field. The fact that the spectrum only contains these two sorts of features and that the splittings associated with them are in the ratio of 2:1 is a result of the uniaxial symmetry of the phase. For this system the component of the quadrupolar tensor along the director is $\tilde{q}_{||}$, giving a splitting of $(3/2)\tilde{q}_{||}$ while the component perpendicular to the director is $\tilde{q}_{\perp}$. Since the tensor is also traceless, $\tilde{q}_{\perp}$ is simply $-\tilde{q}_{||}/2$. This symmetry for the quadrupolar tensor, partially averaged by the rotational motion of the molecules in the liquid crystal phase, follows from the uniaxial symmetry of the phase. Indeed, the uniaxial symmetry for $\tilde{q}$ obtains whatever the shape of the molecule containing the deuterium nuclei.

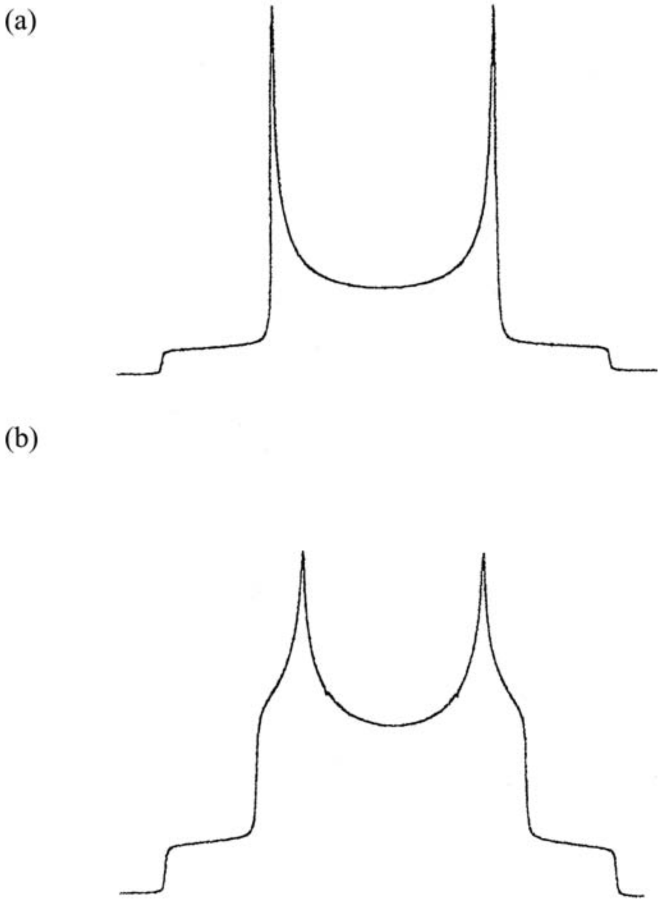


FIGURE 1 The simulated deuterium NMR spectrum for a system containing a single deuteron for which the directors are randomly distributed with respect to the magnetic field for (a) a uniaxial phase, and (b) a biaxial phase.

It follows from this discussion that if the liquid crystal phase is biaxial, as say for a rectangular columnar phase, then the partially averaged quadrupolar tensor will also be biaxial. That is, the three principal components of $\tilde{q}$ will be different, however because the tensor is traceless there are just two independent elements which are expressed as the major element, $\tilde{q}_{ZZ}$, and the biaxiality which is represented by the reduced quantity [9]

$$\tilde{\eta} = (\tilde{q}_{XX} - \tilde{q}_{YY})/\tilde{q}_{ZZ}. \tag{8}$$

This parameter $\tilde{\eta}$ provides a pragmatic characterisation of the phase biaxiality but is not uniquely defined for it is likely to vary, for example, with the location of the deuteron in the molecule [10]. When the magnetic field is parallel to a principal axis or equivalently one of the directors the observed quadrupolar splitting is just three halves of the component of $\tilde{q}$ associated with that axis. In general if the field is at an arbitrary orientation with respect to the three directors, then the quadrupolar splitting is given by

$$\Delta\tilde{v}(\theta,\phi) = (3/2)\tilde{q}_{ZZ}\{(3\cos^2\theta - 1)/2 + (\tilde{\eta}/2)\sin^2\theta\cos 2\phi\}, \tag{9}$$

where θ and $\boldsymbol{\phi}$ are the spherical polar angles made by the field with the principal axes of $\tilde{q}$. It is, however, extremely difficult to prepare a monodomain sample of a biaxial liquid crystal whose orientation can then be varied with respect to the magnetic field of the NMR spectrometer. The alternative is to study a sample in which the directors are randomly arranged. An example of such a powder pattern for a biaxial liquid crystal with a biaxiality parameter $\tilde{\eta}$ of 0.20 is shown in Figure 1(b). It is clear that this NMR spectrum contains three pairs of features, a central pair of horns and two sets of shoulders, which are associated with the different quadrupolar splittings occurring when the field is parallel to the three directors. The pattern for the biaxial phase clearly contrasts with that for the uniaxial phase which has only two pairs of spectral features; it should, therefore, be easy to identify a biaxial liquid crystal phase using deuterium NMR spectroscopy and this is certainly the case, as we shall see.

3. SYSTEM 1: ORIENTATIONAL ORDER AND MOLECULAR GEOMETRY

One of the intriguing features of discotic liquid crystals is that, in addition to being formed by pure materials, these phases can also be induced by mixing two materials. Such chemically-induced liquid crystal phases clearly result from a specific interaction between the two components which favours the formation of the induced phase. The existence of these induced phases provides further clear evidence that molecular shape is not the only factor responsible for the formation of liquid crystals. For the discotic systems chosen to illustrate the power of deuterium NMR spectroscopy in the study of liquid crystals, we have selected two in which the phases are formed by chemical induction.

In the first example the radial multiyne, pentakis(phenylethynyl)phenyldecyl ether (D102) is mixed with 2,4,7-trinitrofluorenone (TNF) [11]; the chemical structures of both materials are shown in Figure 2. The code used to denote this multiyne and the other which we have studied were introduced by the person who synthesised them; they indicate his first name

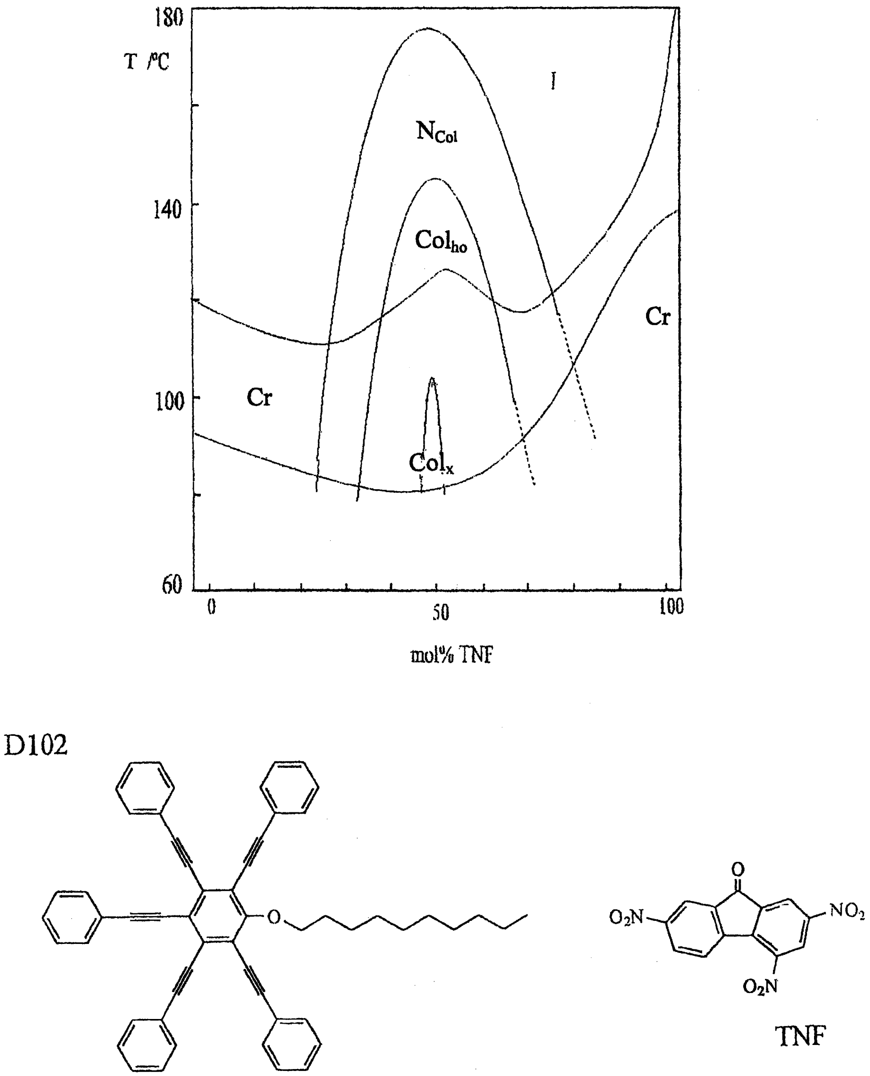


FIGURE 2 The phase diagram for a binary mixture of a radial multiyne (D102) and 2,4,7-trinitroflurorenone (TNF); the chemical structures of both components are given.

(Dirk) and the order in which the compounds were prepared. The phase diagram for the binary mixture is also given in this figure and we can see that whereas the pure components are not mesomorphic their equimolar mixture exhibits two enantiotropic phases, a columnar nematic phase, N_{Col}, and the other a hexagonal columnar phase [11]; there is also a monotropic columnar phase, Col_X, whose structure has not been determined. The nematic phase, N_{Col}, is unlike a conventional nematic formed from discotic molecules in that the D102 and TNF molecules are stacked, on average, alternately in short columns [11] giving a structure in which these aggregates resemble the rod-like molecules of a calamitic nematic. The mixtures have a striking reddish-orange colour which contrasts with the pale yellow appearance of the pure components. It results from a charge-transfer band caused by the electron-rich character of D102 and the high electron affinity of TNF. Although the existence of the charge-transfer band is not in doubt, the role this plays in stabilising the induced phases is questionable. The weakness of the charge-transfer interaction has led to the suggestion that a quadrupolar electrostatic interaction, not to be confused with the quadrupolar spin interaction in NMR spectroscopy, could be responsible for the chemical induction of the liquid crystal phases [12]. This suggestion is supported by the results of a computer simulation study for a mixture of Gay-Berne discs, each with an embedded point quadrupole, but of opposite sign. Not only is a columnar phase induced but a nematic phase also appears which exhibits a local columnar structure in which, on average, the components alternate along the column [12]. A more general model for such phase induction in which the charge is distributed over the two molecules rather than representing it as a point quadrupole has subsequently been developed [13].

In order to study the system using deuterium NMR spectroscopy, we have prepared perdeuteriated TNF-d_5, D102 with the five phenyl rings deuteriated, D102-d_{25} and D102 with the decyloxy chain perdeuteriated, D102-d_{21}. The availability of these deuteriated materials is clearly essential for such spectroscopic investigations and their synthesis is described in section 7. Here D102-d_{25} is denoted by **2**, D102-d_{21} by **1** and TNF-d_5 by **4**. In these studies we have concentrated on the equimolar mixture since this has the longest mesophase range (see Fig. 2). We begin with the results for TNF-d_5 and the NMR spectra of this in the N_{Col} and Col_{ho} phases are shown in Figure 3. In the nematic phase, close to the nematic-isotropic transition there are two doublets with very similar splittings coming from the ordered nematic together with a single peak originating from the isotropic phase. It shows immediately that the system exhibits a biphasic region with co-existing nematic and isotropic phases, as expected for a two component mixture. What is unexpected is that the quadrupolar splittings for the deuterons in TNF are so similar. As we have seen the quadrupolar splittings are proportional to the order parameter for the C-D bonds which, in turn, are determined by the principal components of the ordering matrix and the molecular geometry (see Eq. (6)). If TNF is taken to be planar then one of the principal axes, say z, must be orthogonal to the molecular plane.

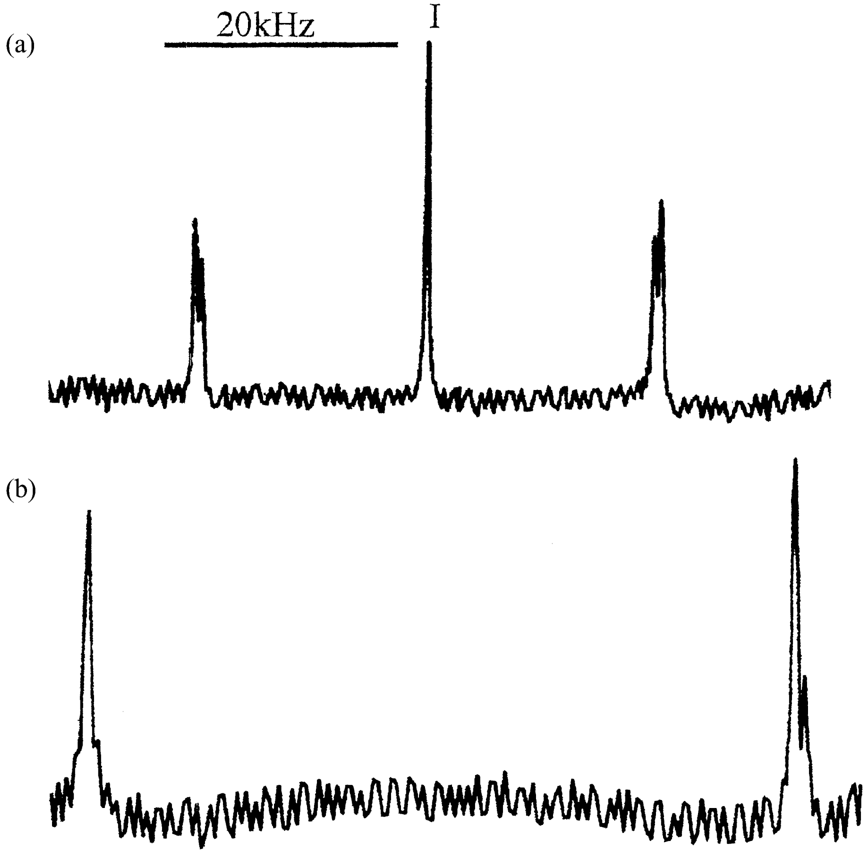


FIGURE 3 The deuterium NMR spectrum of TNF-d_5 in an equimolar mixture of D102 and TNF at (a) $T_{NI} - T = 5°C$ in the N_{Col} phase, and (b) at $T_{NI} - T = 53°C$ in the Col_{ho} phase.

The non-symmetric substitution pattern of the nitro groups makes the location of the remaining principal axes less definite. However, if we ignore this difficulty then we could locate one axis along the C=O bond and the other orthogonal to this and in the plane. Such an intuitive identification of the principal axes for **S** is consistent with their more theoretical location based on the surface tensor model [14] which places the in-plane principal axes just 8° from our more approximate identification [15]. With this approximation, the five deuterons divide into a geometrically equivalent group of three, in positions 1, 5, 8, and a group of two at positions 3, 6. The C-D bonds in these groups make significantly different angles with the x, y principal axes but the same angle, of 90°, with the z axis. It follows from Eq. (6), therefore, that the only way in which the quadrupolar splittings for the two groups of deuterons can be the same is if the biaxiality ($S_{xx} - S_{yy}$) is zero. It seems, therefore, that although TNF is certainly biaxial in shape it finds itself in an environment in which it can rotate about its z axis unhindered. This would be consistent with it being sandwiched in the local nematic columns between the aromatic cores of two D102 molecules. In marked contrast, if TNF-d_5 is dissolved in a calamitic nematic, then the ordering matrix is found to have a large biaxiality [15], presumably because the environment of TNF is significantly less uniform that in a columnar nematic phase. On lowering the temperature for the equimolar mixture of TNF and D102, the orientational order increases significantly as is apparent from the increase in the quadrupolar splitting shown by the spectrum in Figure 3(b). On entering the Col_X phase, the spectrum disappears and we shall return to this unusual observation shortly. The temperature dependence of the quadrupolar splitting for TNF-d_5 is shown in Figure 4 for both the N_{col} and Col_{ho} phases. We see that there is a small temperature range where the two phases coexist, as expected for a binary mixture. Within the nematic phase the quadrupolar splitting exhibits

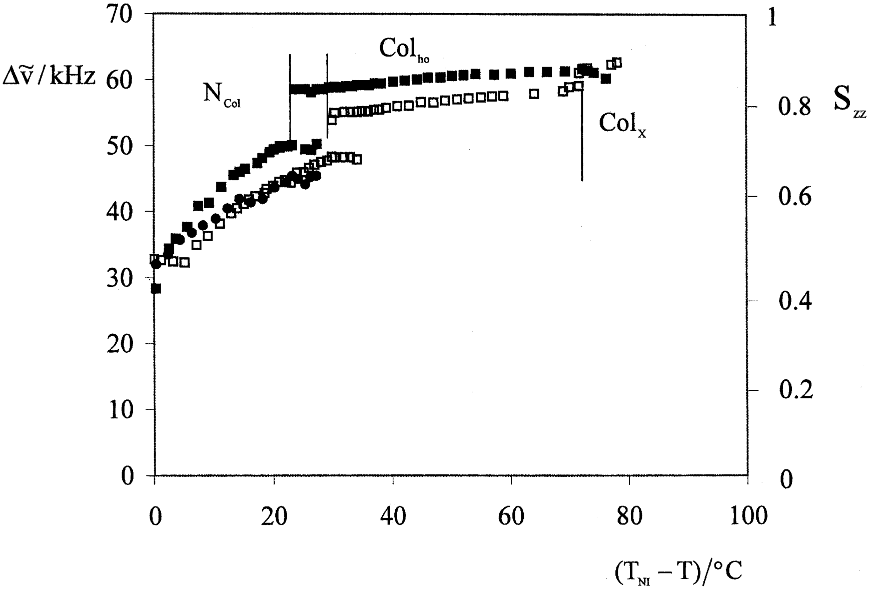


FIGURE 4 The dependence on the shifted temperature, $T_{NI} - T$, of the quadrupolar splittings for TNF-d_5 and D102-d_{25} in an equimolar mixture of D102 and TNF. Also shown are the order parameters, S_{zz}, for an axis perpendicular to the molecular planes for the two components, (■) TNF-d_5 and (□) D102-d_{25}. For comparison the equivalent parameter for the pure mesogen D13 is also shown as (●).

a strong temperature dependence but in the more ordered columnar phase, the splitting is far less sensitive to temperature. The measurement of the quadrupolar splitting is especially important because it provides a route to the orientational order parameter. As we have seen, for a uniaxial disc in a phase with the director aligned at right angles to the field, it follows from Eqs. (1) and (4) that the splitting is directly proportional to the order parameter for the symmetry axis of the disc. We have converted the quadrupolar splitting for TNF-d_5 to the order parameter, which we denote by S_{zz}, and the results are shown in Figure 4.

A knowledge of the order parameter is important, not only to characterise the liquid crystal phase but also to test theories of the phase. For nematic liquid crystals the Maier-Saupe molecular field theory [6] provides, almost certainly, the best description even though the theory is especially simple. One of the predictions of this theory is that uniaxial particles whether disk-like or rod-like forming a nematic phase should have the same orientational order parameters. Our results allow this intriguing prediction to be tested. Thus, at the nematic-isotropic transition the order parameter, S_{zz}^{NI}, for TNF-d_5 is found to be 0.41 which compares favourably with the value of about 0.35 which is typical of that determined for nematics composed of rod-like molecules. In addition, the transitional order parameter is predicted by the Maier-Saupe theory to be 0.429 [6] in remarkably close agreement with experiment. There is a significant jump in the orientational order parameter at the $\mathrm{Col_{ho}} - \mathrm{N_{Col}}$ transition consistent with the first order nature of this. However, by analogy with the SmA-N transition, it might have been expected that the wide nematic range would have made the transition far weaker. The orientational order parameter in the columnar phase is between 0.8 and 0.9 depending on the temperature (see Fig. 4) which indicates that there is a high degree of order in good agreement with the computer simulation results for the generic quadrupolar Gay-Berne model of this system [12].

We now turn to the other component of the binary mixture, namely D102–d_{25}, which was perdeuteriated in the five phenyl rings. From our results for TNF–d_5 we might have anticipated that all of the 25 deuterons would have had the same quadrupolar splittings. However, this is clearly not the case as we can see from the spectra of D102–d_{25} shown in Figure 5 for the nematic and hexagonal columnar phase of the equimolar mixture. The spectral resolution is better in the columnar phase, presumably because the director fluctuations which can broaden the lines in the columnar nematic phase are largely quenched in the hexagonal columnar phase. In any event, we can clearly see four distinct quadrupolar splittings together with a weak central peak coming from an isotropic phase. It is not at all apparent why there should be this small amount of isotropic phase so deep into the columnar phase. We would note, however, that an isotropic

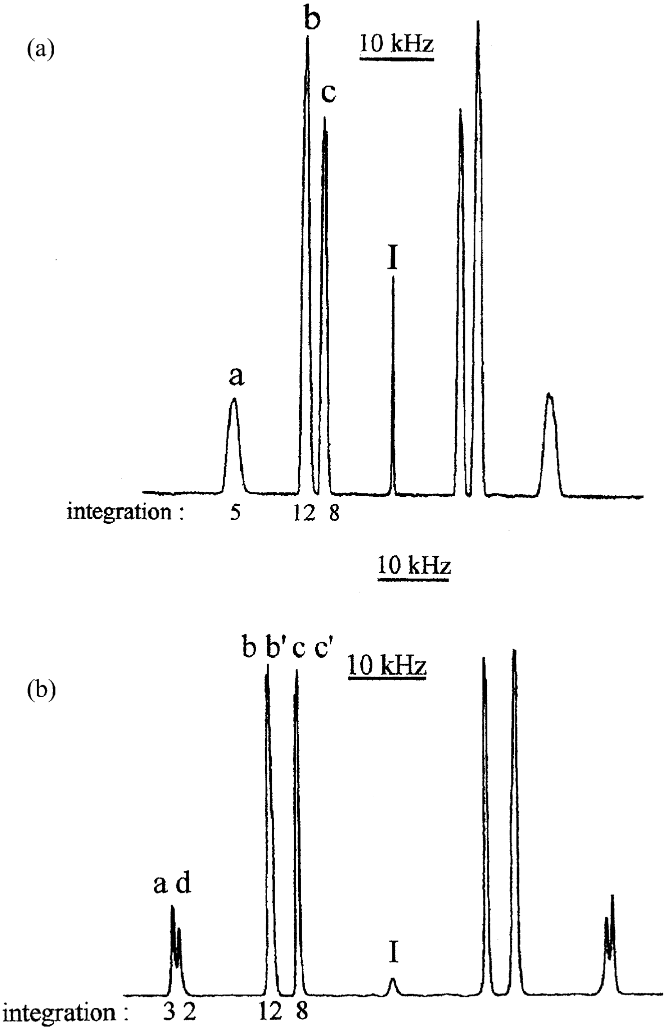


FIGURE 5 The deuterium NMR spectrum of D102-d_{25} in an equimolar mixture of TNF and D102 at (a) $T_{NI} - T = 20°C$ in the N_{Col} phase, and (b) $T_{NI} - T = 50°C$ in the Col_{ho} phase.

peak is also found for the nematic phase even though the system is some 20°C from the nematic-isotropic transition. The four quadrupolar splittings observed for the columnar phase become three in the nematic phase because the difference in the two larger splittings is small and the linewidths have increased. Given the marked inequivalence of the deuterons we are faced with the problem of assigning the splittings to particular deuterons. This is a difficult task which could only be solved unambiguously by specific deuteriation of the rings but this would involve some difficult chemical synthesis. Here, we shall use a more heuristic approach and begin by recalling that the area under a spectral line is proportional to the number of nuclei giving that peak. Integration reveals that in the nematic phase the largest splitting comes from five deuterons, the next largest from twelve and the smallest from eight. There are, of course, just five para deuterons and it seems reasonable to associate the largest splitting with these. The fact that the splittings for these deuterons are essentially the same suggests that, as for TNF–d_5, the biaxiality in the ordering matrix for D102–d_5 is also negligibly small. If this is so then why are the splittings for the other deuterons so different? The answer would seem to be that the rings are twisted out of the molecular plane unlike the structure of TNF which is necessarily planar. This view is supported by an X-ray crystallographic study of the analogous multiyne with six phenyl acetylene groups attached to a central phenyl ring [16]. If the rings are twisted, probably to different extents, then the C-D bonds for the ortho and meta deuterons will make different angles with the effective symmetry axis of the molecule in contrast to the para deuterons and so will give different splittings dependent on the twist angle (see Eqs (1) and (4)). Thus, the para deuterons for the five phenyl rings will be in the average plane of the molecule and so will be orthogonal to its symmetry axis and will have the same quadrupolar splittings.

This partial assignment now allows us to determine the order parameter, S_{zz}, for D102-d_{25} using the splittings for the five para deuterons. The results for this in the N_{Col}, Col_{ho} and Col_X phases are shown in Figure 4, again as a function of the shifted temperature. The order parameter at the nematic-isotropic transition, S_{zz}^{NI}, is 0.48 which is very similar to that of TNF-d_5 especially given the quite different molecular structures of these two components of the mesogenic mixture. It would seem, therefore, that the orientations of the two components are highly correlated. We see, from Figure 4, that the orientational order parameter is more or less constant over a small temperature region which would be consistent with the existence of a biphasic region with coexisting isotropic and nematic phases [17]. It then grows with decreasing temperature to a value of 0.71 at the transition to the Col_{ho} phase; this again is very similar to the result found for TNF-d_5. Within the hexagonal columnar phase the orientational order parameter determined from the averaged splitting for the para deuterons is found to grow from 0.81 to 0.85, which is slightly smaller than that found for TNF-d_5. In view of the significant difference in the molecular structure of the two components it is not really possible to explain these small differences. Surprisingly we were able to record a spectrum for D102-d_{25} in the unidentified columnar phase which is in stark contrast to the absence of a spectrum for TNF-d_5. The orientational order parameter in the Col_X phase is about 0.9 which is somewhat higher than for the preceding Col_{ho} phase; this is perhaps to be expected since it is a lower temperature phase.

We now come to the molecular geometry of D102-d_{25}, in particular the twist angles for the phenyl rings which cause the molecule to deviate from planarity although the conformationally averaged structure should be planar. From the structure of D102 it is to be expected that two pairs of rings would be equivalent as indicated by the labelling shown in Figure 2 with one unique ring. The twist angles for this need not be the same and so we should see three different quadrupolar splittings for the ortho/meta deuterons. This follows because as we have seen the quadrupolar splittings are related to the order parameter, S_{zz} and the angle made by the C-D bond with the z axis. However, only two quadrupolar splittings are observed coming from the twenty ortho/meta deuterons in the five rings. This means that the twist angles for three rings are the same but different to those for the two remaining rings. If we now assume that the phenyl rings have a regular hexagonal structure and denote the twist angle by ε, that is the angle between the normal to the central phenyl ring and one attached to it, then

$$\cos\gamma = (3/4)^{1/2}\sin\varepsilon. \tag{10}$$

This gives the quadrupolar splittings for the ortho/meta deuterons, which are the same for a given ring, as

$$\Delta\tilde{v}_{o/m} = (3/32)q_{CD}S_{zz}(9\sin^2\varepsilon - 4), \tag{11}$$

where S_{zz} is available from the quadrupolar splitting for the para-deuterons. This can, in fact, be used to write Eq. (11) as

$$\Delta\tilde{v}_{o/m}/\Delta\tilde{v}_p = (9\sin^2\varepsilon - 4). \tag{12}$$

There is now one complication which relates to the fact that the signs of the quadrupolar splittings are not available from spectra such as those in Figure 5. We have, therefore, to consider both signs for the ratio $\Delta\tilde{v}_{o/m}/\Delta\tilde{v}_p$ which will give two values for the twist angle, ε. In addition we have two splittings for the ortho/meta deuterons, the larger associated with twelve deuterons and so coming from three phenyl rings and the smaller associated with eight deuterons and so coming from two phenyl rings. Clearly one of the rings in the set of three must be the unique phenyl in D102-d_{25} but we are not able to make any assignment for the remaining four rings. The twist angles calculated from the quadrupolar splittings are shown in Figure 6. For the ratio of the splittings, $\Delta\tilde{v}_{o/m}/\Delta\tilde{v}_p$, taken to be negative the twist angles are approximately 30° whereas if the splittings are positive, the angles are much larger at about 55°.

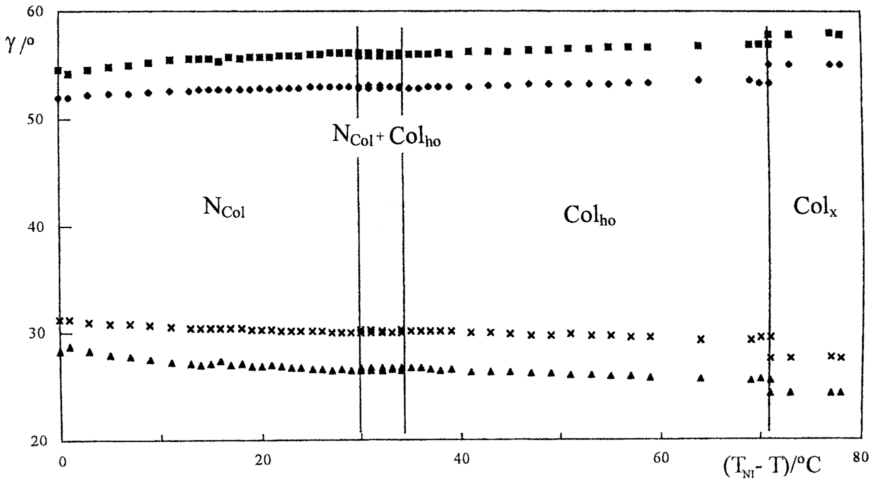


FIGURE 6 The dependence of the twist angles, ε, for the five phenyl rings in D102 on the shifted temperature, T_{NI} – T, for the two choices of the sign of the ratio $\Delta\tilde{\nu}_{o/m}/\Delta\tilde{\nu}_p$, (a) positive, and (b) negative.

We see that the twist angles, for both choices of relative sign, are essentially temperature independent in the nematic and hexagonal columnar phase. In addition they do not change at the Col_{ho}-N_{col} phase transition which seems physically reasonable. However, for the smaller twist angles on going to lower temperatures the angles decrease by a small amount making the molecule slightly more planar which is also physically realistic. In contrast, the larger twist angles increase on lowering the temperature which is unexpected. It should be stressed, however, that in both cases the changes are small. It might be expected that π-conjugation would favour a planar structure for D102 and so we expect the rings to adopt the smaller of the two sets of twists. This would also be in accord with the X-ray structure of the analogous molecule [16]. However, the deviation from planarity was found to be just 11° which is significantly smaller than that given by NMR. This may result simply from the difference in the phase, crystal versus liquid crystal, or it could result from the perturbation of the structure by the decyloxy chain in D102-d_{25}. This difference in the twist angles between the liquid crystal and crystal phases is consistent with that found for biphenyl. In the crystal phase the rings are planar whereas in the nematic phase biphenyl has the rings twisted by about 35° with respect to each other [18]. Again steric forces between neighbouring protons are taken to be responsible for the twist of the rings. In any event the twist of the phenyl rings out of the molecular plane of

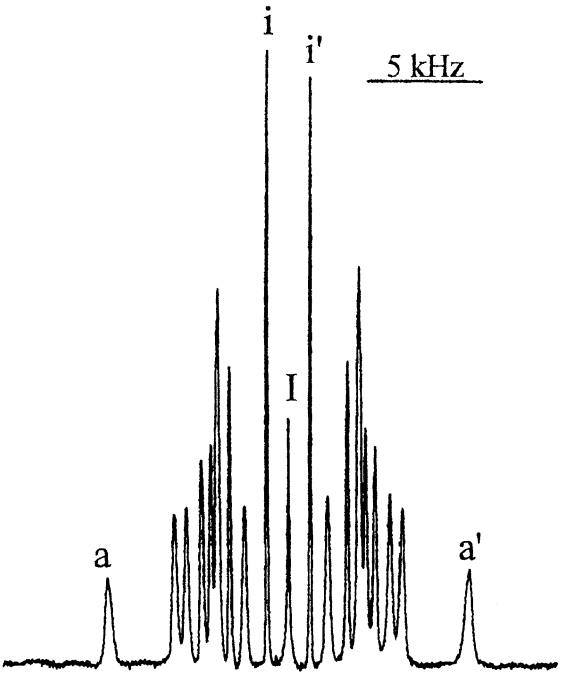


FIGURE 7 The deuterium NMR spectrum of D102-d_{21} in the Col_{ho} phase formed by an equimolar mixture of TNF and D102 at a shifted temperature, $T_{NI} - T$, of about 41°C. An expanded version of half of this symmetric spectrum is also shown.

D102 is almost certainly caused by steric overlap between the ortho deuterons on neighbouring rings.

We have attempted to explore the geometry of the chain in D102 by studying the system with the perdeuteriated chain. In addition, this will also give the orientational order parameters for the C-D bonds along the chain. This information is important, not only as a way of characterising the order but also because it allows the influence of chain flexibility on its orientational order to be evaluated and compared with theoretical predictions. The beautiful spectrum of D102-d_{21} is shown in Figure 7 for the hexagonal columnar phase formed by the equimolar mixture of TNF and D102. A similar spectrum was obtained for the columnar nematic phase but as we have seen, the linewidths are somewhat larger in this phase and so the resolution is not quite so impressive as in the Col_{ho} phase. There are nine well-resolved quadrupolar doublets but we expect to see ten from the ten groups of equivalent deuterons in the decyloxy chain. This implies that two of the groups of deuterons have very similar quadrupolar splittings and by expanding the spectrum and showing just half in Figure 7 we can see that the peak labelled f has a shoulder which is just discernible. Before we consider a more detailed analysis, two features are immediately observable from the spectra in Figure 7. The first of these is the presence of the isotropic peak for the sample which is in the columnar phase far from the nematic-isotropic transition. This could result from a spatial variation in the concentration of the components but the observation of such an isotropic peak for different samples makes this explanation seem unlikely. The other spectral feature is that the quadrupolar splittings are significantly smaller than those for the deuterons attached to the phenyl rings in D102-d_{25}. This implies that further motional averaging of the quadrupolar interactions is taking place and that this is associated with the conformational changes in the decyloxy chain [8].

We now return to the observation of the complete set of quadrupolar splittings and the difficult task of assigning these to positions in the chain. Of course, this could be achieved by preparing D102 with a specifically deuteriated chain but only with considerable difficulty and so we shall first explore simpler procedures. As we have seen, we can use the areas of the peaks to determine the number of deuterons responsible for them. This shows that whereas most peaks are associated with two deuterons, the composite peak, f, has four as we had already implied and i has an intensity coming from three deuterons. It is reasonable to identify this quadrupolar splitting as coming from the methyl deuterons which is consistent with this being the smallest splitting, as found for other systems [19]. Examination of the expanded half spectrum in Figure 7 reveals that with the exception of peak h all of the others are symmetrically spaced with respect to the centre of the spectrum. This suggests that the deuterons responsible for peak h have a slightly different chemical shift to the others. The only reason for this difference would be the location of the CD_2 group next to the oxygen whose high electronegativity would cause the chemical shift to change. If this analysis is correct then it would mean that the next smallest splitting comes from the methylene group closest to the aromatic core of D102. This would be a remarkable result for it is generally observed that such a methylene group would have the largest splitting [19].

In an attempt to confirm this unusual result and also to assign all of the quadrupolar splittings to positions in the chain, we have adopted the following approach. It might be expected that the orientational order would decrease monotonically along the chain as a result of conformational changes. This would seem to imply that the splittings should also decrease in the same way but numerous studies of both calamitic and discotic mesogens have revealed that the splittings often alternate along the chain. However, although the order may not decrease monotonically along the chain, it has been suggested that the chain dynamics should increase monotonically [20]. Since the NMR spin-lattice relaxation time,

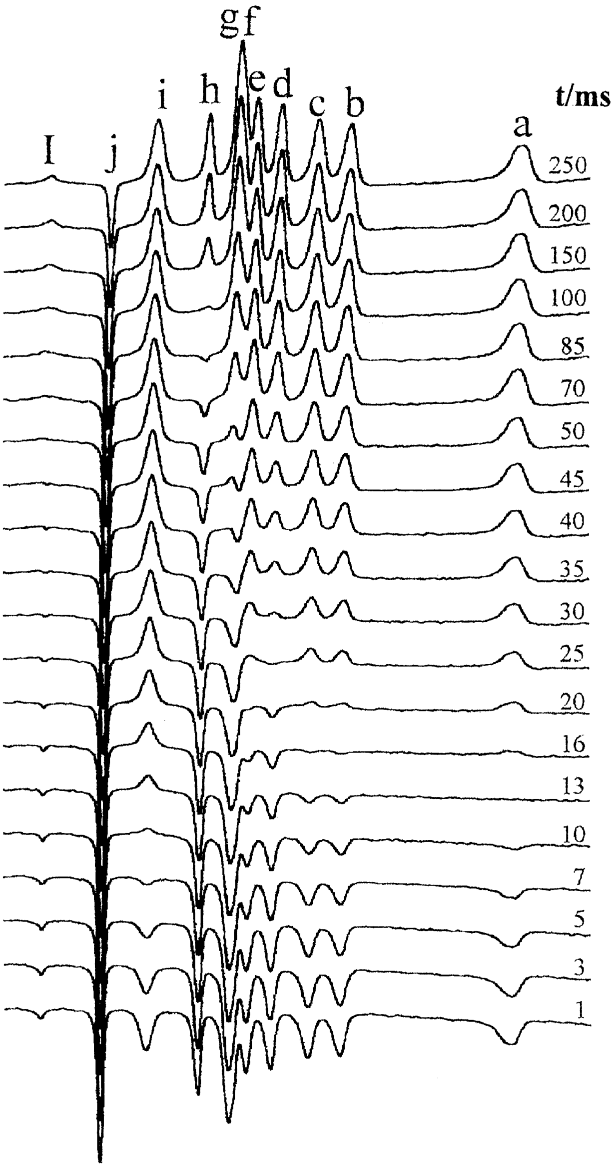


FIGURE 8 The spectra measured as a function of time during the inversion-recovery experiment for D102-d_{21} in the hexagonal columnar phase of the equimolar mixture of TNF and D102 at a shifted temperature of 43°C; only half of the symmetric spectrum is shown.

T_1, is inversely proportional to the correlation time determining the conformational dynamics, it is expected that T_1 should increase monotonically along the chain from the point of attachment to the core to its end. This behaviour is in agreement with the results of a number of studies [21]. We have determined the spin-lattice relaxation times using an inversion-recovery experiment in which the populations of the spin levels are inverted. As a consequence the spectral intensities are also inverted and we monitor the intensities of all the spectral lines as a function of time as they return to their equilibrium values. The spectra observed in such an experiment for D102-d_{21} in its hexagonal columnar phase at a shifted temperature of 43°C are shown in Figure 8. The first spectrum, or rather half of the symmetric spectrum, recorded just 1ms after the initial inversion shows that all of the lines have been inverted. As time increases we expect the intensities to grow, pass through zero and reach an equivalent positive intensity to the initial negative value. This process is readily seen for the outer spectral line a, corresponding to the largest quadrupolar splitting. In contrast the line labelled j retains its negative intensity, indicating a long spin-lattice relaxation time in comparison to those for other peaks. However, this is to be expected because peak j corresponds to the methyl deuterons and so should indeed have

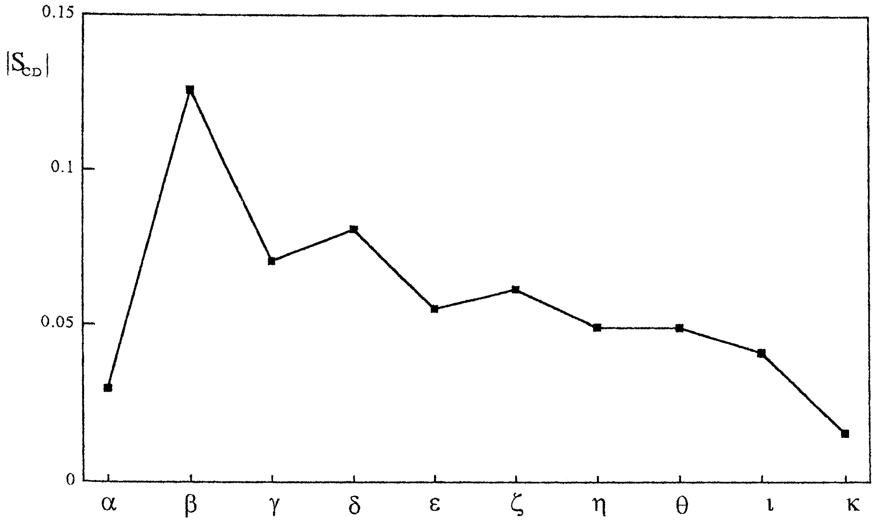


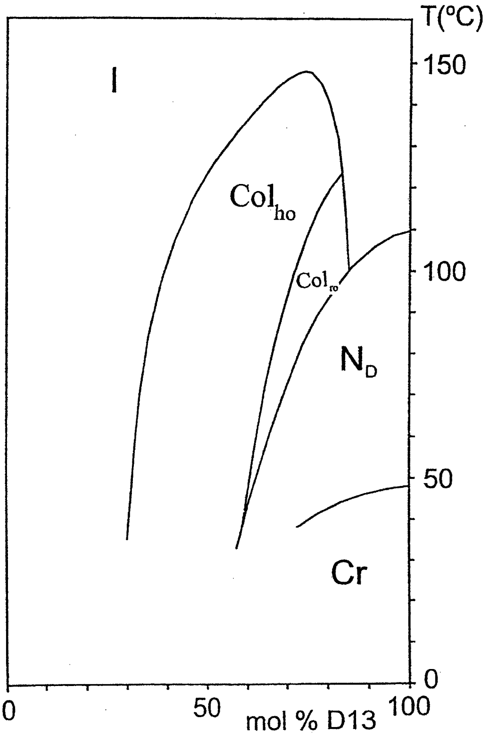
FIGURE 9 The variation of the modulus of the order parameter, $|S_{CD}|$ for the deuterons in the decyloxy chain of D102-d_{21} with their position in the chain for the equimolar mixture of TNF and D102 in the Col_{ho} phase at a shifted temperature of 43°C.

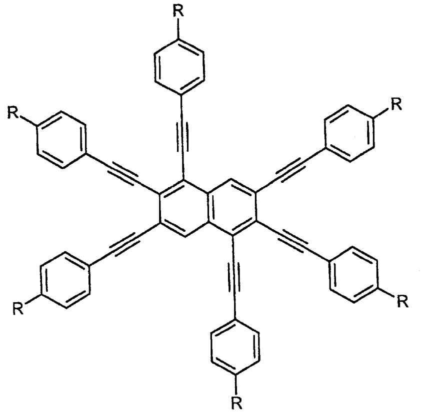
the longest value of T_1. In marked contrast the intensity of peak j corresponding to the next smallest splitting increases rapidly and, in fact, has the shortest spin relaxation time. This is exactly what is to be expected if the deuterons giving this peak were at the end of the chain closest to the core, as we had previously speculated. To be absolutely certain of this especially unusual result we have prepared D102-d_2 with the α-position specifically deuteriated. The deuterium NMR spectrum of this material in an equimolar mixture with TNF consists of the expected single quadrupolar doublet, and the magnitude of the quadrupolar splitting is equal at the same shifted temperature to that of the next smallest splitting found for the perdeuteriated decylocy chain [15]. Given this valuable confirmation of the assignment of the next smallest splitting to the pair of deuterons in the α-methylene group in the decyloxy chain, we have used the values of T_1 to assign the remaining splittings and hence the C-D bond order parameters to the other groups in the chain. This assignment is shown in Figure 9 where the position along the chain is labelled with the letters α, β, ...κ. We see that the modulus of the order parameter $|S_{CD}|$ alternates along the chain although this alteration is attenuated until there is a large drop in $|S_{CD}|$ for the methyl deuterons. This final reduction is a consequence of the additional averaging of the quadrupolar interaction caused by the rotation of the methyl group about the terminal C-C bond.

The results shown in Figure 9 present a challenge to theories of chain ordering in liquid crystalline systems [22]. We shall not deal with our attempts to fit the results for D102 here but note that the agreement between theory and experiment is convincing [15] even though the chain is in an usually inhomogeneous local environment with two phenyl rings on each side of it, unlike the situation for other discotic materials, where there are other chains on either side [19]. What is important for our studies is that the order parameter $|S_{CD}|$ for the α-position is particularly sensitive to the torsional angle defined as that between the normal to the central phenyl ring and the normal to the $C_{ar}OC_{al}$ plane. For a zero torsional angle the α-carbon atom lies in the plane of the ring and for a 90° torsional angle the carbon atom is immediately above the ring. For ether linked chains, the torsional angle is usually zero [16]. What we find for D102 is that to account for the very small order parameter of the deuterons on the first methylene group, the torsional angle needs to be about 60°. If the chain were twisted just in this way then the two C-D bonds of the α-methylene group would make significantly different angles with the normal to the molecular plane and so would have different quadrupolar splittings (see Eq. (4)). The fact that these different splittings are not observed in the spectra of D102-d_{21} (see Fig. 7) clearly demonstrates that the torsional angle for the chain must jump between equal but opposite values. This dynamic process will then average the different quadrupolar splittings and so restore the equivalence of the α-deuterons. The large alternating value of the torsional angle undoubtedly results from the steric interactions of the chain with the neighbouring phenyl rings. This arrangement for the chain causes D102 to deviate from a disc-like shape; indeed it has a scorpion-like appearance which could help explain the absence of a liquid crystal phase for the pure material and the formation of a chemically-induced nematic phase and not just a columnar phase. This situation obtains because the formation of a columnar phase results, in part, from a strong interaction between the discotic molecules when they are in a face-to-face configuration. This is most likely to occur when as many atoms are as close to each other as possible. Molecules with a planar core such as the triphenylenes will allow this to happen. In contrast for discotic molecules such as D102 the twist of the phenyl rings, especially if this is not regular, together with that for the decyloxy chain, will reduce the number of effective atomic contacts.

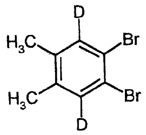
4. SYSTEM 2: ORIENTATIONAL ORDER AND PHASE SYMMETRY

The other binary mixture with which we have chosen to illustrate the importance of NMR spectroscopy shows quite remarkable behaviour. One component is the radial multiyne, 2,3,4,6,7,8-hexakis(4-nonylphenyl ethynyl)naphthalene. The phase sequence, namely Cr -N – I, can be changed dramatically by the addition of relatively small molecules such as 4,5-dibromo-o-xylene (DBOX), as the phase diagram in Figure 10 shows [23]. Thus for 75 mol % of D13 the mixture exhibits a hexagonal columnar phase, a rectangular columnar phase and a re-entrant nematic phase on cooling. This change in phase behaviour seems really quite remarkable although it should be noted that reducing the length of the terminal chains from nine to eight carbon atoms produces the same phase sequence [23]. The phase behaviour of the equimolar mixture of D13 and DBOX is very different to that for the previous mixture in that only a hexagonal columnar phase is formed. The precise role of the small molecules in inducing the phases is not clear. However, what is known is that the molecule must possess an electric dipole moment, for example 1,2,4,5-tetramethylbenzene which is isosteric to DBOX does not induce a phase but simply depresses the nematic-isotropic transition. In addition, the larger the dipole moment the higher is the maximum temperature for the hexagonal columnar to isotropic transition. It has also been suggested that the ability of the phase inductors to fit into the gaps left near the two unsubstituted positions on the naphthalene core is also important. It is clearly of interest to investigate the orientational order of the two components especially to see how they compare with each other





D13



DBOX

FIGURE 10 The phase diagram for a binary mixture of D13 and DBOX; the chemical structures of the two components are also given.

and with other discotic systems. To this end we have specifically deuteriated D13 at the two vacant positions 1 and 5 in the naphthalene core, D13-d_2; and also at the two unsubstituted positions, 3 and 6, on the phenyl ring of DBOX to give DBOX-d_2. The syntheses of these specifically deuteriated compounds is described in section 7 where D13-d_2 is denoted by **3** and DBOX-d_2 by **5**.

We begin with the pure mesogen D13-d_2; this gave the expected simple NMR spectrum containing a single quadrupolar doublet since the two deuterons are equivalent. It is not possible, therefore, to estimate the biaxiality in the ordering matrix of D13 but if we assume that, like D102, the ordering matrix is uniaxial then we can calculate the order parameter for the axis orthogonal to the plane of the naphthalene core; this gives the results shown in Figure 4. We can see from this that the transitional order parameter, S_{zz}^{NI}, is 0.46 which is essentially the same as that found for D102 in the equimolar mixture of TNF and D102. It would seem, therefore, that the local columnar structure in the N_{Col} phase has essentially no influence on the orientational order parameters of the components in comparison with a conventional nematic formed from disc-like molecules. In contrast, the entropy change, $\Delta S/R$, at the nematic-isotropic transition does appear

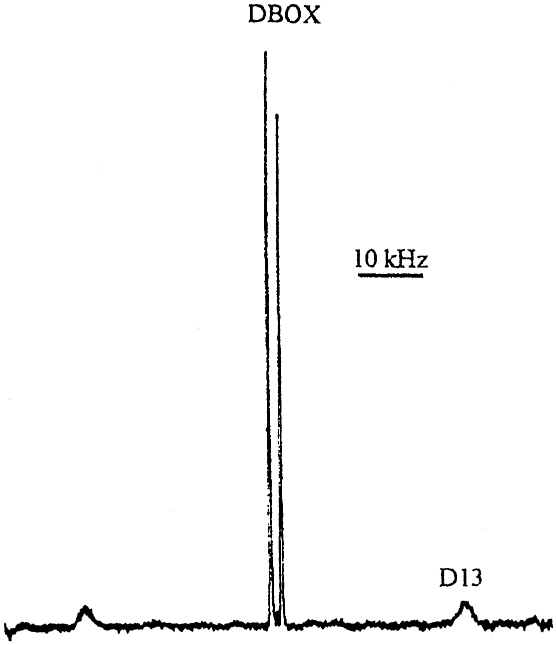


FIGURE 11 The deuterium NMR spectrum of an equimolar mixture of D13-d_2 and DBOX-d_2 in the hexagonal columnar phase at a shifted temperature, $T_I - T$, of 50°C.

to be sensitive to this structure. Thus for D13, the transitional entropy is 0.03 [21] which is very small in comparison with the value of 0.16 found for the columnar nematic-isotropic transition exhibited by the equimolar mixture of TNF and D102 [13]. It is also of interest that $\Delta S/R$ for nematics formed by rod-like molecules are higher than those formed from disc-like molecules, being typically about 0.3.

We now consider the orientational order of the two components in the equimolar mixture of D13 and DBOX which, as we can see from Figure 10, forms just a Col_{ho} phase over a wide temperature range. The NMR spectrum of the columnar phase 50°C from the transition to the isotropic phase is shown in Figure 11. Since both components are partially deuteriated, the spectrum contains two quadrupolar doublets; the strong peaks with a small quadrupolar splitting come from DBOX-d_2 while the doublet from D13-d_2 has a small height and a large splitting. The dramatic difference in line heights for the two doublets originates in the significant difference in linewidths. This difference is probably caused by the faster reorientation of DBOX in comparison with D13 because of the considerably larger size of D13. The lines broaden further as the temperature is lowered but differentially so that the spectral lines for DBOX-d_2 are still discernible after those from D13-d_2 are no longer apparent. The fact that the spectrum in Figure 11 contains just simple quadrupolar doublets means that the director in the sample is uniformly aligned with respect to the field. This is somewhat surprising because it shows that the magnetic field of the spectrometer is able to align the column axes despite the high viscosity of

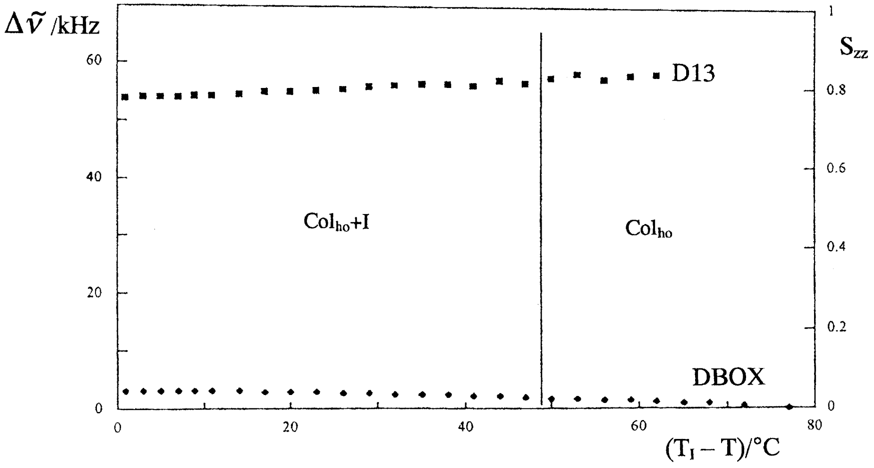


FIGURE 12 The dependence of the quadrupolar splittings and the associated order parameters for (■) D13-d_2 and (◆) DBOX-d_2 on the shifted temperature, $T_I - T$.

this ordered phase. This may occur because the sample was prepared by cooling from the isotropic phase; it passes, therefore, through a biphasic region in which columnar and isotropic phases coexist and that facilities alignment by the magnetic field.

The temperature dependence of the two quadrupolar splittings together with the order parameters calculated from them are shown in Figure 12. The most striking feature of these results is the dramatic difference in the orientational order of the two components of this chemically-induced phase. Thus while the order parameter for D13-d_2 in the columnar phase is typically about 0.8, which compares well with that for D102 in the columnar phase formed by its equimolar mixture with TNF (see Fig. 4), the order parameter for DBOX-d_2 is only about 0.02. This huge difference certainly suggests that DBOX is not sandwiched between the D13 discs unlike TNF with D102. This result provides further evidence for the suggestion that DBOX and similar phase inductors reside in the bay regions of D13 where they tumble more or less freely [23]. The filling of these regions by the small molecules implies a steric mechanism for the phase induction but the need for the inductors to possess an electric dipole moment shows that attractive forces must also be involved.

Another curious feature of this, and indeed the other system exhibiting chemically-induced liquid crystal phases, is the observation of an isotropic peak in the spectra over a wide temperature range. Since the isotropic peak is relatively sharp in comparison with the quadrupolar doublets coming from the coexisting liquid crystal phases, NMR spectroscopy is especially sensitive to the occurrence of the isotropic phase; indeed this would be extremely difficult to detect with other techniques. For the equimolar mixture of D13 and DBOX, the peak from the coexisting isotropic phase can be seen over about 50°C as is apparent from the results shown in Figure 12. Such an extended biphasic region contrasts with the behaviour for conventional mixtures where the biphasic region results from the first order character of the phase transition and the phases coexist over just a few degrees. However, during the NMR experiments we have noticed that as the sample is held at relatively high temperatures (see Fig. 10), that its colour passes from pale yellow, to dark yellow and eventually to brown. Associated with this colour change, presumably caused by the thermal decomposition of D13, was an increase in the intensity of the isotropic peak in the NMR spectrum. The decomposition of D13 might result in the creation of concentration gradients within the sample and so result in the appearance of small isotropic domains.

The mixture containing 75 mol% of D13 and 25 mol% of DBOX is fascinating because it exhibits a reentrant nematic phase and a rectangular columnar phase in addition to the hexagonal columnar phase. Here we use this system to illustrate how NMR spectroscopy can be used to establish the symmetry of a liquid crystal phase since the rectangular phase is biaxial whereas its hexagonal counterpart is uniaxial. As we have seen this can be achieved by measuring the principal components of a partially averaged quadrupolar tensor. These components can be determined by recording the spectrum of a sample in which the three directors are randomly aligned with respect to the magnetic field of the spectrometer. Here we show that this need not be the case, provided two of the directors are randomly aligned.

Since the deuterium NMR spectrum of DBOX-d_2 is so much stronger than that of D13-d_2 it is this deuteriated component which was used to explore the phase symmetry of the columnar phases. We started in the reentrant nematic phase of the mixture of D13 (75 mol%) and DBOX-d_2 (25 mol%). This is especially convenient because the director is aligned orthogonal to the field as was clearly apparent from the simple quadrupolar doublet in the spectrum. As the temperature was increased a broad feature appeared between the two nematic peaks corresponding to the formation of the $\mathrm{Col_{ro}}$ phase. The spectra of DBOX-d_2 recorded as a function of temperature within this rectangular columnar are shown in Figure 13 together with one at 385 K just inside the hexagonal columnar phase. All of the spectra contain, as we have come to expect, an isotropic component but this represents a small fraction of the sample; we shall ignore it in future discussions of these spectra. The powder-like features of the spectra show that the directors of the biaxial rectangular columnar phase are not uniformly aligned with respect to the magnetic field. In addition the absence of central horns in the spectrum (see Fig. 1) suggests that it is just two of the three directors which are randomly oriented with respect to the field. This is to be expected because the $\mathrm{Col_{ro}}$ phase is formed through a relatively weak transition from the nematic phase which would allow the director that was orthogonal to the field to remain so aligned and to become the column axis in the $\mathrm{Col_{ro}}$ phase. Then, as the discs tilt within a column, the columnar cross-section becomes elliptical creating a biaxiality which is also responsible for the rectangular organisation of the columns. From the appearance of the spectra it would seem that the two directors are randomly arranged with respect to the magnetic field, presumably the tilt of the molecular discs within a column takes place without any preference for the tilt direction. This analysis is supported by the observation that, as the temperature is increased, so the width of the two broad features decreased until an essentially sharp quadrupolar doublet appeared on entering the uniaxial hexagonal columnar phase. However, the observation of a random arrangement of the two directors with respect to the magnetic field is somewhat surprising because it might have been expected that the director associated with the most negative component of the magnetic susceptibility would be aligned parallel to the magnetic field. As a result the

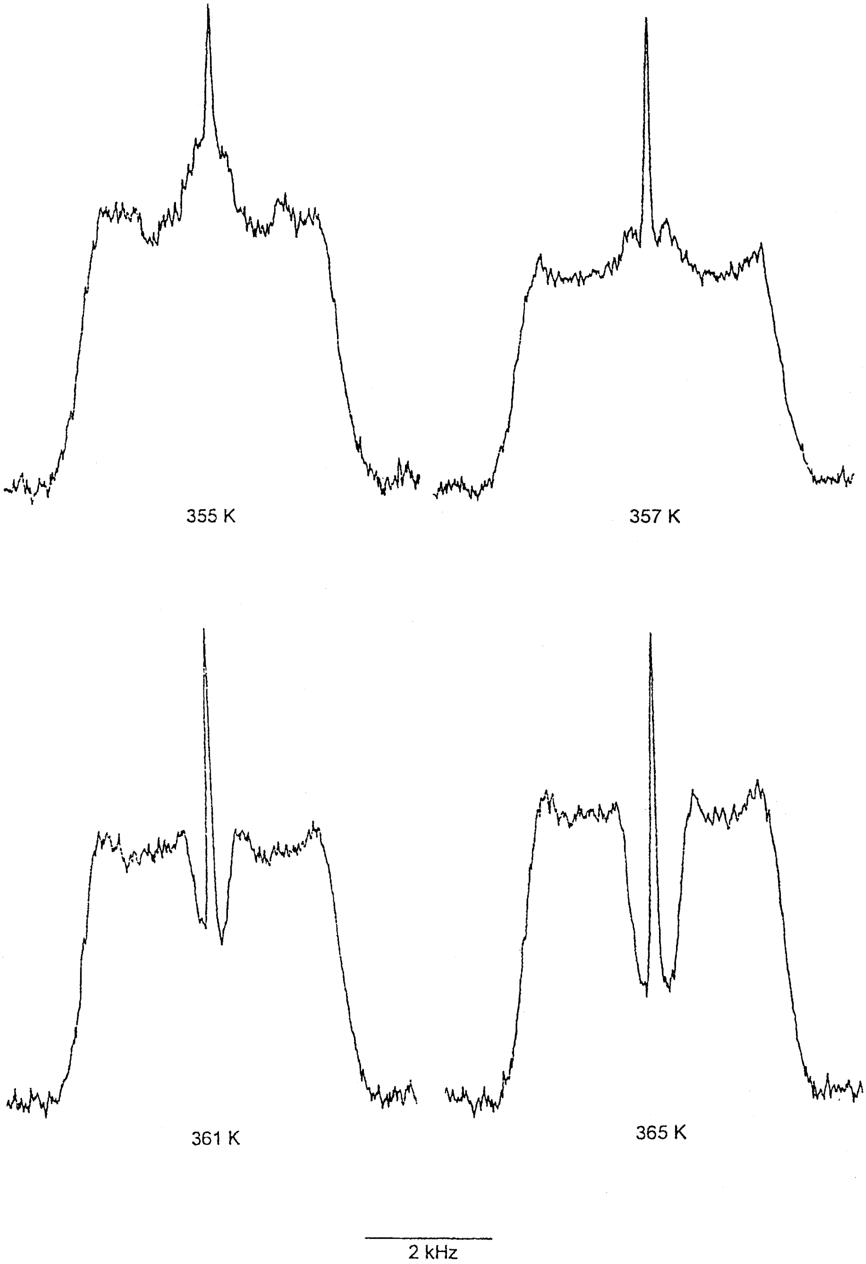


FIGURE 13 The deuterium NMR spectra of DBOX-d_2 recorded as a function of temperature within the Col_{ro} phase and just inside the Col_{ho} phase at 385 K.

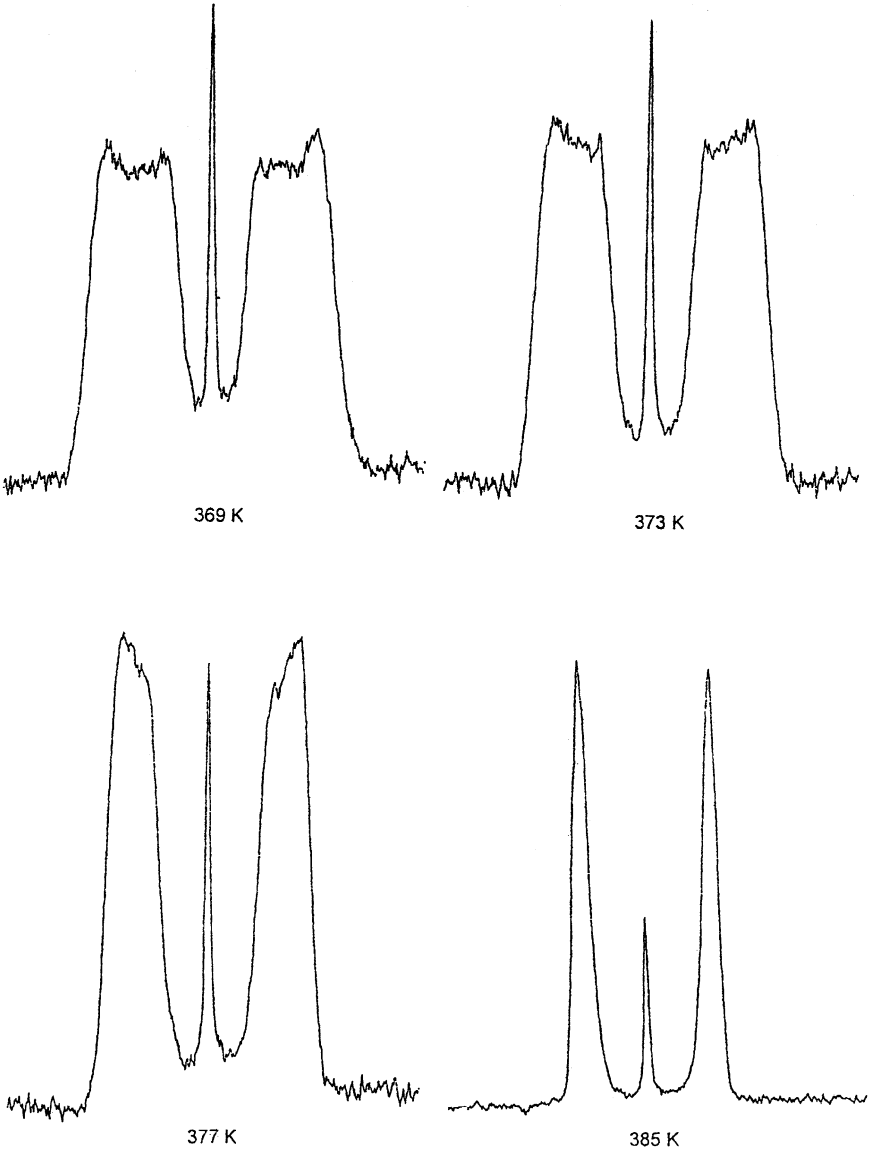


FIGURE 13 Continued.

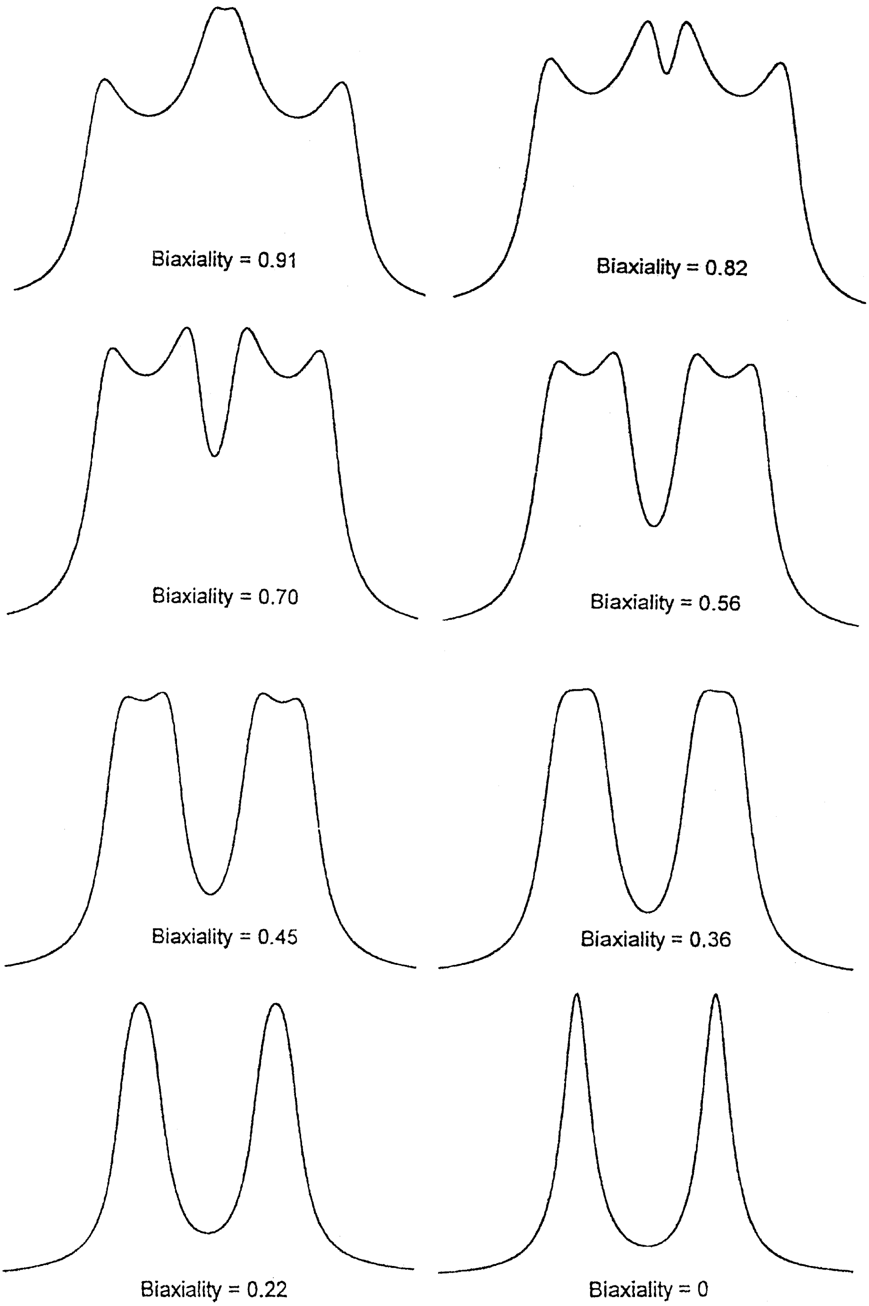


FIGURE 14 The simulated deuterium NMR spectrum of a biaxial rectangular columnar phase for which the magnetic field is randomly distributed in a plane formed by two of the directors. The spectra were simulated for a range of biaxialities, $\tilde{\eta}$, in the partially averaged quadrupolar tensor.

spectra should consist of a simple quadrupolar doublet. The fact that this does not occur may indicate that when the rectangular columnar phase is formed, the director distribution is random and that the high viscosity of the $\mathrm{Col_{ro}}$ phase prevents the appropriate director from being aligned by the magnetic field. The behaviour for the $\mathrm{Col_{ro}}$ phase formed by cooling from its hexagonal counterpart is quite different. Now the spectrum consists of a single quadrupolar doublet, albeit with relatively broad lines, which suggests that at the transition, the tilt direction of the discs is more or less uniformly aligned by the magnetic field.

To confirm this qualitative interpretation of the NMR spectra from the rectangular columnar phase and to determine the biaxiality in the partially averaged quadrupolar tensor, $\tilde{q}$, we have simulated the powder patterns. To do this the magnetic field is assumed to be randomly distributed in a plane formed by two of the directors taken to be along the major and minor axes of the elliptical columnar cross-section. The quadrupolar splitting is then given by (see Eq. (9))

$$\Delta\tilde{v}(\phi) = (3/4)\tilde{q}_{ZZ}(-1 + \tilde{\eta}\cos 2\phi) \tag{13}$$

since one director is orthogonal to the field and the powder pattern is obtained by summing spectra from all orientations of the other two directors with respect to the field. The spectra were simulated for a range of biaxiality parameters, $\tilde{\eta}$, and are shown in Figure 14. It is immediately apparent that the agreement between the simulated spectra and the experimental is very close. The variation in the simulated spectra with $\tilde{\eta}$ is relatively easy to understand. For the largest biaxiality the quadrupolar splitting associated with one of the directors is essentially zero which gives the broad central feature with a small splitting while for the other director the quadrupolar splitting is large. In the simulations as the biaxiality, $\tilde{\eta}$, is reduced so the splitting for the central peaks increases while that for the outer peaks decreases. This process continues as $\tilde{\eta}$ is decreased until no indication of the four peaks is apparent in the spectrum even though $\tilde{\eta}$ is still 0.22. The effect of setting $\tilde{\eta}$ to zero corresponding to a uniaxial phase is simply to decrease the widths of the two spectral lines. Comparison of the simulated with the experimental spectra allows us to estimate the biaxiality, $\tilde{\eta}$. This is related to the biaxiality of the rectangular columnar phase that results from the tilt of the disc-like molecules in the columns and the ordering of the tilt directions in the plane orthogonal to the column axes. Just after the formation of the $\mathrm{Col_{ro}}$ phase at 355 K the spectrum corresponds to $\tilde{\eta}$ of about 0.9 which is close to the maximum value for $\tilde{\eta}$ of unity. The biaxiality in $\tilde{q}$ then decreases more or less linearly with increasing temperature until it disappears at the transition to the columnar hexagonal phase when the tilt of the discs in the columns vanishes.

5. CONCLUSIONS

The deuterium NMR experiments that we have described have clearly provided a wealth of information concerning the behaviour of two chemically-induced discotic liquid crystals and here we draw together our primary conclusions. We begin with the orientational order for the components of these systems. For the binary mixture of D102 and TNF the Saupe ordering matrices for the two components are essentially cylindrically symmetric which indicates the lack of in-plane anisotropy in the interactions between the two molecules. The order parameters for the effective symmetry axes of the components are almost the same, suggesting a strong out-of-plane interaction between TNF and D102. In addition the order parameters in the columnar nematic phase are comparable to that for the radial multiyne D13 and for its mixture with DBOX. This equivalence is in keeping with the predictions of universality by the Maier-Saupe molecular field theory of nematics. More importantly the values of the orientational order parameters for nematics formed from disc-like molecules are similar to those composed of rod-like molecules, a result also predicted by the Maier-Saupe theory. The orientational order in the hexagonal columnar phase formed by D102 and TNF is found to be high for both components and comparable to that for D13 in the $\mathrm{Col}_{\mathrm{ho}}$ phase formed with DBOX. However, the order parameter determined for DBOX is a factor of approximately 40 smaller than D13 showing that the molecule tumbles more or less freely and indicating that the mechanism of induction is quite different to that in the D102/TNF mixture.

The availability of suitably deuteriated versions of D102 has allowed us to explore the geometry of this molecule in both the columnar nematic and hexagonal columnar phases. It is found that the five phenyl rings of the radial multiyne are twisted out of the molecular plane by approximately 30° and that this angle is essentially independent of temperature and the liquid crystal phase. It results, presumably, from steric interactions between the ortho hydrogens on neighbouring phenyl rings, in contrast, the higher order of the crystal phase causes a significant reduction in the twist angle. In addition, the decyloxy chain is found to be located above the molecular plane with a twist angle which fluctuates between $\pm 60°$. Again steric interactions, now between the chain and the neighbouring phenyl rings, are thought to be responsible for this conformation which gives D102 a scorpion-like appearance.

The biaxial symmetry of the rectangular columnar phase formed by the mixture of D13 and DBOX on heating the nematic phase is clearly revealed by the NMR spectrum of DBOX-d_2. The magnitude of the biaxiality measured for the partially averaged quadrupolar tensor is initially large but then decreases essentially linearly with increasing temperature until it vanishes at the transition to the uniaxial hexagonal columnar phase. This change in the phase biaxiality is clearly associated with the reduction in the tilt angle of the discs within the columns. In marked contrast the spectrum of the rectangular columnar phase formed by cooling the Col_{ho} phase does not indicate the biaxial nature of the Col_{ro} phase. Presumably the magnetic field is able to control the tilt direction at the Col_{ho}-Col_{ro} transition but not for the N_{Re}-Col_{ro} transition.

It is certainly apparent that deuterium NMR spectroscopy is an extremely powerful technique for the study of discotic liquid crystals.

6. EXPERIMENTAL

6.1. Syntheses of the Three Deuteriated Radial Multiynes 1,2,3, their Precursors Together with the Phase Inductors, Pentadeutero-Trinitrofluorenone 4, and Dibromodideutero-o-Xylene 5

6.1.1 Pentakis(Phenylethynyl)Phenyl-Perdeuterodecyl Ether (1)

The synthesis of **1** required five steps [23]:

1) perdeuteriation of decanoic acid;
2) its reduction to perdeuterodecanol;
3) sulphonylation of the perdeuteriated decanol;
4) preparation of pentabromo-phenyl-perdeuterodecyl ether; and
5) fivefold CC-coupling reaction of the ether with phenylacetylene.

Step 1: A mixture of 8.61 g (50 mmol) of decanoic acid, 11.28 g (110 mmol) NaOD in a D_2O solution (40%), and 3.5 g of the catalyst Pt/activated carbon (10% Pt) in 100 ml D_2O stirred for 8 days at 180°C. Yield: 6.23 g (65%) $C_{10}HD_{19}O_2$ (m.w. 191.4) as a yellowish solid, m.p. 28°C. The degree of deuteriation determined by MS was greater than 95%.

Step 2: 6.23 g (32.6 mmol) of $C_9D_{19}COOH$, was dissolved in 100 ml of dry tetrahydrofuran, and added dropwise under argon to a stirred suspension of 3.42 g (82 mmol) $LiAlD_4$ in 150 ml of dry tetrahydrofuran. This mixture was refluxed and stirred under argon for 5 h and thereafter for 18 h at room temperature. Following hydrolysis, extraction with diethylether, washing the combined extracts with dilute hydrochloric acid and subsequently with saturated aqueous sodium chloride solution, the ethereal phase was dried over anhydrous magnesium sulphate. After evaporation of the diethyl-ether under reduced pressure, 6.36 g of crude perdeuterodecanol, $C_{10}HD_{21}O$ (m.w. 179.4) were obtained as an oily material.

Step 3: This intermediate product was mixed with 70 ml of dry pyridine under argon, ice cooling, and stirring and then with 7.60 g (42 mmol) of 4-toluene-sulphonic acid chloride added in portions. The stirring of this mixture was continued for about 10 min and then for a further 3 h under argon and reflux. After cooling to room temperature, the reaction mixture was poured onto 400 g ice/200 ml concentrated hydrochloric acid and extracted with diethylether. The combined extracts were washed in succession with dilute hydrochloric acid, saturated aqueous sodium carbonate and sodium chloride solutions, dried over anhydrous magnesium sulphate, and the solvent removed under reduced pressure. Yield: 9.93 g (83% based on nonadecadeutero-decanoic acid) perdeuterodecyl 4-toluenesulphonylate, $C_{17}H_7D_{21}O_3S$ (m.w. 333.6), as a pale yellow oil, which crystallised on refrigeration.

Step 4: A mixture consisting of 29.32 g (60 mmol) of commercially available pentabromophenol, 0.15 g ($\approx$60 mmol) sodium hydride, and 9.93 g (27 mmol) of the tosylate, prepared in step 3, in 150 ml of dry dimethylformamide was stirred for 26 h at 80°C and for 60 h at room temperature. The product was crystallised from acetone and then from acetone/ethanol which yielded 10.2 g (58%) of white crystalline pentabromophenyl-perdeuterodecyl ether, $C_{16}D_{21}Br_5O$ (m.w. 645.5); m. p. 46°C;. high-resolution (MS) data of the molecular ion: calculated 644.8806, found 644.8827.

Step 5: The reaction of 3.25 g (5 mmol) of the ether, prepared in the previous step, with 5.11 g (50 mmol) of commercially available phenylacetylene in 50 ml triethylamine catalysed by 250 mg palladium(II)-bis-(triphenylphosphine)chloride, 250 mg copper(I) iodide, and 500 mg triphenylphosphine for 42 h at room temperature gave 2.27 g (60%) of the final, yellow, crystalline product **1**, $C_{56}H_{25}D_{21}O$ (m.w. 756.1). This was purified by column chromatography on 300 ml silicagel 60 with a mixture of petroleum ether and diethylether (starting at 100:1 and finishing at 50:1) as elutant followed by several crystallisations from acetone; m.p. 116.2°C; IR (CCl_4, cm^{-1}): 2211 ($C{\equiv}C$); high-resolution (MS) data of the molecular ion: calculated 755.4845, found 755.4867.

6.1.2 Pentakis(Pentadeuterophenylethynyl)Phenyl-Decyl Ether (2)

The synthesis of **2** was carried out in four steps [24]:

1) preparation of the pentabromophenyl-decylether;
2) acetylation of perdeuterobenzene;

3) transformation of this ketone into pentadeutero-phenyl-acetylene; and
4) a fivefold CC-coupling reaction of the pentabromophenyl-decyl ether of step 1 with the pentadeuteriated phenylacetylene.

Step 1: A mixture containing 24.43 g (50 mmol) pentabromophenol, 0.15 g ($\approx$60 mmol) sodium hydride, and 15.48 g (70 mmol) 1-bromodecane in 150 ml of dry dimethylformamide (commercially available chemicals) was first stirred for 26 h at 80°C and then for 60 h at room temperature. The usual work-up procedure followed by two subsequent crystallisations of the crude product from acetone yielded 23.48 g (75%) of the desired, colourless, pentabromo-phenyl-decyl ether, $C_{16}H_{21}Br_5O$ (m.w. 628.9), m.p. 49°C; MS peaks (%): 628 (3) [M^+], 487 (62) [M^+- $C_{10}H_{20}$].

Step 2: The following mixture of commercially available chemicals in 200 ml carbon disulphide was stirred for 24 h at room temperature: 1) 25.25 g (0.30 mol) perdeuterobenzene, 2) 27.45 g (0.35 mol) acetylchloride, and 3) 53.00 g (0.40 mol) aluminum trichloride. The usual work-up procedure, followed by distillation of the crude product, yielded 30.59 g (81%) of the desired pentadeuterophenyl-methyl ketone, $C_8H_3D_5O$ (m.w. 125.2), as a colourless liquid; b.p. 80°C/30 hPa; MS (%): 125 (83) [M^+].

Step 3: 30.05 g (0.24 mol) of the pentadeuterophenyl-methyl-ketone was added dropwise to 56.00 g (0.27 mol) phosphorous pentachloride over a period of 1 h while stirring and cooling with a mixture of ice/sodium chloride/water. Following the addition the reaction mixture was stirred for a further 20 h at room temperature. The phosphorous oxychloride formed was evaporated under reduced pressure, and the crude products, 38.30 g of a yellow 1:1 mixture consisting of 1-chloro-1-pentadeuterophenyl-ethene, $C_8H_2D_5Cl$ (m.w. 143.9), and of 1,1-dichloro-1-pentadeuterophenyl-ethane, $C_8H_3D_5Cl_2$ (m.w. 180.6), were distilled under vacuum (oil pump) over a Vigreux column; boiling range 32–60°C/10–26 Pa. 23 g (142 mmol) of this mixture of the two deuteriated compounds and 50.20 g (0.45 mol) potassium t-butanolate in a mixture of 300 ml diethylether and 120 ml tetrahydrofuran under argon were first stirred for 20 h at room temperature, then refluxed for 5 h, and finally for 84 h, again at room temperature. Yield: 6.60 g (43%) pentadeuterophenyl-acetylene, C_8HD_5 (m.w. 107.2), colourless liquid after the usual work-up and distillation, b.p. $\approx$ 80°C / 250 hPa; GC/MS (%): 107 (100) [M^+].

Step 4: As for the fivefold CC-coupling reaction in step 5 of sub-section 6.1.1, 3.14 g (5 mmol) pentabromophenyl-decyl ether and 5.35 g (50 mmol) pentadeutero-phenyl-acetylene catalysed by 250 mg palladium(II) bis (triphenylphosphine)chloride, 250 mg copper(I) iodide, and 500 mg triphenylphosphine in 50 ml triethylamine was stirred for 63 h at room temperature. This yielded, after the usual work-up procedure described previously, 2.21 g (58%) of the final, yellow, crystalline product **2**, $C_{56}H_{21}D_{25}O$ (m.w. 760.1); m.p. 117.7°C; IR (CCl_4, cm^{-1}): 2212 (C≡C); MS (%): 760 (46) [M^+]. The degree of deuteriation was greater than 99%.

6.1.3 1,5-Dideutero-2,3,4,6,7,8-Hexakis(4-Nonylphenylethynyl)Naphthalene (3)

The synthesis of **3** was accomplished in six steps following the procedure developed by Praefcke *et al.* [25]. The six steps were

1) perdeuteriation of naphthalene;
2) bromination to hexabromonaphthalene;
3) acetylation of nonylbenzene;
4) transformation of this ketone to the corresponding 2-chloroethene;
5) dehydrochlorination of the chloroethene to yield the nonylphenylacetylene; and
6) the six-fold CC-coupling of the hexabromonaphthalene and nonylphenylacetylene.

Steps 3, 4, 5 and 6 are analogous to those which we have encountered in the preparation of **2** and described in the subsection 6.1.2.

Step 1: 5.0 g (39 mmol) of naphthalene was dissolved in 20.0 g (240 mmol) of perdeuterobenzene and 4 ml of a 2 M solution of the ethylaluminium dichloride catalyst [26] in hexane was added by syringe. The solution was stirred for 48 h under a constant flow of nitrogen. D_2O (2 ml) was added, shaken and then 20 ml of H_2O was added, again with shaking. The aqueous layer was discarded and the benzene evaporated to leave 4.7 g of perdeuteronaphthalene. The degree of deuteriation was found by proton NMR to be about 85% which is essentially the maximum possible for this catalytic exchange mechanism. Repeating the procedure increased the degree of deuteriation to greater than 98%.

Step 2: 2.5 g (19 mmol) of the perdeuterionaphthalene was added, stepwise, to a stirred solution of 4.0 g (15 mmol) aluminium tribromide in 40 g (250 mmol) of bromine at 0°C for 3 h and then left for 12 h at room temperature. The reaction mixture was poured onto ice and aqueous sodium disulphite added. A dark brown solid was removed by filtration and recrystallised twice from toluene to give dark red crystals of 1,5-dideutero-2,3,4,6,7,8-hexabromonaphthalene $C_{10}D_2Br_6$ (m.w. 603.6); m.p. 311–312°C (IR nujol mull, cm^{-1}): 1534 (C-C), 507 (C-Br).

Step 3: 10.0 g (50 mmol) of nonylbenzene was added slowly to a stirred mixture of 8 g (60 mmol) anhydrous aluminium trichloride and 4.3 g (55 mmol) of acetyl chloride in dry carbon tetrachloride. The reaction mixture was cooled in an ice bath for 1 h after which it was stirred for another hour at room temperature before being poured onto ice and concentrated hydrochloric acid. The organic layer was washed with 2 M hydrochloric acid (twice) sodium carbonate and water. The organic component was dried over 4 Å molecular sieves for 12 h and then the solvent was removed to give the crude product. This was purified by distillation on a Kugelrohr apparatus to give 4-nonylacetophenone as a colourless liquid $C_{17}H_{26}O$ (m.w. 246.4). Yield 7.1 g (59%) IR (liquid, cm^{-1}): 1686 (C=O).

Step 4: 20.2 g (82 mmol) of the 4-nonylbenzophenone was added dropwise to 16.5 g (75 mmol) of phosphorous pentachloride cooled by an ice/sodium chloride/water bath. The mixture was stirred for 1 h and then for a further 12 h at room temperature. The major by-product, phosphorous oxychloride was removed by distillation under reduced pressure. The desired product was purified by further distillation on a Kugelrohr apparatus to give a yield of 20.7 g (64%) of a clear liquid 1-(4-nonylphenyl)-2-chloroethane, $C_{17}H_{25}Cl$ (m.w. 264.8).

Step 5: 18.5 g (70 mmol) of the chloroethane produced in the previous step and 20.9 g (190 mmol) of potassium t-butanolate were refluxed in 225 ml of t-butanol for 36 h at 110°C. After the reaction mixture had been cooled it was poured onto an ice/water slush and the product extracted with diethyl ether. The organic component was washed with a saturated solution of sodium chloride and dried over anhydrous magnesium sulphate. The solvent was removed by evaporation and the crude product was purified by distillation on a Kugelrohr apparatus. This gave 7.8 g (50%) of pure 4-nonylphenyl-acetylene $C_{17}H_{24}$ (m.w. 228.4). IR (film, cm^{-1}): 1644 (C-C).

Step 6: In the final step 1.35 g (2.2 mmol) of the perdeuteriohexabromonaphthalene was added to 4.7 g (20 mmol) of 4-nonylphenyl-acetylene in 25 ml of degassed triethylamine. The catalyst system comprising of 100 mg palladium (II) bis(triphenylphosphine) dichloride, 100 mg copper (I) iodide and 200 mg triphenylphosphine was then introduced and the mixture was purged continuously with nitrogen, heated to 105°C and stirred for 18 h. After cooling, 150 ml of light petroleum ether was added with stirring; a dark brown suspension was formed which was removed by filtration. The solvent was evaporated from the remaining solution, diethyl ether added and the solution was washed with 2 M hydrochloric acid, saturated aqueous sodium chloride and then dried over anhydrous magnesium sulphate. The solvent was removed to leave a brown viscous oil which was washed with hot acetone and further purified by column chromatography using flash silica and a mixture of light petroleum ether and ethylacetate (100:1) as eluent. The product was obtained as brown crystals which were recrystallised twice from a mixture of acetone and 1,2-dichlorobenzene (20:3) to give 2.1 g (75%)

yellow crystals of 1,5-dideutero-2,3,4,6,7,8-hexakis(4-nonylphenylethynyl)naphthalene $C_{112}H_{138}D_2$ (m.w. 1488.3). T_{NI}=110.5°C. IR (nujol mull, cm^{-1}): 2198 (C≡C), 1772, 1607 (C-C), 1020, 894, 833. MS (Argon FAB): 1484 [M^+].

6.1.4 1,3,5,8-Pentadeutero-2,4,7-Trinitrofluerenone (4)

The synthesis of the perdeuteriated version of the phase inductor 2,4,7-trinitrofluorenone involved three steps [27]. These were:

1) deuteriation of fluorene in the aromatic sites;
2) oxidation of fluorene to give the perdeuteriated fluorenone; and
3) nitration to give the desired product **4**

6.1.5 3,6-Dideutero-4,5-Dibromo-o-Xylene (5)

The synthesis of this phase inductor with two deuterons in the phenyl ring was accomplished in a single step using the catalytic exchange procedure described in subsection 7.1.3.

0.44 g (1.7 mmol) of 4,5-dibromo-o-xylene was added to 2.0 g (24 mmol) of perdeuterobenzene and the system purged with nitrogen. 0.4 ml of a hexane solution of the catalyst, ethylaluminium dichloride, was added and the mixture left for 2 h. The reaction was quenched by the addition of 5 ml D_2O, the organic layer was left to evaporate and 0.38 g (77%) of the product was obtained. The degree of deuteriation was found by proton NMR to be approximately 70%. It is not essential to achieve 100% deuteriation since the deuterium NMR spectrum originates solely from the deuteriated material. However, the greater the extent of deuteriation, the stronger the NMR spectrum will be.

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