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Electric field N.M.R. of pretransitional effects in liquid crystals

A solute study

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Pretransitional effects in the isotropic phase of liquid crystals are manifest in the N.M.R. spectra of solutes recorded in the presence of an applied electric field. The temperature dependence of the quadrupolar splittings of p-xylene-d_{10} in the isotropic phase of the nematogen 4-n-pentyl-4′-cyanobiphenyl is investigated, and proves to be as expected from the Landau–de Gennes theory for pretransitional effects. The influence of temperature in the biphasic region of the phase diagram is very striking: the orientational ordering of the solute is temperature independent. The applied electric field not only determines the ordering of the solute, but also has a clear effect on the transition temperature. Electric field N.M.R. of solutes to study pretransitional effects is an alternative to the investigation of the nematogen itself.

1. Introduction

Liquid crystals in the isotropic phase often show a pronounced pretransitional behaviour when approaching the transition to the nematic phase. This phenomenon has been known for a long time, and it has been studied by several techniques. Amongst them, the electro-optical (Kerr) and magneto-optical (Cotton–Mouton) effects have been employed frequently. Spectroscopic methods to study pretransitional behaviour are also available, and N.M.R. spectroscopy is one of them. The advantages of a spectroscopic method compared to bulk oriented techniques have been pointed out [1]. The first N.M.R. reports dealt with the pretransitional characteristics of spin–lattice relaxation [2]. Of more recent date are the investigations of line-splittings in the N.M.R. spectra of the liquid crystal molecules in the pretransitional region. These splittings are of quadrupolar or dipolar origin, and they are induced by partial orientation of the molecules by the magnetic field of the spectrometer [3] or by an applied electric field [4]. The effects observed are much larger than in normal liquids and solutions exposed to orienting electric or magnetic fields [5].

An alternative to the use of N.M.R. to study the nematogen itself is the use of solute probe molecules. A widespread use of probe molecules is found in the study of molecular dynamics [6, 7]. Pretransitional magnetic field alignment effects have also been investigated by N.M.R. of solutes [1, 8]. Here we report a study of pretransitional electric field alignment effects, manifested in the N.M.R. spectra of the solute.

Upon dissolving a non-mesomorphic solute in a liquid crystal, two effects play a role. Firstly, the transition temperature is shifted to lower temperatures, and secondly, in the phase diagram of the system a region appears where the isotropic and nematic phases can coexist. The limiting temperatures of this biphasic region are denoted T_N

(at the low temperature side) and T_I (at the high temperature side); T_N is the temperature below which only the nematic phase is thermodynamically stable; above T_I only the isotropic phase can exist. The width of the coexistence region is determined by the concentration of the solute. In the present case of 2·7 mol per cent *p*-xylene-d_{10} in the liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB), the biphasic region is 0·6°C wide, a value in agreement with the observation of Oweimreen *et al.* [9]. This situation, with two transitions, is in contrast with that found in *pure* nematogens, where only one transition is found, i.e. a nematic-to-isotropic phase transition at temperature, T_NI.

Transitions from isotropic to nematic phase can conveniently be monitored by N.M.R. This is achieved by recording the integrals of the isotropic phase N.M.R. signals of the solute or the solvent as a function of the temperature. The nematic phase is reached when a sharp decrease of the integrals is observed. This method, applied before [1, 4], has been adopted in this work. Spectra were recorded in the isotropic and the biphasic regions, and occasionally in the nematic phase. The temperature behaviour of the effects also is investigated, as is the influence of the electric field on the phase transition.

2. Experimental

The liquid crystal, 5CB, was obtained from BDH Chemicals and used without further purification; *p*-xylene-d_{10} was purchased from Janssen Chimica, Belgium (99 per cent D), and was also used as such. The solute was dissolved in 5CB to 2·7 mol per cent. The Teflon electric field N.M.R. sample cell has been described before [10]; no essential changes were made. The electrode separation within the cell was 4 mm. The N.M.R. spectra were recorded with a Bruker WM 250 spectrometer (magnetic field 5·9 T), and in some cases with a wide-bore Bruker WH-180 spectrometer.

Temperature regulation is crucial in the present experiments. It was achieved in the way indicated previously [4]. The temperature stability was always better than 0·04°C, with a temperature gradient over the cell better than 0·02°C during an experiment. The temperatures were measured with copper-constantan thermocouples.

3. Theory

The spin hamiltonian describing the energy of an oriented spin system can be written

$$H = H_\mathrm{Z} + H_\mathrm{s} + H_\mathrm{J} + H_\mathrm{Q} + H_\mathrm{D}. \tag{1}$$

The subscripts refer to the Zeeman interaction with the magnetic field, the chemical shift contribution, the scalar (indirect) spin–spin coupling, the quadrupolar interaction (for nuclei with spin $I \geqslant 1$) and the dipolar (direct) spin–spin coupling. Of these terms, the last two are anisotropic spin interactions, which are zero in the isotropic (non-oriented) case and show up upon partial orientation of the molecule.

Of these anisotropic interactions, we shall only consider the quadrupolar coupling, since the nucleus of interest is the deuteron. In the limit of a strong magnetic field, such that the nuclear spins are quantized along the direction of the field (the laboratory z' axis), H_Q can be written as [11]

$$H_\mathrm{Q} = \frac{eQ}{4I(2I-1)}[3I_{z'}I_{z'} - I^2]\,V_{z'z'}, \tag{2}$$

where I is the nuclear spin, $V_{z'z'}$ is the electric field gradient in the direction of the magnetic field at the nucleus, $I_{z'}$ and I^2 are spin operators and eQ is the nuclear quadrupole moment. It is often more convenient to express $V_{z'z'}$ in terms of the components V_{ii} in its principal axis system, which has (often) a fixed orientation in the molecular frame. For deuterons the electric field gradient tensor is nearly axially symmetric. Therefore, the asymmetry parameter η may be neglected for our purpose and only $V_{zz} = eq$ remains. If it is further assumed that the methyl groups rotate very fast compared with the reorientational motion of the molecule, and taking tetrahedral angles for the methyl C–D bonds and a hexagonal geometry for the aromatic ring, we obtain for the quadrupolar splitting of the methyl and ring deuterons, respectively [5]

$$\Delta\nu_{\mathrm{Me}} = -\frac{1}{2}\left(\frac{e^2qQ}{h}\right)_{\mathrm{Me}} \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle, \qquad (3a)$$

$$\Delta\nu_{\mathrm{Ar}} = -\frac{3}{16}\left(\frac{e^2qQ}{h}\right)_{\mathrm{Ar}} \{\langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle + \tfrac{9}{2}\langle \sin^2\theta\cos 2\phi\rangle\}. \qquad (3b)$$

Here θ and ϕ are the polar angles describing the orientation of the magnetic field in the molecular frame (see figure 1). The deuteron quadrupolar coupling constants, needed to calculate the orientational parameters from the observed quadrupolar splittings, are known from other sources: 165 kHz and 186 kHz for the methyl and aromatic deuterons respectively [12, 13]. Since the sign of the splittings cannot be derived from the spectra, the signs of the orientational order parameters have to be deduced from auxiliary information. In the subsequent discussion this matter is returned to.

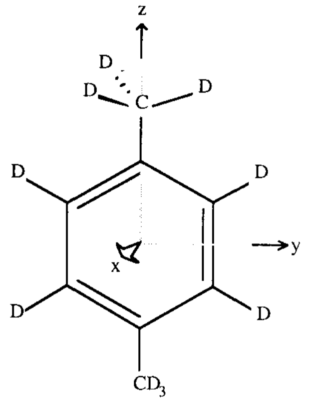

Figure 1. The molecular axis system defined for p-xylene-d_{10}.

4. Results and discussion

4.1. *The isotropic phase*

^{2}H N.M.R. spectra of p-xylene-d_{10}, dissolved in 5CB, were recorded in the isotropic state as a function of the applied voltage and temperature. Figure 2 shows the observed splitting versus the square of the electric field strength. The steeper of the two lines always reflects the splitting of the methyl deuteron resonance. As can be seen, a linear relationship between splitting and squared voltage is found. The methyl splitting is about 200 Hz at an electric field of $4{\cdot}5 \times 10^6\,\mathrm{V\,m^{-1}}$, close to the phase transition. These effects are much larger than expected on the basis of the direct

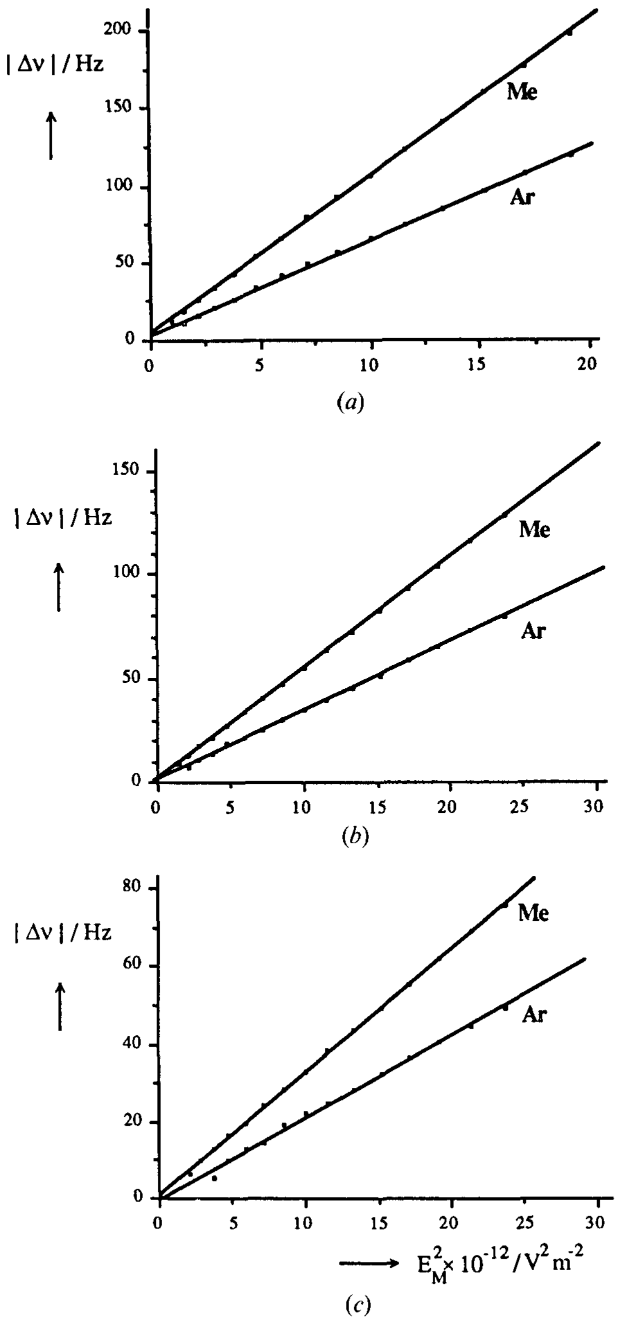

Figure 2. ^{2}H quadrupolar splitting as a function of E^2; (*a*) $T = T_1$; (*b*) $T = T_1 + 1{\cdot}33°$C; (*c*) $T = T_1 + 3{\cdot}60°$C. The two or three points at lowest field strengths have a low accuracy.

interaction between the anisotropic molecular polarizability of the solute and the applied field [14], and should therefore be attributed to an indirect alignment effect, i.e. the probe molecules are oriented via anisotropic interactions with the solvent, which itself is oriented uniformly by the applied electric and/or magnetic field [4].

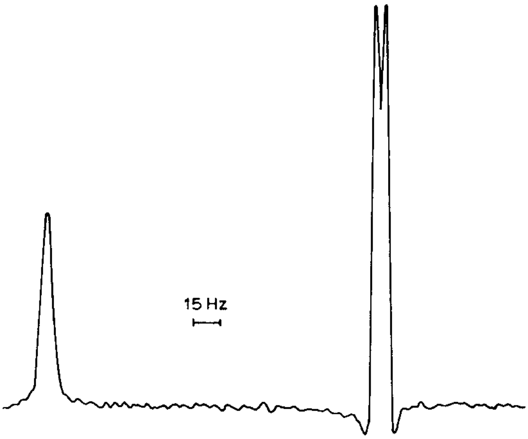

Figure 3. ^2H N.M.R. spectrum of *p*-xylene-d_{10} in 5CB, at T_I + 1°C (magnetic field strength 5·9 T).

The intercept of the straight lines in figure 2 is non-zero and tends to decrease with increasing temperature. This indicates the presence of a residual orientation mechanism in the absence of the electric field. The effect should be attributed to the magnetic field induced contribution to the splitting. An independent check of this expectation was made by measuring the ^2H N.M.R. spectrum of the solute in 5CB in a normal spinning N.M.R. sample tube (which allows a better resolution than achievable in the electric field N.M.R. cell). The result is shown in figure 3; a magnetic field induced splitting of approximately 5 Hz is observed for the methyl deuterons at $T = T_I + 1°C$. The splitting could not be resolved for the aromatic deuterons, but in view of the observed line broadening, it is definitely present. An electric field N.M.R. experiment on the Bruker WH 180 (4·2 T) spectrometer leads to an essentially zero intercept in the $\Delta\nu$ versus E^2 plot. This is to be expected, since the magnetic field induced order is proportional to the square of the magnetic field strength. Magnetic field induced pretransitional effects in the spectra of solutes have been studied by Attard *et al.* [1, 8].

The effect of the temperature on the order of the solute is depicted in figure 4(*a*). The (absolute) value of $\Delta\nu_{Me}$, which is linearly proportional to the ordering of the solute (see equation (8)), is plotted reciprocally against $(T - T_I)$. According to the Landau–de Gennes theory [15] for pretransitional behaviour in liquid crystals, the electric field induced solvent order should be proportional to $(T - T^*)^{-1}$ for temperatures not too close to T^*. The order is expected to be complete at $T = T^*$, the fictitious temperature at which the second order isotropic-to-nematic phase transition would take place. For a second order phase transition, the change of, for example, the free energy and entropy is continuous, in contrast to the discontinuities found for first order transitions. In the Landau-de-Gennes expansion of the free energy in the order parameter S, a continuity of the entropy at the transition temperature ($\Delta s = 0$) would lead to a second order transition at $T^* = T_{NI}$. Since for liquid crystals Δs is very small, T^* is not found at T_{NI}, but at a slightly lower temperature [15]. The isotropic-to-nematic transition is often called nearly second order, or weakly first order, for this reason. As the order of the solute is determined by that of the solvent, the reciprocal of $\Delta\nu_{Me}$ should be proportional to the temperature. This is borne out experimentally, and T^* is found 2°C below T_I (1·4°C below T_N).

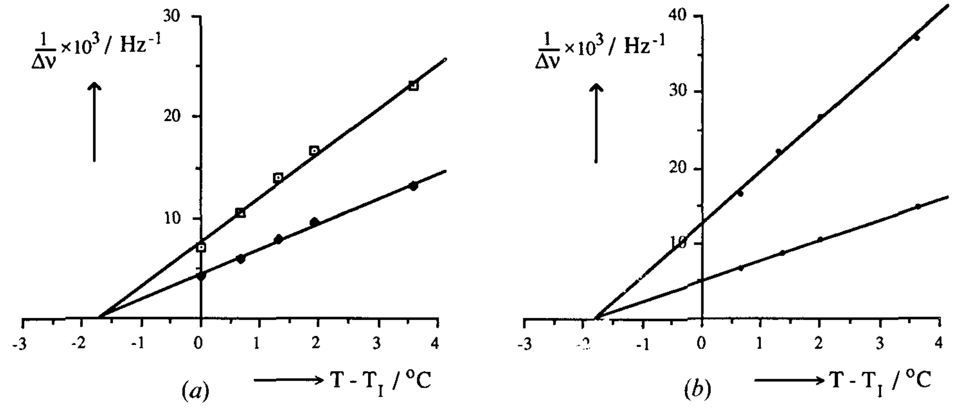

Figure 4. (*a*) Reciprocal of $\Delta\nu_{Me}$ of the solute versus $T - T_I$, at $E = 4{\cdot}9 \times 10^6\,\mathrm{V\,m^{-1}}$ (steeper line) and at $3{\cdot}7 \times 10^6\,\mathrm{V\,m^{-1}}$. (*b*) Reciprocal of the ^{1}H dipolar splittings of the α-methylene protons (steeper line), and the methyl protons of 5CB versus $T - T_I$ ($E = 4{\cdot}8 \times 10^6\,\mathrm{V\,m^{-1}}$).

An analogous experiment can be performed by monitoring the orientation of the solvent as a function of the temperature. To this end the dipolar splittings of the α-methylene and the terminal methyl-group protons of 5CB were measured in the ^{1}H electric field N.M.R. spectra of the solvent. Their reciprocals are plotted against temperature in figure 4(*b*), giving a value of 1·8°C for $T^* - T_I$.

For *pure* 5CB, T^* was found to be approximately 1·1°C below T_{NI} [4]. In both the pure compound and the mixture, the nematic phase has already been reached before the second order transition can occur. A similar observation has been made for the system Phase V/anthracene [1].

4.2. *The orientation order parameters*

Thus far, only the absolute values of the observed quadrupolar splittings were referred to in the discussion. Also of relevance are of course the signs of the two orientational parameters for the solute. They can be deduced once a choice of sign has been made for the observed splittings. To this end, it is assumed that $\langle \frac{3}{2}\cos^2\theta - \frac{1}{2}\rangle$ is positive for *p*-xylene, since the long molecular axis will preferably be parallel to the orientation axis of 5CB, which is parallel to the magnetic (and electric) field. Hence $\Delta\nu_{Me}$ is negative (cf. equation (3)).

The sign of the other orientational order parameter is less easily deduced. The N.M.R. spectrum of the solute in the biphasic region might be of help. The signs of the orientational parameters in this region are likely to be equal for the constituting phases [1, 8]. It is assumed that the main dipolar effects observed in the spectrum in the nematic phase originate from dipolar couplings between the methyl deuterons (D_{Me}) on the one hand, and between aromatic deuterons in adjacent positions on the ring (D_{Ar}) on the other. The appearance of the spectrum could then only be simulated adequately with opposite signs of D_{Me} and the quadrupolar coupling $\Delta\nu_{Me}$, and of D_{Ar} and $\Delta\nu_{Ar}$. Since $\langle \frac{3}{2}\cos^2\theta - \frac{1}{2}\rangle$ is taken positive, $\Delta\nu_{Me}$ is negative (for a positive quadrupolar coupling constant; see equation (3)). Evaluating the expression for the dipolar coupling [16], a positive sign is found for D_{Me}, and a negative one for D_{Ar}. Consequently, by the result of the simulation concerning the relative signs, $\Delta\nu_{Ar}$ is positive. By substitution of the experimentally observed $\Delta\nu_{Ar}$ and $\Delta\nu_{Me}$ into equation (8),

$\langle \sin^2\theta \cos 2\phi \rangle$ can be calculated; its sign proves to be negative. Similar observations, i.e. $\Delta\nu_{Ar}$ and $\Delta\nu_{Me}$ positive and negative respectively, with a resulting negative $\langle \sin^2\theta \cos 2\phi \rangle$ have been made for *p*-xylene in Phase V [8]. Finally, by the assumption indicated, the same signs are adopted for the solute in the isotropic phase.

The two order parameters in the isotropic phase can now be deduced from electric field N.M.R. spectra. Their magnitudes are typically of the order of 10^{-4} to 10^{-3}. These values should be compared to the orientational order in the nematic phase ($\sim 10^{-1}$) on the one hand, and to the electric field induced order in normal liquids ($\sim 10^{-5}$ to 10^{-4}) on the other. In the pretransitional region of the isotropic liquid crystal, the order of the solute that can be reached is intermediate between that in the nematic phase and that in normal liquids. Nevertheless, the potential of mean torque, to which the solute molecules are subjected according to mean field theory, is still very weak. This explains why a plot of $\langle \sin^2\theta \cos 2\phi \rangle$ versus $\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$, for different electric field strengths at a given temperature, gives a straight line through the origin (cf. figure 5). Due to the weakness of the orienting potential, i.e. $U(\Omega) \ll kT$, the series expansion of the distribution function,

$$f(\Omega) = Z^{-1}\exp[-U(\Omega)/kT], \tag{4}$$

can be truncated after the linear terms. In equation (4) Z is the orientational partition function and $U(\Omega)$ is the ordering potential. If $U(\Omega)$ is expanded in spherical harmonics, each order parameter can be related to a single expansion coefficient due to the orthogonality of the spherical harmonics. This is the same reasoning as followed by Attard *et al.* [8] to explain the temperature independence of the ratio $\langle \sin^2\theta \cos 2\phi \rangle / \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$ (or, rather, of the corresponding ratio $(S_{xx} - S_{yy})/S_{zz}$) [1, 8]. We also found this ratio to be temperature independent, with a value of $-0{\cdot}54$, but this is not so surprising in view of the small temperature range studied (T_I to $T_I + 4$°C).

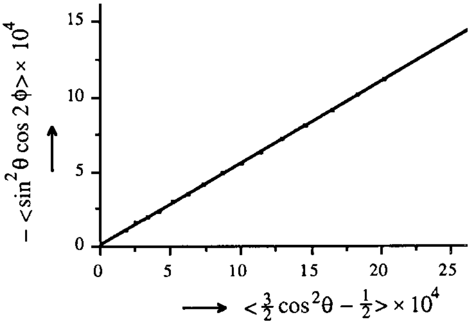

Figure 5. $\langle \sin^2\theta \cos 2\phi \rangle$ versus $\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$, at $T = T_I + 0{\cdot}66$°C.

4.3. *The biphasic region*

In this part of the phase diagram, the spectra of the solute in the nematic and isotropic phases can be observed separately. This means that the exchange of the solute between the two phases is in the slow motion regime. From the ratio of the observed quadrupolar splittings in the two phases, the exchange rate is estimated to be slower than $100\,\mathrm{s}^{-1}$. An estimate from solute spectra of both phases in a study of magnetic field induced pretransitional behaviour arrived at a rate of at most $10^4\,\mathrm{s}^{-1}$ [8].

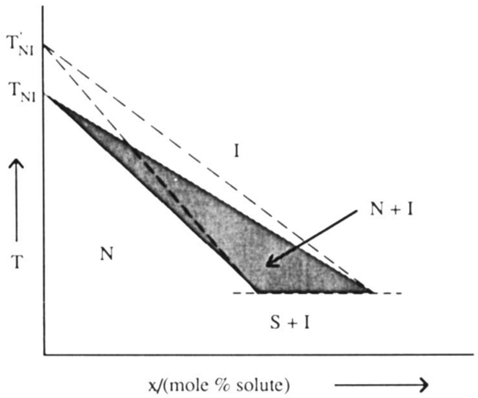

Figure 6. Phase diagram of the biphasic region (see text for explanation).

A second interesting feature emerges in the biphasic region: at a given electric field strength, the quadrupolar splittings of the solute in the isotropic phase are independent of temperature. The effect can be understood by looking at the phase diagram (cf. figure 6). Upon lowering the temperature within the biphasic region the composition of the isotropic phase changes such that, when considered separately, this phase has a T_I that is always equal to the actual temperature of the sample [8]. Thus, the reduced temperature T/T_I is effectively unity throughout the biphasic region. In mean-field approaches it is this reduced temperature that determines the properties of the system, for example the orientational order [17].

As before in the isotropic phase, the ratio of the two orientational parameters of the solute in the isotropic part of the biphasic region was investigated. The result is a constant value of $-0{\cdot}53 \pm 0{\cdot}01$. This is close to that observed in the isotropic phase ($-0{\cdot}54$) and also to that measured in the nematic phase: $-0{\cdot}52$, at $T = T_N - 1°C$. These observations seem to imply that no basic change takes place in the orientational ordering mechanism of the solute; it is ordered by the same anisotropic interactions with the solvent, be the latter oriented by electric or magnetic fields. The fact that both the dielectric and the diamagnetic anisotropy of 5CB is positive is probably important. It means that in this case both fields tend to align 5CB with its long axis parallel to the field. Only the strength of the orienting potential is different for the two fields.

4.4. *The effect of the electric field on the phase transition*

In a previous paper [4] the influence of the applied field on the value of the transition temperature was mentioned. The observation made was a non-linear relation between the dipolar spin–spin coupling between certain protons of the pure liquid crystal and the square of the applied electric field. An explanation was found in an increase of the nematic-to-isotropic transition temperature under the influence of the electric field. Experimental evidence for the influence of externally applied fields (either magnetic or electric) has been reported occasionally. Strong magnetic fields were shown to increase T_{NI} slightly [18], but the relatively weak diamagnetic anisotropy of liquid crystals was argued to be a prohibitive factor for more pronounced shifts [19, 20]. More promising in this respect are strongly polar nematogens, which have a substantial dielectric anisotropy. The early experiments of Helfrich [21], who observed a shift of about 1 K in an electric field of $10^7 \mathrm{V\,m^{-1}}$, supports this expectation [20]. Several other reports on the influence of electric fields on the temperature of the nematic-to-isotropic transition have appeared [22].

Investigations regarding the effects of applied external fields on transition temperatures are of relevance in view of the feasibility of attaining a critical system. The increase of T_{NI} with the applied field is expected to end at a critical point in the T–E phase diagram. Beyond this point, denoted ($T_{\mathrm{NI,cr}}$; E_{cr}), the nematic and isotropic phases are indistinguishable, and the first order phase transition has disappeared. The value of $T_{\mathrm{NI,cr}}$ with respect to the field-free $T_{\mathrm{NI,0}} = T_{\mathrm{NI}}$, and the magnitude of E_{cr} (and H_{cr}), has been calculated by several theoretical approaches. In the well-known Maier–Saupe molecular field approximation [24] $T_{\mathrm{NI,cr}}$ is calculated to be approximately 15°C above $T_{\mathrm{NI,0}}$ for 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) [19, 25] (a frequently used model liquid crystal, since an abundance of experimental data is available for this compound). A calculation at a level just beyond the Maier–Saupe theory, arrived at a value of 12°C above the field-free transition point of MBBA [19]. E_{cr} is about $3 \times 10^8 \mathrm{V\,m^{-1}}$ in both approaches, and probably within reach experimentally by using a very intense and focused laser beam [19] (the electric field is then of optical frequency). Critical magnetic fields, of approximately 800 T, are not attainable with current technologies. The phenomenological theory of Landau–de Gennes [15] for the nematic-to-isotropic transition has also been used to calculate the effects of external fields [19]. The values of the critical fields and critical temperatures are however an order of magnitude, or more, smaller: $T_{\mathrm{NI,cr}} = T_{\mathrm{NI,0}} + 0{\cdot}5$°C, $E_{\mathrm{cr}} = 3 \times 10^7 \mathrm{V\,m^{-1}}$ and $H_{\mathrm{cr}} = 100$ T.

In a recent paper, using a mean-field point of view, it was calculated that for *strongly polar* nematogens with a cyano end group (e.g. 5CB) the critical point is reached with an effective internal electric field of $9{\cdot}6 \times 10^7 \mathrm{V\,m^{-1}}$, at 6°C above $T_{\mathrm{NI,0}}$ [20]. Furthermore, the shift of T_{NI} is found to be proportional to E^2, as also reported by others [23]. It would be of interest to see whether the present electric field N.M.R. result could give any evidence for or against the different theoretical predictions. To this end, the integral of the signal of isotropic 5CB was measured in the biphasic region, at four different strengths of the electric field. The results are shown in figure 7, in which the integral is plotted against the square of the electric field. Because of technical difficulties, only four data points could be obtained. Nevertheless, it is clear that figure 7 is in accord with an E^2 dependence of T_{I}. The data do not preclude a stronger than E^2 relationship of the integrated fraction, but even if this were the case, it would still be in agreement with a linear dependence of T_{I} on E^2. This can be shown, without having knowledge of its precise shape, by assuming that the biphasic region in the phase diagram has a triangular form, and that the crystalline–nematic and crystalline–isotropic transitions are not affected by the electric field (see figure 6). These assumptions seem reasonable in view of the small solute concentrations used. Then two effects will contribute to the field dependence of the amount of isotropic liquid in the biphasic region at a fixed temperature. The phase lines are tilted towards higher temperatures as well as to higher solute concentration. Simple geometric arguments then show that the isotropic part of the biphasic region decreases with the electric field strength acccording to

$$\text{Integral (isotr.)} = (A - BE^2)/(C + DE^2).$$

The constants A to D are determined by the shape of the phase diagram and by the shift of T_{NI} with increasing field.

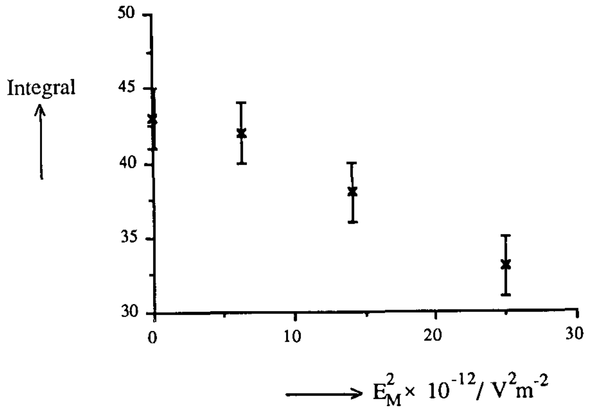

Figure 7. Integrated intensity (in arbitrary units) of the isotropic 5CB signal in the biphasic region, versus the square of the electric field. The vertical bars indicate estimated errors.

It may seem puzzling that the E^2 dependence of the solute deuteron splitting in the isotropic phase is represented by straight lines as shown in figure 2. If the splittings depend on $T - T_I$, they should show positive deviations from linearity when going to higher field. Clearly, the splittings depend only on $T - T^*$, with T^* being independent of the electric field strength. This behaviour is in contrast to that found for dipolar splittings of methylene and methyl protons in pure, isotropic 5CB [4]. Here, positive deviations from linearity were in fact ascribed to a decrease of $T - T_{NI}$ with increasing electric field. A clue to understanding such behaviour might be the breakdown of the Landau–de Gennes model, due to the high degree of ordering of the liquid crystal molecules. More experimental work is needed to clarify this point, however.

5. Conclusions

The use of solute molecules to trace electric field induced pretranstional effects in N.M.R. is shown to be a good alternative to the study of the nematogen itself. The pretransitional effects are clearly established, and have been interpreted by the Landau–de Gennes theory. The presence of the solute results in a biphasic region in the phase diagram of the system, where the isotropic and nematic phase coexist. The temperature behaviour of the orientational order in this region is striking, since a change of temperature gives no change in the solute order. When calculating the ratio of the two orientational parameters of the solute from the N.M.R. spectra in the nematic and isotropic phases, a marked degree of constancy is found. This probably points at a strong similarity of the ordering mechanisms that play a role in the ordering of the solvent in the different phases. Finally, a clear influence of the applied electric field on the phase transition as such is observed, which has been explained only tentatively. Further research should be done to gain a better insight into the effects of the field.

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