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Broadband dielectric studies of weakly polar and non-polar liquid crystals

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Complex dielectric permittivities, for two orientations of the director **n**, parallel (**E** || **n**) and perpendicular (**E** \perp **n**) to the probing electric field **E**, of the weakly polar liquid crystals (LCs) 4,4'-dihexylazoxybenzene (D6AOB) and 4,4'-diheptylazoxybenzene (D7AOB) as well as the non-polar LC diheptylazobenzene (D7AB) have been measured in the frequency range 75 kHz to 1 GHz. The measurements were performed in the nematic, smectic and isotropic phases of the LCs. The dielectric anisotropies $\Delta \varepsilon$ ($=\varepsilon_{\parallel}-\varepsilon_{\perp}$) obtained from the values of dielectric permittivities at 100 kHz in the nematic phase were found to increase with decreasing temperature. However, for the DnAOBs, the $\Delta \varepsilon$ values are somewhat smaller than that for D7AB which does not have a permanent dipole moment. In the nematic phase two molecular relaxation processes were observed for both DnAOBs in each of the orientations parallel and perpendicular. The four processes merge into two separate processes in the isotropic phase. For D7AB no orientational relaxations were observed in the experimental frequency range.

1. Introduction

The orientational ordering in liquid crystalline systems depends on the shape of the molecules and the intermolecular interactions that mainly arise from anisotropic short range as well as long range forces. An example of the latter are dipole-dipole interactions [1, 2]. Molecular factors such as intermolecular forces play an important role in determining the stability and properties of liquid crystal phases. It is useful to know the correlation between macroscopic liquid crystal properties, e.g. the dielectric permittivity, and molecular properties such as the dipole moment, in order to understand the properties of liquid crystals. Although consideration of the permanent dipole moment alone is inconclusive for forecasting liquid crystalline behaviour, because other properties such as induced dipole moments and structural conformations have more importance, it has an influence on the melting points as well as on the transition temperatures. As such, a detailed knowledge of long range interactions is needed, and this has not vet been completely understood. The importance of the long range interaction is a matter of current controversy and is an important topic of recent studies [3-5].

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To understand the relationship between dielectric permittivity (dielectric constant) and molecular properties has long been an objective of dielectric studies [6-10]. The large frequency range offered by the dielectric spectroscopic method makes this ideal for studying the dynamics of dipolar motions that could exist in a wide range of frequencies. Various dielectric investigations on liquid crystals have already been reported but most of the studies have involved molecules having a strong dipole moment [7-10]. However, studies on liquid crystals with a weak dipole moment could also provide important information for understanding the nature of molecular interactions responsible for the formation of mesophases. With this as our aim, we have studied liquid crystals (LCs) that have no dipole moments and have compared them with those having a weak dipole moment. Dielectric spectroscopy was the ideal method for such investigations. In addition, two members from the same homologous series of 4.4'-dialkylazoxybenzenes, having weak dipole moments, were studied to see the influence of the size of the molecules.

2. Experimental

Our study concerns the non-polar liquid crystal 4, 4'-diheptylazobenzene (D7AB), symmetric in structure and having a planar conformation [11]. The weakly

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polar liquid crystals 4,4'-dihexylazoxybenzene (D6AOB) and 4,4'-diheptylazoxybenzene (D7AOB) with similar end groups were also studied and were used as obtained from Sigma-Aldrich. D7AB was obtained from AWAT Co. Ltd, Poland [12]. The DnAOBs are symmetric at the end groups and almost symmetric in the central part with a non-planar conformation [11]. The almost symmetric structure of such molecules gives an added advantage that the deviation of the molecular long axis from the direction of the orienting magnetic field is minimal. The azobenzene has a nematic phase at room temperatures and becomes isotropic above 47.3°C. D6AOB has the following sequence of phase transitions: Cr 23°C N 53.1°C I, while D7AOB has the sequence Cr 32°C SmA 53°C N 70.0°C I. The dipole moments in both dialkylazoxybenzenes (DnAOB) have an angle of 64.9° from the molecular axis and a magnitude of 1.70 D [13].

Real (ε') and imaginary (ε'') parts of the complex dielectric permittivity (ε^*) were measured in the frequency range 75 kHz to 1 GHz. 7AB was measured between 34 and 62°C. D6AOB was measured between 30 and 65°C, while D7AOB was measured in the temperature range 34 to 90°C. In the frequency range 75 kHz to 30 MHz, a Hewlett-Packard HP4285A precision LCR meter was used for measurement. The sample cell consisted of a parallel plate capacitor type with a guard ring to eliminate the stray capacitance caused by the edge effect. The cell was housed in an oven that could be placed between magnets with parallel and perpendicular field orientations. The distance between two electrodes was about 200 µm. Temperatures were controlled using an oven designed to accommodate the low frequency cell [14].

In the frequency range 1 MHz to 1 GHz an HP4291B RF impedance analyser was used in combination with a home made cell [15] connected to the test head supplied by HP. The cell was centred inside a temperature controlled cylindrical cavity such that it could be placed in a magnetic field. A circulating fluid inside the walls of the cylindrical cavity controlled the temperature. The temperature was measured using an HP 2850 quartz thermometer probe close to the sample cell. The sample thickness in such measurement was about 150 μ m. The accuracy and stability of the controlled temperature was better than 0.01 K.

The data at low frequencies and high frequency of the two Impedance Analysers overlap in the frequencies between 1 and 30 MHz. For analysis, we used the data measured by the LCR meter between the frequencies from 75 kHz to 1 MHz, and by the Impedance Analyser in the frequency range 1 MHz to 1 GHz. The absolute values of data in the high frequency range were adjusted according to the values at 1 MHz obtained by the LCR meter. The strengths of the applied magnetic field were around 0.5 T for the low frequency measurements and about 0.4 T for the high frequency measurements.

3. Results and discussion

3.1. Dielectric permittivity

The static dielectric permittivity ε' of the azoxybenzenes and azobenzene, measured at 100 kHz as function of temperature for **E** \parallel **n** and **E** \perp **n** orientations, are shown in figure 1. The values ε_{\parallel} and ε_{\perp} represent the dielectric constants for the applied electric field E parallel and perpendicular to the macroscopic molecular orientation n, respectively. The dielectric anisotropy $\Delta \varepsilon$ (= ε_{\parallel} - ε_{\perp}), obtained from the values of dielectric permittivities below the isotropic (I) to nematic (N) phase transition, was found to increase with decreasing temperature. However, for the dialkylazoxybenzenes $\Delta \varepsilon$ values are somewhat smaller than for diheptylazobenzene (which does not possess a permanent dipole moment) in the nematic phase [6, 11]. The contribution of the electronic polarizability to ε' is greater in the direction along the molecular long axis than perpendicular to it [6, 11]. Consequently for D7AB $\Delta \varepsilon$ is positive, as there are no additional contributions from dipolar relaxation because the permanent dipole moment is zero. For DnAOBs there is an additional permanent dipole moment, which contributes slightly more in the perpendicular case than in parallel alignment.

For D7AOB a reversal in the sign of the dielectric anisotropy is seen around the nematic to smectic A (SmA) transition. The change in sign is caused by a



Figure 1. Temperature dependence of the static dielectric permittivity ε' (measured at 100 kHz) of D6AOB (\bigcirc), D7AOB (\triangle), and D7AB (\square) in the nematic phase with parallel (||) and perpendicular (\bot) orientations and in isotropic phases. Dashed lines represent $(\varepsilon'_{\parallel} + 2\varepsilon'_{\perp})/3$.

decrease in the value of ε_{\parallel} with decreasing temperature on entering the smectic phase, whereas ε_{\perp} increases anomalously. The decrease of ε_{\parallel} in the SmA phase results from the smaller distance between the molecules than between different planes, leading to an increased antiparallel correlation between the components of the dipole moments along the molecular long axis [6]. Consequently, the effective dipole moment in this direction is reduced, causing a decrease of ε_{\parallel} . The absolute values of the static dielectric permittivity for DnAOBs with a weak dipole moment is much smaller than for LCs with a strong a dipole moment such as 5CB, which has values 18.5 and 7.0 at 25°C for parallel and perpendicular alignments respectively [16, 17], or 6CB [15].

3.2. Field parallel to director

In order to study the rotational motions of the molecules, dielectric relaxation spectra were obtained at various temperatures. It was found that DnAOBs have two clear molecular relaxation processes in the anisotropic phase, for the case in which the probing field is parallel to the director. The measurements on D7AB, consisting of molecules without dipole moments, showed no interesting spectra and were found to be flat over the whole frequency range. The frequency dependences of the dielectric permittivities for the DnAOBs in the nematic phase for parallel alignment are shown in figure 2. The figure represents typical relaxation spectra observed in the nematic phase with parallel alignment. Similar spectra were also observed in the smectic phase of D7AOB. The spectra were analysed by fitting them to the empirical Havriliak-Negami formula [18] represented by:

$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \sum_{j} \frac{\Delta \varepsilon_{j}}{\left[1 + \left(i2\pi f \tau_{j}\right)^{1-\alpha_{j}}\right]^{\beta_{j}}}$$
(1)

where ε_{∞} is the high frequency limit of the permittivity, $\Delta \varepsilon_j$ the dielectric strength, τ_j the mean relaxation time, and *j* is the number of the relaxation process. The exponents α_j and β_j describe the symmetric and asymmetric distribution of relaxation times. In the figure the solid lines represent the fitting of such curve to the data. In figure 2(*b*), for the parallel alignment, the dashed lines and the dash-dot-dot lines represent the resolution into two molecular relaxation processes for D6AOB and D7AOB, respectively.

The values of the fitting parameters are presented in the table. The first process has a characteristic frequency of 2 MHz while the second process has a characteristic frequency of 0.5 GHz. The slow process for both liquid crystals is more prominent, as can be seen from figure 1, where both processes are clearly obvious, the fast process going out of range. The two



Figure 2. Frequency dependence of the real (*a*) and imaginary (*b*) parts of the dielectric permittivity of nematic D6AOB (\bigcirc) and D7AOB (\Box) measured for **E** || **n** at 45.2 and 60.5°C, respectively. Solid lines are fits to equation (1). Broken lines (dashed—D6AOB; dash-dot-dot—D7AOB) represent deconvolution into elementary contributions.

processes for D6AOB and D7AOB are qualitatively similar, with the minor difference that in the case of D7AOB the ratio of dielectric strengths of the fast process to the slow process is always smaller than for D6AOB. The slower relaxation process is attributed to molecular rotation around the short axes. The values of the relaxation times are similar to those of LCs with strong dipole moments [16, 17]. The relaxation time τ_1^{\parallel} depends strongly on the length of the molecules, as can be seen by comparing the relaxation times obtained for D6AOB and D7AOB. Such a strong dependence of the relaxation times of the process corresponding to the rotation around short axis is known in general for LCs [7-10]. In comparison with LCs having strong dipole moments, it can be inferred that the strength of the dipole moment has a small or maybe no influence on the relaxation times.

The MHz process was found to be close to a Debyetype whereas the GHz process was of non-Debye-type. The slow process was slightly asymmetric for D6AOB

Table. Parameters obtained from fitting of the imaginary part of the dielectric permittivity of nematic D6AOB and D7AOB measured for $E \parallel n$ and $E \perp n$, and isotropic D6AOB and D7AOB.

Process	$\Delta \varepsilon_{i}$	$\tau_{\rm i}/{\rm ns}$	αί	β_{i}
		D6AOB		
$\varepsilon^{\parallel}(\omega, T = 45.2)$	2°C)			
1	0.51	69.46	0	0.94
2	0.48	0.26	0.12	1
$\underline{\varepsilon}^{\perp}(\omega, T=45.$	3°C)			
1	0.05	44.58	0	1
1′	0.07	3.2	0	1
2	0.86	0.32	0.05	1
$\underline{\varepsilon}^{iso}(\omega, T = 55)$	<u>.8°C)</u>			
1	0.25	12.23	0	0.75
2	0.77	0.23	0.1	1
		D7AOB		
$\varepsilon^{\parallel}(\omega, T = 60.5)$	5°C)			
1	0.46	83.48	0	1
2	0.22	0.32	0.04	1
$\underline{\varepsilon}^{\perp}(\omega, T = 60.$	<u>6°C)</u>			
1	0.06	85.40	0.02	1
2	0.78	0.22	0.12	1
$\underline{\varepsilon}^{iso}(\omega, T = 78)$.0°C)			
1	0.16	5.61	0	0.97
2	1.01	0.06	0.28	1

with β increasing linearly from a value of 0.9 at 35°C to a value of 1.0 at the N–I transition. The value for D7AOB was close to 1.0 at all temperatures in the anisotropic phase. The α parameter for the fast process, however, increased monotonously from 0.1 at low temperatures to 0.2 around the transition in the case of D6AOB. For D7AOB the processes evolved from a Debye-like process at low temperatures in the smectic phase to a non-Debye type with α around 0.4 near the transition. These values however cannot be taken strictly as the process is close to the high frequency limit of measurement. The origin of the fast process will be discussed later in the paper.

3.3. Field perpendicular to director

In the case where the director is perpendicular to the probing field, two relaxation processes with similar relaxation times were observed, the slow process being much weaker than the fast process. The frequency dependences of the dielectric permittivities for the DnAOBs in the nematic phase for perpendicular alignment are shown in figure 3; the spectrum is typical of all spectra observed in the perpendicular alignment at all temperatures. The two relaxation processes observed in perpendicular alignment, as can be seen by comparing figures 2 and 3. However the relaxation times τ_1^1 of the weak process and τ_2^1 were close to the values of



Figure 3. Frequency dependence of the real (a) and imaginary (b) parts of the dielectric permittivity of nematic D6AOB (○) and D7AOB (□) measured for E ⊥ n at 45.3 and 60.6°C respectively. Solid lines are fits to equation (1). Broken lines (dashed—D6AOB; dash-dot-dot—D7AOB) represent deconvolution into elementary contributions.

the respective slow and fast processes observed in parallel alignment. The processes were found to be close to Debye-type. In the case of D6AOB a third minor intermediate process, with characteristic frequency about 50 MHz, was needed in order to achieve a good fitting to the experimental result.

For the analysis of all spectra for D6AOB in the nematic phase three relaxation processes were taken into account, as a resolution into two Havriliak–Negami processes was not possible. In the case of D7AOB this intermediate process was not needed. In figure 3 (b) the dielectric spectra for perpendicular alignment with three separated processes are shown by dashed curves for D6AOB. The intermediate process showed no temperature dependence and had constant relaxation strength in the nematic phase. The process however disappears in the isotropic phase. This process seems to arise from precessional motion around the long axes. However, it

cannot be ruled out that the process may arise from the instrument, as the signal is quite weak for low dielectric constant materials, as in the case of DnAOBs.

The clear fast process τ_2^{\perp} is attributed to the rotation of molecules around long axes. This can be correlated with the fact that the dipole moment has a larger perpendicular component. Consequently there should be a greater amplitude of the projection of the molecular dipole moment in the direction of the field for perpendicular alignment than in the case of parallel alignment. This should therefore lead to a higher value of the dielectric strength. In the imaginary part of the spectrum this will cause a loss with a greater amplitude for $\varepsilon_2^{\prime\prime\perp}$ than for $\varepsilon_1^{\prime\prime\parallel}$. On comparing the amplitudes from the MHz process in figure 2 and the high frequency process in figure 3 we observe that the amplitude in the second case is indeed greater. In order to get quantitative agreement we can consider the contribution of μ_1 and μ_t to ε^{\parallel} and ε^{\perp} , respectively, based on existing theory [7-9]. It is known from the theory that for rotation around the short axes $\Delta \varepsilon_1^{\parallel} \sim \mu_1^2 (1+2S)$ and for rotation around the long axis $\Delta \varepsilon_{2}^{\perp} \sim \frac{1}{2} \mu_{t}^{2} (1+2S)$, where S is the orientational order parameter. Hence from the ratio of μ_l to μ_t one can estimate the value of the angle β , the angle between the dipole moment and the molecular long axis. Using the values of the dielectric strength obtained from the fitting we find that β is equal to 61.2° for D6AOB and 61.3° for D7AOB. These values are quite close to the reported values [13] and confirm that the fast process in the perpendicular alignment is due to the rotation of molecules around the long axis. In order to understand the nature of the slow process observed for perpendicular alignment, the temperature dependence of relaxation times maybe useful and hence will be considered later in this section.

3.4. The molecular relaxation processes

All the four processes—two from parallel alignment, two from perpendicular alignment—converge into two clear relaxation processes in the isotropic phase, with characteristic frequencies around 10 MHz and 1 GHz, respectively. A typical frequency dependence of the dielectric permittivities for the DnAOBs in the isotropic phase is shown in figure 4. For all the measurements made at different temperatures, two distinct dielectric relaxations are always seen in the measured frequency region. The slow process was, however, asymmetric with $\alpha = 0$ and β around 0.75. The fast process was a non-Debye-type with α decreasing with increasing temperatures. The dielectric strength of the slow process increases slightly with temperature while that of the fast process decreases with temperature as shown in figure 5.



Figure 4. The frequency dependence of the real (*a*) and imaginary (*b*) parts of the dielectric permittivity of isotropic D6AOB (○) and D7AOB (□) measured at 54.8 and 78.0°C respectively. Solid lines are fits to equation (1). Broken lines (dashed—D6AOB; dash-dot-dot—D7AOB) represent deconvolution into elementary contributions.

In the case of D7AOB the trend seemed to be similar, however a quantitative conclusion on the fast process could not be achieved as the process had moved out of the measuring frequency range. In the isotropic phase the dielectric spectrum is a weighted sum of all relaxation processes. The dominant process is related to the rotation of the dipole moment around the long axis, whereas the slow process is due to rotation around the short axis.

In Figure 5 we show the plots of the different dielectric strengths obtained from fitting. For D6AOB the dielectric strength of $\varepsilon_1^{\parallel}$ at the transition reduces to half of its value at low temperatures. The dielectric strength of the fast process $\varepsilon_2^{\parallel}$ close to the phase transition is almost double its value at low temperatures for both azoxybenzenes. This could be because the molecular movements such as rotation around the short axis depend on the order parameter value (*S*) such that $\Delta \varepsilon \propto S$. In the case of D7AOB the trend is



Figure 5. Temperature dependence of the dielectric strength for the different processes. (a) 6AOB—parallel, perpendicular and isotropic cases; (b) 7AOB—parallel, perpendicular and isotropic cases.

similar where the dielectric strengths become almost equal to each other around the phase transition temperature. The dielectric strength of the fast process $\varepsilon_2^{\parallel}$ increases slightly upon entering the nematic phase of D7AOB from the smectic phase. For perpendicular alignment the dielectric strength of the slow process ε_1^{\perp} is more or less constant for the azoxybenzenes, while that of the fast GHz process ε_2^{\perp} decreases linearly with increasing temperature.

In order to understand the nature of the molecular motions we need additionally to consider the temperature dependence of the relaxation times of the processes. We show the plots of relaxation times against temperature in figure 6 and 7. The temperature dependence of the relaxation times in the anisotropic and isotropic phase are of Arrhenius type. In figure 6 we plot the relaxation times corresponding to rotation around the short axis in the case of $\mathbf{E} \parallel \mathbf{n}$ for the



Figure 6. Temperature dependence of the relaxation times of processes with MHz frequency range for 6AOB in the nematic phase: parallel alignment (○), perpendicular alignment (●), isotropic phase (∇); and for 7AOB in the nematic phase: parallel alignment (□), perpendicular alignment (■) and isotropic phase (△). Lines represent fits with Arrhenius temperature dependence.



Figure 7. Temperature dependence of the relaxation times of processes in the GHz frequency range for 6AOB in the nematic phase: parallel alignment (○); perpendicular alignment (●), isotropic phase (◇); and for 7AOB in the nematic phase: parallel alignment (□), perpendicular alignment (■). Lines represent fits with Arrhenius temperature dependence. Inset shows the temperature dependence of the relaxation times for the intermediate process for 6AOB in perpendicular alignment.

D*n*AOBs. In addition we plot the relaxation times of the slow process observed in perpendicular alignment, for both D6AOB and D7AOB. The relaxation times τ_1^{\parallel} and τ_1^{\perp} for the D*n*AOBs seem to be close in value in the nematic phase. Considering one particular temperature for both analogues of D*n*AOB, the relaxation process for D7AOB is slower than for D6AOB as the viscosity

of D7AOB could be greater than for D6AOB. For D6AOB in parallel alignment the activation energy for the slow process was found to be 81.2 kJ mol^{-1} in the nematic phase while it was 47.5 kJ mol^{-1} in the isotropic phase. Similar values were obtained for D7AOB, 87.7 and 52.2 kJ mol^{-1} in the nematic and isotropic phases, respectively. The value in the smectic phase of D7AOB was found to be 63.1 kJ mol^{-1} .

On plotting the relaxation times of the slow MHz processes observed in perpendicular alignment it can be seen that the relaxation times as well as the activation energies are comparable, although slightly faster for hexylazoxybenzene, suggesting that the origin of this process is the same. The activation energy in the nematic phases for this process was 86.0 and $94.0 \,\mathrm{kJ \, mol^{-1}}$ for D6AOB and D7AOB, respectively. Based on detailed work on the origin of relaxation processes measured at different angles of the orienting field with respect to the probing field, performed by Jadżyn et al. [19, 20], we can conclude that the slow process in perpendicular alignment is of similar origin to that of rotation around the short axis, but for molecules tending towards parallel alignment. It was shown that such a process is present in the case in which nonperfect molecular alignment with respect to the director exists [19].

In figure 7 the relaxation times of the fast processes are shown. In addition to the relaxation times obtained for $\mathbf{E} \perp \mathbf{n}$, the relaxation times of the fast process observed in parallel alignment are also shown. In the inset of the figure the relaxation times of the intermediate process observed for D6AOB for perpendicular alignment is plotted. The open symbols represent rotation around the long axis. It can be seen from the figure that the relaxation times are faster for hexylazoxybenzene. In both azoxybenzenes the process moves out of the measurement range leading to a difficulty in fitting the data. The activation energies were found to be low for both DnAOBs, 29.8 and 23.4 kJ mol^{-1} for D6AOB and D7AOB, respectively, in the nematic phases and 17.5 kJ mol^{-1} in the smectic phase for D7AOB. A low value of the activation energy such as these accounts for the almost free rotation of the molecules around the long axis. The process becomes slower as it enters the isotropic phase because in the nematic phase there is less restriction to rotation around the long axis in comparison with the rotation in an environment of randomly distributed molecules of the isotropic phase. The filled symbols represent the high frequency processes observed for perpendicular alignment. The values of the relaxation times are close to those corresponding to rotation around the long axis. The slight discrepancies are due mainly to weakness of the process (small dielectric strength) hence leading to a difficulty in

obtaining a good fit. The activation energies were 23.5 and 37.3 kJ mol^{-1} for D6AOB and D7AOB, respectively in their nematic phases, while it was 24.6 kJ mol⁻¹ for D7AOB in the smectic phase.

We now consider the origin of the fast process for the parallel alignment. We found that the relaxation times of the fast process were similar in magnitude to those of rotation around the long axis. However, the large dielectric strength and its order parameter-like dependence on temperature $(\Delta \varepsilon \propto 1-S)$ suggests that the origin of this process could be due to molecular rotation on the cone around the director **n**. Since the component of the dipole moment is larger in the perpendicular direction, the fast process in parallel alignment due to conical motion could have a larger dielectric strength in comparison with conical motion around the director in perpendicular alignment. For $\varepsilon_2^{\parallel}$ the contribution of μ_t decreases with increasing value of *S*.

4. Conclusion

Weakly- and non-polar liquid crystals have been studied by dielectric spectroscopy. For non-polar LCs the dielectric permittivity depends only on the polarizability of the substance. For weakly-polar liquid crystals four dipolar relaxation processes could be observed in the nematic phase-two for parallel alignment and two for perpendicular alignment. In the case of parallel alignment the processes were observed with the characteristic frequencies 2 MHz and 1 GHz. The slow frequency process is due to the rotation of molecules around their short axes while the GHz process is due to molecular rotation on the cone around the director. In the case of perpendicular alignment the relaxation processes had similar characteristic frequencies. The slow process in the perpendicular alignment is of similar origin to the slow process observed in the parallel case, as there could be some molecules parallel to the electric field due to imperfect alignment of the phase. The GHz process in the perpendicular alignment has been attributed to the rotation of molecules around their long axes. The four processes converge into two clear processes in the isotropic phase. All the processes are qualitatively and quantitatively similar to those observed for strongly polar liquid crystals, suggesting that the strength of the dipole moment has little influence on the liquid crystalline properties.

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