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Pretransitional behaviour in the vicinity of the isotropic–nematic transition of strongly polar compounds

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Abstract

The isotropic–nematic transition, being weakly first order, exhibits pretransitional effects signifying the appearance of the nematic-like regions in the isotropic phase. In the isotropic phase, strongly polar liquid crystals, such as the popular alkyl and alkoxy cyano biphenyl behave in a non-standard fashion: whereas far away from the transition the dielectric constant ϵ_{iso} has a $1/T$ dependence (a feature also commonly seen in polar liquids), on approaching the nematic phase the trend reverses resulting in a maximum in ϵ_{iso} , at a temperature slightly above the transition, an effect explained on the basis of short-range correlations with an antiparallel association of the neighbouring molecules. Recently, there has been a revival in studies on this behaviour to possibly associate it with the order of transition. Here we report dielectric measurements carried in the vicinity of this transition for a number of compounds having different molecular structures including a bent core system, but with a common feature that the molecules possess a strong terminal polar group, nitro in one case and cyano in the rest. Surprisingly, the convex shape of the thermal variation of ϵ_{iso} was more an exception than the rule. In materials that exhibit such an anomaly we find a linear correlation between $\delta\epsilon = (\epsilon_{\text{peak}} - \epsilon_{\text{IN}})/\epsilon_{\text{IN}}$ and $\delta T = T_{\text{peak}} - T_{\text{IN}}$, where ϵ_{peak} is the maximum value of the dielectric constant in the isotropic phase, ϵ_{IN} the value at the transition, and T_{peak} and T_{IN} the corresponding temperatures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Investigations on the pretransitional effects in the vicinity of the isotropic–nematic (I–N) transition have been carried out with a variety of probes, especially with a view to observe the critical behaviour considering the fact that the transition is a weakly first order one. The pretransitional effects reveal that an appreciable degree of nematic-like short-range order persists above the transition temperature in the isotropic phase. These effects have been probed using, amongst others, magnetic [1–3] and electric birefringence [3, 4], light scattering [2, 5], and linear [6–13] and nonlinear dielectric constant [14] measurements.

The temperature (T) dependence of ϵ , the dielectric constant in the isotropic phase, is expected to be proportional

to $\mu^2/k_{\text{B}}T$, where μ is the dipole moment and k_{B} is the Boltzmann constant. Thus the normally expected behaviour is just a linear increase of ϵ as the temperature is lowered. While this is true for polar compounds, strongly polar liquid crystals, especially alkyl/alkoxy cyano biphenyls, exhibit a peculiar behaviour. Far away from the transition to the nematic, ϵ increases with a decrease of temperature, but in the vicinity of the transition has a reverse behaviour after passing through a maximum in the value—a feature that we refer to here as the convex-shaped anomaly (CSA for short). First observed by Bradshaw and Raynes [6], it has been explained on the basis of the theoretical work by Madhusudana and Chandrasekhar [15]. Molecules with a strong polar terminal group, such as CN or NO₂ have a tendency to form antiparallel pairs in order to reduce the dipolar contribution to the free energy. The CSA

of the dielectric permittivity is due to the coupling between the antiparallel arrangement and the growing short-range nematic ordering. Over the years a number of studies [6–12, 16] have been reported to understand the correlation between the molecular structural parameters and the appearance of the CSA. An important outcome of these results is that such a behaviour is exclusively observed in systems containing the CN group at the terminal position. In fact, a slight reduction in the dipole moment by substituting the CN group with the NCS group makes the feature disappear [11] and has been explained as being due to the molecular organization in the pseudo-nematic domains not being as efficient as in the case of CN derivatives. There also appears to be an inherent suggestion that the presence of the terminal CN group invariably results in the CSA. Suggestions have also been put forth [11, 17] that the thermal strength of the I–N transition plays a decisive role: the CSA is absent in materials with a strong first order character. To get a better understanding of the CSA, we have investigated a number of structurally different compounds, all possessing the terminal CN group (pointing along the long molecular axis), and one compound having a NO₂ group. Also studied are two non-conventional compounds with a banana shape, but having an alkyl cyanobiphenyl entity. Our studies suggest that it is not one unique factor, but several factors which influence the appearance and magnitude of the CSA.

2. Experimental details

The structural formulae of the materials used are given in table 1, along with their phase sequence. The materials were chosen to have variety in the molecular structures: calamitic compounds with (i) the core of the molecule having bridging groups, whose dipole moments are either additive (nOBCAB, with the terminal alkyl chain $n = 8, 9$ and 11) or subtractive (10 OPCBOB) with respect to the terminal CN dipole; (ii) alkyl (5CB, 6CB, 7CB, 8CB and 10CB) and alkoxy (5OCB, 6OCB and 8OCB) cyanobiphenyls which have a very stiff core; (iii) a compound having a NO₂ terminal group (NPOOB); (iv) a compound in which a bent core mesogen is tethered to an alkyl cyanobiphenyl entity (SC170); (v) a compound in which two mesogenic entities are linked through an alkyl spacer having an odd number of carbon atoms, resulting in an overall bent shape of the molecule (SC422); (vi) a commercially available eutectic mixture (E7) consisting of mainly cyanobiphenyls and a cyano terphenyl, and binary mixtures of two different compositions of the stiff core 8OCB and the bent core SC170 (95 and 80 mol% of 8OCB in SC170). While the alkyl/alkoxy biphenyls and the mixture E7 were procured from commercial sources (Merck and Frinton), the other materials were synthesized in our laboratory. It may be noted that except 10CB, which has the isotropic–smectic A transition, all the materials exhibit the I–N transition.

For dielectric studies the samples were sandwiched between indium-tin oxide (ITO) coated glass plates treated with either a polyamide solution and uni-directionally rubbed or treated with a silane solution to get uniform planar or homeotropic alignment of the molecules yielding dielectric constants perpendicular (ϵ_{\perp}) and parallel (ϵ_{\parallel}) to the nematic

director respectively. Dielectric permittivity measurements were done using an impedance analyzer (HP4194A). The data presented were collected at a fixed frequency of 10 kHz, which is well below the relaxation frequency of any dielectric mode for the materials over the temperature ranges under study.

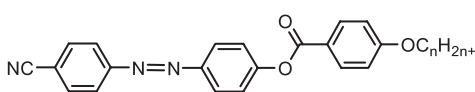
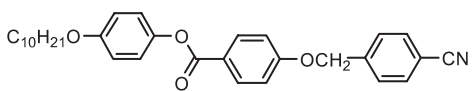
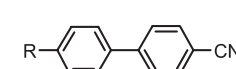
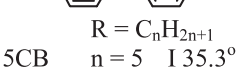
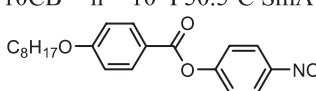
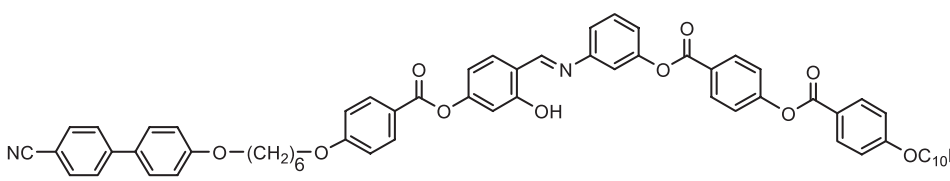
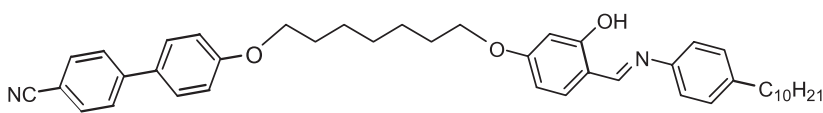
3. Results and discussion

Figure 1 shows the temperature dependent static dielectric permittivities ϵ_{\parallel} and ϵ_{\perp} for 7 materials, representing the different categories of the compounds studied here: the alkyl and alkoxy cyanobiphenyls (figures 1(a) and (b)), the nitro compound (figure 1(c)), two other rod-like cyano compounds (figures 1(d) and (e)) and the banana-shaped compounds (figures 1(f) and (g)). To be noticed is the feature that all the compounds possess a large positive dielectric anisotropy ϵ_a . In fact, except in the case of 10OPCBOB, which has the bridging group ester dipole point in the opposite direction to that of the terminal cyano dipole, the anisotropy is $\epsilon_a > 6$. More important, from the viewpoint of this study, is the qualitatively different behaviour of ϵ immediately above the transition: while the first three compounds exhibit the CSA feature, surprisingly the other four compounds have a simple linear dependence on temperature, despite having the strongly polar cyano terminal group (figure 2). It may be mentioned that the non-CSA feature shown in figure 2 for 8OBCAB is observed for its higher homologues 9 and 11OBCAB (which exhibit the partially bilayer smectic A and reentrant phases), for the banana-shaped compounds SC170 and SC422, and also for the 80% 8OCB/SC170 mixture. In the following we look at the influence of various parameters such as the strength of the (first order) transition, the extent of cancellation of the parallel component of the molecular dipole moment (μ_{\parallel}), the stiffness, and length of the molecules on the appearance and strength of the CSA effect.

3.1. Strength of the transition

In a recent paper Ginovska *et al* [11], concluded from the static dielectric permittivity data in the isotropic phase near the I–N transition that the hardly observed pretransitional effects (taken to be equivalent to the nonlinear behaviour of the permittivity) in less polar mesogens signifies the strong first order character of the transition. In contrast, the large pretransitional effects seen for strongly polar compounds are argued to be due to the transition being close to second order. There is an inherent lacuna in this argument: non-polar compounds in which the dipole-driven antiparallel correlation is ruled out should always have a strong first order transition. In a subsequent work, Van Roie *et al* [12] reported heat capacity and dielectric measurements on a number of compounds, polar as well as non-polar. This work showed that there is no direct connection between the value of the latent heat and the size of the pretransitional effect observed in the dielectric constant mentioned above. To find out whether this is true for the materials studied here, we have carried out differential scanning calorimetry (DSC) measurements of representative compounds. Table 2 lists the transition latent heat (ΔH)

Table 1. Molecular structure and the associated transition temperatures of the compounds studied.

	
n = 8	8OBCAB I 255.2°C N 98.8°C SmA
n = 9	9OBCAB I 249 N 212°C SmA
n = 11	11OBCAB I 236°C N 227°C SmA
	
	10OPCBOB I 162°C N 141°C SmA
	
	R = C _n H _{2n+1}
5CB	n = 5 I 35.3°C N
6CB	n = 6 I 29.0°C N
7CB	n = 7 I 42.8°C N
8CB	n = 8 I 40.5°C N
10CB	n = 10 I 50.5°C SmA
	
	R = OC _n H _{2n+1}
5OCB	n = 5 I 68°C N
6OCB	n = 6 I 75.5°C N
8OCB	n = 8 I 80°C N 67°C SmA
	
	NPOOB I 68°C N 61°C SmA
	
	SC170 I 162°C N 136°C SmA
	
	SC422 I 140°C N 91°C SmA
	E7 I 60.5°C N

values, determined from DSC scans conducted at a cooling rate of $1\text{ }^{\circ}\text{C min}^{-1}$. Obviously, there is no strict correlation between ΔH and the observation of the CSA. For example, 8OCB and 8OBCAB have comparable ΔH values and while the former shows the CSA, the latter compound does not. More interestingly, SC170 which has a much smaller ΔH value than 8OCB does not exhibit a CSA feature. We provide in figure 2, a further proof for the argument of Van Roie *et al* [11]. As already mentioned 10CB exhibits a direct transition from the isotropic to the smectic A phase and as expected the transition is about an order of magnitude stronger (thermally) than the typical N-I transition. If there were to be a strict correlation

between the strength of the transition and the appearance of the pretransitional effect, then this material should not have shown such an effect, contrary to the data displayed in figure 2. This observation is corroborated by the data seen in two earlier reports [6, 8] also confirming this observation. Such a feature has also been seen for a material that exhibits the isotropic to Crystal E transition, again another thermally strong transition [9].

3.2. Cancellation of the μ_{\parallel}

Let us recall that the CSA effect has been reported only in molecules possessing a strong terminal dipole moment.

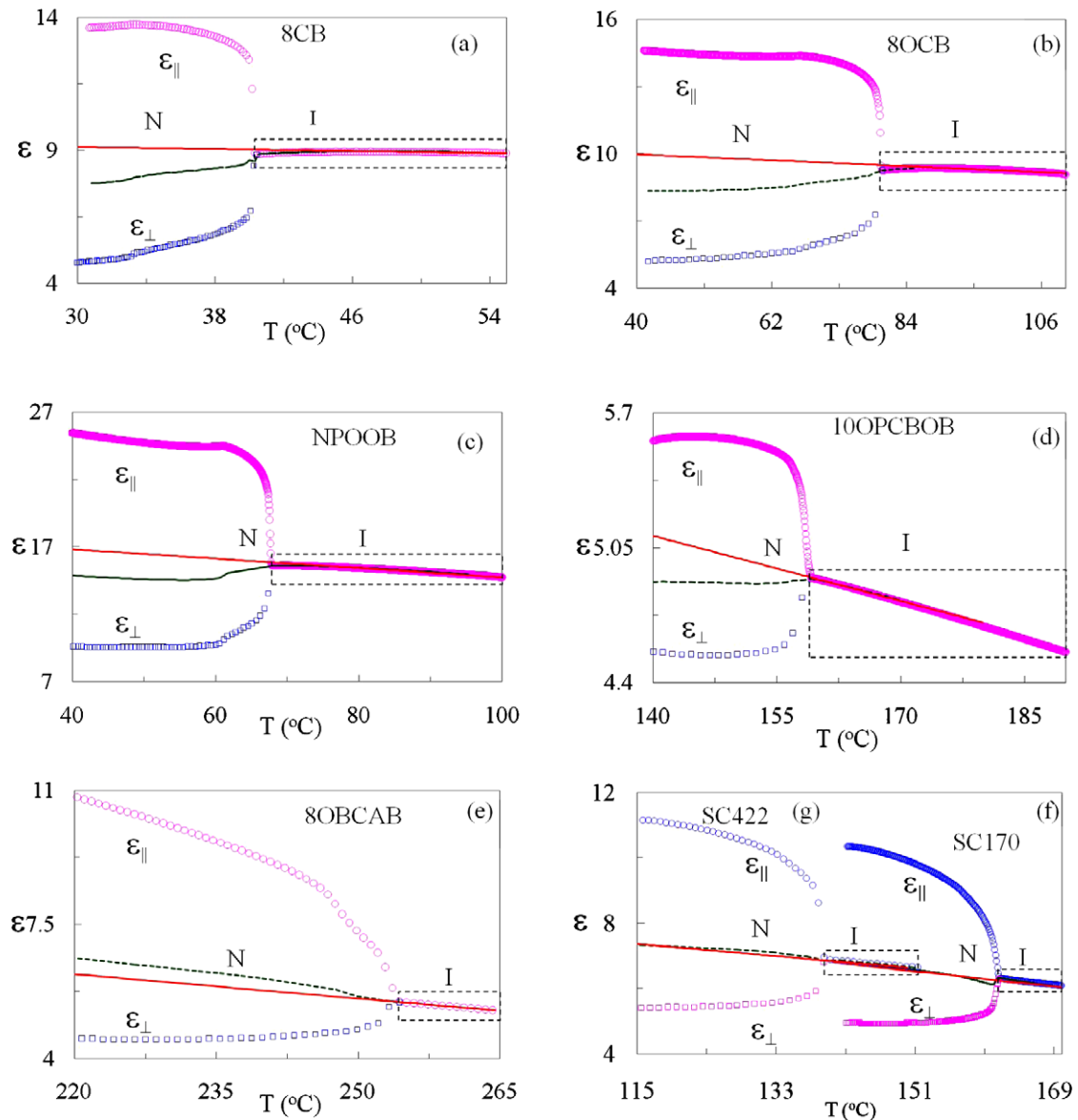


Figure 1. Static measurements of the parallel ($\epsilon_{||}$) and perpendicular (ϵ_{\perp}) dielectric constants near the isotropic–nematic (I–N) transition for (a) 8CB, (b) 8OCB, (c) NPOOB, (d) 10OPCBOB, (e) 8OBCAB, (f) SC170 and (g) SC422. The calculated ϵ_{avg} is represented as a dotted line. The linear extrapolation of ϵ in the isotropic phase into the mesophase region is shown as a solid line. The region enclosed in dotted boxes is shown on an enlarged (normalized) scale in figure 2.

Table 2. Transition enthalpy for the I–N transition of selected compounds.

Compound	ΔH ($J g^{-1}$)
1 8OBCAB	1.3
2 11OBCAB	0.7
3 10OPCBOB	2.5
4 8OCB	1.4
5 NPOOB	0.6
6 SC170	0.4
7 SC422	0.9

Owing to the tendency to reduce the dipolar contribution to the free energy, neighbouring molecules orient such that their terminal dipoles are antiparallel. Performing experiments

on binary mixtures of a strongly polar (5CB)/weakly polar (MBBA) system, Drozd-Rzoska *et al* concluded that the detection of pretransitional behaviour is possible only if the cancellation of the component of the dipole moment parallel to the main axis of the rod-like molecule is substantial [10]. This observation suggests that a strong dipole moment along the long axis and the concomitant antiparallel pairing in the isotropic phase ensures the appearance of the anomalous pretransitional behaviour. The data shown for the strongly polar systems, 8OBCAB, 10OPCBOB and the two banana-shaped systems (SC170 and SC422) clearly shows that this feature is not universal. In fact, the nOBCABs have a much larger dipole moment than cyanobiphenyls and also exhibit the partially bilayer smectic A and reentrant phases, features which arise from molecules correlated in a strong antiparallel fashion.

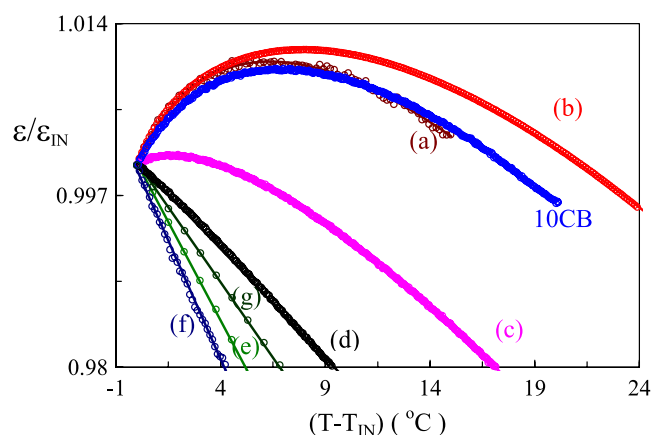


Figure 2. Thermal variation of the normalized dielectric constant in the immediate vicinity of the I–N transition for the compounds shown in figure 1 (the alphabetic labelling used to indicate the compounds is the same as in figure 1). Note that the dependence is monotonic and linear right up to the transition for the last three of these compounds, the first three compounds show a convex-shaped anomaly (CSA) behaviour. To be noticed is that 10CB, which has an isotropic–smectic A transition also exhibits the CSA feature. The solid line through the data represents a fit to equation (1) and a straight line for the compounds having CSA and non-CSA features, respectively.

Even the presence of the alkyl cyanobiphenyl units in SC170 and SC422 does not lead to the CSA behaviour. The fact that nOBCABs have a much higher dielectric constant than the corresponding alkoxy cyanobiphenyls rules out the possibility of limitations of the measurement technique as a cause quoted for the absence of the CSA feature in certain systems.

3.3. Stiffness of the molecule

As seen in the previous sections, while the strength of the dipole moment along the long molecular axis and the strength of the first order of the I–N transformation do play a role, neither can be considered to be the sole controlling parameter. We suggest that the stiffness of the molecule is also important. If the central (core) portion of the molecule is flexible (thus making it less rod-like), the other two factors do not ensure the appearance of the CSA feature. This is supported by comparing the behaviour of the nOBCABs and the alkyl cyanobiphenyls. Of course, the greater the flexibility, resulting from the presence of bridging groups between the phenyl rings, the less the chance of observing the CSA. It is possible that the presence of dipoles in the central region (present in nOBCABs, but absent in cyanobiphenyls) creates a situation conducive to soft repulsions between neighbouring molecules in the lateral direction. This in turn may then reduce, notwithstanding the effect due to the strong terminal dipole, the tendency for antiparallel pair formation, at least at low densities, as would be the case near the I–N transition. A good demonstration of the sensitivity of the CSA to molecular features is shown in figure 3 depicting the data for the two mixtures of the 8OCB/SC170 binary system, in which it is seen that, although both components possess the terminal CN group, addition of about 20% of the bent core system with a flexible middle

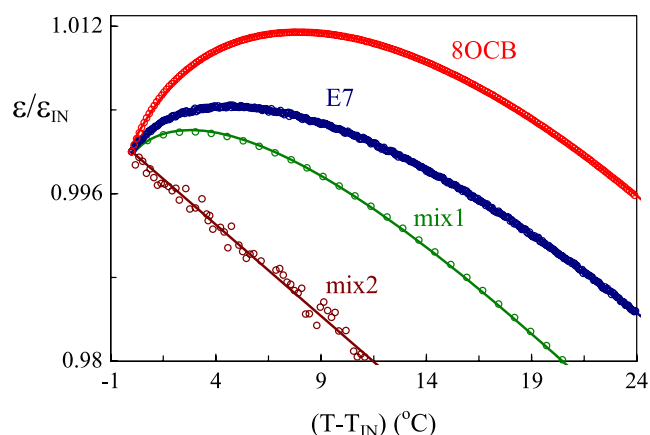


Figure 3. Demonstration of the sensitivity of the CSA on the stiffness/flexibility of the central (core) of the constituent molecules. The CSA which is strong for 8OCB diminishes significantly by adding just 5% of the bent core molecule SC170 (mix1: 95% 8OCB/SC170) completely vanishes for mix2 (80% 8OCB/SC170). To show the effect is not due to molecules of different length, data for the E7 mixture is also shown.

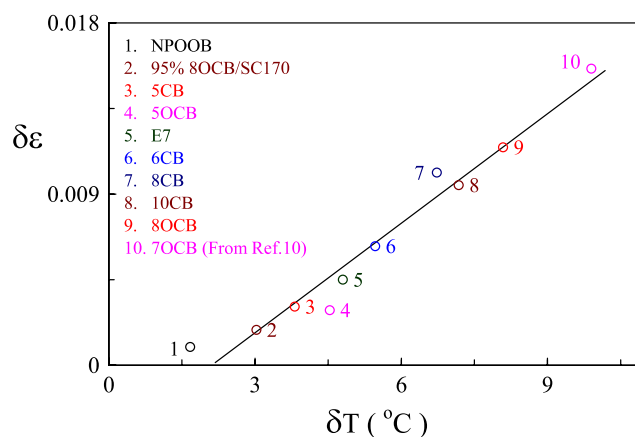


Figure 4. Diagram to show the interdependence of $\delta\epsilon = (\epsilon_{\text{peak}} - \epsilon_{\text{IN}})/\epsilon_{\text{IN}}$ and $\delta T = T_{\text{peak}} - T_{\text{IN}}$, where ϵ_{peak} is the maximum value of the dielectric constant in the isotropic phase, ϵ_{IN} the value at the transition, and T_{peak} and T_{IN} the corresponding temperatures for a number of materials exhibiting the CSA behaviour.

portion makes the CSA vanish. The presence of molecules of differing length cannot be the cause for this behaviour as the CSA does exist for E7, a mixture having four types of molecules different in their length, but of course possessing a stiff central core.

As a possible quantification of the strength of the CSA, we use two parameters $\delta\epsilon = (\epsilon_{\text{peak}} - \epsilon_{\text{IN}})/\epsilon_{\text{IN}}$ and $\delta T = T_{\text{peak}} - T_{\text{IN}}$, where ϵ_{peak} is the maximum value of the dielectric constant in the isotropic phase, ϵ_{IN} the value at the transition, and T_{peak} and T_{IN} the corresponding temperatures. These parameters are definable only for those materials which have the CSA feature. For the various materials studied here and also reported in the literature, it is noticed that these two parameters are interdependent. Figure 4 shows that $\delta\epsilon$ has a nearly linear relation with δT , suggesting perhaps that both

have the same molecular origin. Notice that even the mixture of 8OCB that has 5% bent core molecule SC170 also fits into this picture.

An association that is seen from the data in figures 2 and 3 is that, especially for cyanobiphenyls (for which extensive data is available), both $\delta\epsilon$ and δT increase with increasing length of the terminal chain. Figure 5 shows the data for the nCBs separately to highlight this observation, a possible explanation for which could be the following. Within a given homologous series, the antiparallel correlation becomes favourable with increasing length of the molecule, perhaps even in the isotropic phase, thus increasing the temperature range of the CSA. This is supported by the fact that for example in the cyanobiphenyl series, ϵ_{iso} decreases with increasing chain length. A caveat should be added here. It appears that the monotonic increase in the CSA range would be valid when only one kind of pretransitional fluctuation (nematic-like) is present. Fluctuations of additional order (say, smectic-like) would limit the range, perhaps owing to the possibility of the nanophase segregation between the core and the chain part being the dominant issue. Notice that the appearance of smectic correlations can also lead the system towards a smectic–nematic–isotropic triple point and finally to a direct isotropic–smectic transition regime, an obvious situation for reduction in pretransitional effects.

An important point of the theory of Madhusudana and Chandrasekhar [15] is that the manifestation of the antiparallel correlations can be seen in the average dielectric constant in the mesophase (ϵ_{avg}) being lower than ϵ_{extr} , the extrapolated isotropic value i.e., the parameter $\epsilon_{\text{diff}} (= \epsilon_{\text{avg}} - \epsilon_{\text{extr}})$ being negative. Further, the data on cyanobiphenyls was used to propose that materials having negative ϵ_{diff} exhibit such correlations in the isotropic phase as well. However, this is not borne out by the experimental data. For example, 10PCBOB and SC170, despite having negative ϵ_{diff} do not show the CSA behaviour in the isotropic phase. On the other hand, the compound like 8OBCAB has a positive ϵ_{diff} . Thus the appearance of the CSA appears to be dependent on several factors, with the major role being played by the stiffness of the central rigid portion of the molecule.

Quantitative description of the temperature dependence of the CSA has been performed on a number of cyano compounds (particularly the biphenyls) by Thoen and Menu [8], and by Rzoska's group [9, 10, 16]. The basis for this analysis is the dielectric effect near the critical solution point in binary mixtures of ordinary liquids [18]. The functional form used to describe the temperature dependence of the dielectric constant has also been borrowed for the liquid crystal case and is given by

$$\epsilon = \epsilon_{\text{IN}} + At + Bt^\phi \quad (1)$$

where $t = (T - T_{\text{IN}})/T_{\text{IN}}$, with T_{IN} as the transition temperature and ϵ_{IN} the corresponding dielectric constant. Various cyano group systems have yielded $\phi \sim 0.5$, a value significant as being that predicted for a tricritical point. As shown in figure 2 for all the materials studied here and exhibiting the CSA the data in the isotropic phase could be described by equation (1) with an exponent of 0.5. Especially interesting was the fact that even the 95% mixture with the

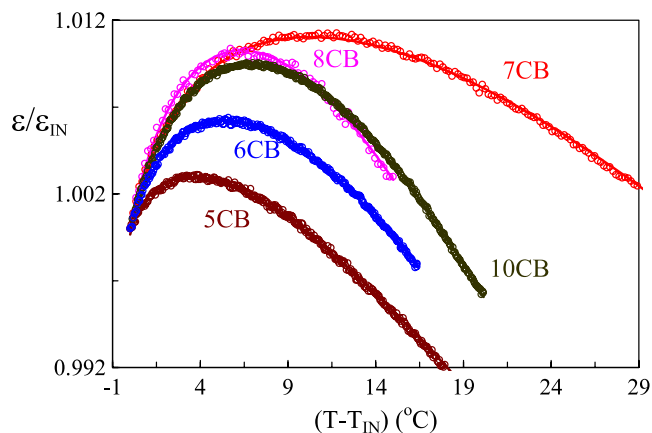


Figure 5. Plot to show the dependence of the magnitude of the CSA on the chain length of the alkyl cyanobiphenyl molecule.

bent core system conformed to this description, suggesting that fluid-like critical behaviour is universal irrespective of the shape of the constituent molecules.

Another interesting finding of these studies is that there appears to be a correlation between the existence of the CSA behaviour and the slope of the temperature dependence of ϵ deep in the isotropic phase. Denoting this parameter ϵ_{slope} as the slope of the $\epsilon/\epsilon_{\text{IN}}$ versus $T - T_{\text{IN}}$ curves, we find that all the alkyl/alkoxy cyano biphenyls have an ϵ_{slope} value in the range of $\sim 1 \times 10^{-3} \text{ K}^{-1}$, the materials not exhibiting the non-CSA behaviour show a factor of 2–3 times higher values. Let us recall the fact that deep in the isotropic phase, the $\mu^2/k_{\text{B}}T$ term gives a negative temperature dependence for ϵ and that an increasing nematic-like short-range order in conjunction with antiparallel correlations in the vicinity of the I–N transition results in a positive temperature dependence. Thus a smaller value may facilitate the antiparallel correlations to dominate the behaviour of ϵ results in the CSA feature.

4. Summary

We have conducted dielectric measurements on a number of liquid crystalline systems of varied molecular structures and exhibiting the isotropic–nematic transition with a view to understanding the dielectric anomaly seen immediately above the nematic–isotropic transition in, generally, cyanobiphenyl compounds. Our studies demonstrate that there is no single factor that controls the CSA feature. Instead, several factors, such as the magnitude of the dipole moment along the molecular axis, the order of the transition and most importantly, the stiffness/flexibility of the core part of the constituent molecules decide the appearance as well as the magnitude of this anomaly. Experiments are underway to find out if the stiffness of the molecules can be quantified in terms of the elastic constants of the medium. The stiffness/flexibility parameter can also be looked at from the point of soft repulsions that can be caused by the presence of lateral dipoles present in the central portion of the molecule. It may be recalled here that the electric field effects obtained in a system having a central dipole, as against in a simple cyanobiphenyl,

were analyzed in terms of the existence of short-range polar order [19]. If indeed true, such a feature explains the behaviour observed for example, in nOBCABs.

Acknowledgments

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