Nematic twist-bend phase of a bent liquid crystal dimer: field-induced deformations of the helical structure and macroscopic polarization

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Abstract
The twist-bend nematic (N\textsubscript{tb}) phase is a recent addition to the family of nematic (N) phases of liquid crystals (LCs). A net polar order in the N\textsubscript{tb} phase under an external electric field is interesting and it was predicted in several recent theoretical studies. We investigated the field-induced polarization behaviour, dielectric, and electro-optic properties of a bent LC dimer CB7CB in the N and N\textsubscript{tb} phases. A threshold-dependent polarization current response was obtained in both the phases under triangular and square-wave input electric fields, existing till frequencies as high as 150 Hz. The polarization switching times were found in \(\sim\)1 ms region, especially in the N phase. In the N\textsubscript{tb} phase, electric field-induced deformation of the helical structure was observed, like ferroelectric LCs. Dielectric measurements revealed the presence of cybotactic clusters via collective relaxations. The dielectric anisotropy (\(\Delta\varepsilon\)) is negative at the frequencies of polarization measurements. The net polarization resulted from field-induced reorientation of cybotactic clusters and additionally from the field-induced deformation of helical structures in the N\textsubscript{tb} phase. We explored the possibility of ionic contributions to the net polarization by synthesizing TiO\textsubscript{2} nanoparticles (NPs) dispersed CB7CB LC nanocomposite. Incorporation of the NPs resulted in reduction of the collective order, increase in the ionic impurity content and conductivity, but an extinction of the field-induced polarization response. Our results demonstrate that the net polarization has competing contributions from both ferroelectric-like and ionic origin (up to \(\sim\)10 Hz) in the LC phases, but it becomes dominantly ferroelectric-like at higher frequencies.

Supplementary material for this article is available online

Keywords: liquid crystals, twist-bend nematic, polarization, ferroelectric

(Some figures may appear in colour only in the online journal)
1. Introduction

The liquid crystals (LCs) comprised of bent-shaped molecules (bent-core LCs or BLCs) are often considered as the material for next-generation displays and electro-optic devices [1–3]. The latest inclusion in the nematic phase sequence of BLCs is the twist-bend nematic (N_{tb}) phase. It was first proposed by Meyer in 1973 in the nematic phases with spontaneous polarization (i.e. in a ferroelectric nematic) [4, 5]. Following this, in 1999, Lorman and Mettout predicted a new mesophase for curved molecules with a transverse circular polar order—similar to Meyer’s N_{ab} phase [5, 6]. In 2001, in an alternative approach, Dozov showed that the twist deformation in the N_{tb} phase of bent-shaped molecules is not spontaneous, but it is imposed by the spontaneous bend deformation, enabling a ‘third dimension escape’ for \( \vec{n} \) [7]. In the past few decades, several such models for the N_{tb} phase have been proposed based on both polar and apolar interactions [5–12]. In the N_{tb} phase, the nematic director (\( \vec{n} \)) draws an oblique helicoid maintaining a constant oblique angle \( \theta \) with the z-axis (the helix axis), such that \( 0 < \theta < \pi/2 \). The N_{tb} phase is thus chiral, even though it is constituted of achiral mesogens [13]. While theoretical predictions of the N_{tb} phase were made long ago, experimental realizations were made only recently [13, 14]. Cestari et al., in their pioneering paper [14], first reported the experimental identification of this phase in a bent LC dimer CB7CB which is the most studied dimer to exhibit this phase. At that time, they marked this phase as ‘X’ (or N_{X}, as identified in the literature [5]), which was subsequently established as the N_{tb} phase [13, 14].

The N_{tb} phase is an example of spontaneous chiral symmetry breaking in LCs, reminiscent of the helical smectic C\(^\ast\) (SmC\(^\ast\)) phase [8, 11]. Due to chirality and the spontaneous breaking of mirror symmetry, this phase is expected to be locally polar and may also exhibit the heli-electric nature [5–7, 11, 15]. In the N_{tb} phase, the local polar order (pointing along the bend-direction) is modulated in a helix and hence averages to zero globally, similar to the ferroelectric SmC\(^\ast\) LCs [8, 15]. Therefore, in the N_{tb} phase, the helical structure needs to be deformed or unwound to obtain macroscopic polar behaviour. Pajak et al., in a recent theoretical investigation, have demonstrated that under a sufficiently large electric field, the twist-bend helix can be unwound giving rise to a globally polar nematic phase (N_{P}) with non-vanishing polarization [11]. Similar predictions were also made by Merkel et al., where they report flexoelectric polarization and electroclinic effect arising due to this polarization [16]. Through dielectric studies, they also report low-frequency collective relaxations and a large polar order (dielectric strength \( \sim 800 \)) in the N_{tb} phase. In a recent study, Sreenilayam et al. have reported spontaneous polarization in the N_{tb} phase of a hockey shaped achiral rigid BLC [17]. They report polarization values \( \sim 5 \) nC cm\(^{-2}\) due to partially unwound N_{tb} helices under a bias electric field of 2.2 V \( \mu \)m\(^{-1}\). A net polar order in the N_{tb} phase is interesting, new and it may find application in fast-switching electro-optic devices. A detailed and rigorous investigation of the N and N_{tb} phases of BLCs is therefore essential for gaining significant insight into the polar nature and interesting switching behaviour.

Recently, a group of researchers have developed an independent model to describe the new and exciting N_{tb} phase [18, 19]. They identify the N_{ab} phase of bent LC dimer CB7CB and its higher homologues as the polar-twisted nematic (N_{pt}) phase. They also discuss that the high-temperature nematic (N) phase of CB7CB is a cybotactic nematic phase consisting of polar-twisted clusters (N_{cybpt}) [19]. It is consistent with the report by Krishnamurthy et al., where they propose clusters with a helical internal structure present in the high-temperature N phase of flexible BLCs, such as CB7CB [20]. The term ‘cybotactic’ originates from the Greek word cybotaxis meaning space arrangement, because these clusters are more ordered compared to the surrounding nematic environment [1]. The cybotactic clusters exhibited by the majority of BLCs are locally polar (with large transverse dipole moments), and they are known to give rise to a net ferroelectric polarization under an external electric field above a certain threshold [1, 3, 21–28]. Therefore, under a strong external electric field—(a) in the high-temperature N phase, a net polar response is expected due to reorientation of the polar clusters, and (b) in the N_{ab} phase, a net polar order is expected due to unwinding (complete or partial) of the helical structure, under the condition \( E \) (electric field) \( \perp \) (helix axis) [5, 12, 29].

In this paper, we report the field-induced effects leading to polarization in the nematic (N) and the twist-bend nematic (N_{tb}) phases of a bent LC dimer CB7CB (1′′, 7′′-bis(4-cyanobiphenyl-4′-yl)heptane). We performed the optical, dielectric, and electro-optic measurements in the different mesophases of CB7CB. A net polarization response is obtained in both the N and N_{tb} phases under an external electric field of both triangular and square-wave nature. The origin of this polarization is explored through its frequency and thickness dependence, electro-optic, conductivity, and dielectric measurements. The possible extent of ionic impurity contribution to this net polarization is also investigated by synthesizing 1 wt% TiO\(_2\) nanoparticles (NPs) dispersed CB7CB LC nanocomposite and through a brief study of its optical, dielectric, conductivity, and electro-optical properties. Additional details are available under electronic supporting information (ESI).

2. Experimental details

2.1. Materials

The chemical formula of the LC compound 1′′, 7′′-bis(4-cyanobiphenyl-4′-yl)heptane (CB7CB) is shown in figure 1 and the related synthetic scheme details are available under the ESI. The phase transition temperatures of the compound were determined using a Perkin-Elmer Diamond differential scanning calorimetry (DSC), and also using an Olympus BX-51P polarizing optical microscope (POM). The DSC measurements were taken at a heating and cooling rate of 5 °C min\(^{-1}\). Before use, the DSC was calibrated using pure indium as a standard. The POM measurements were taken only in the
cooking cooling and at a lower rate of cooling (0.5 °C min⁻¹). The isotropic to N transition was observed at ~115.5 °C, and the N to N crystal transition was observed at ~103 °C. The obtained transition temperatures are summarized in ESI table T1, along with the ones reported by other researchers, for comparison [13, 15, 30–33]. The apparent difference between the obtained transition temperatures (POM and DSC) is possibly because of the difference in the rate of cooling and the different confinement conditions.

2.2. Methods

2.2.1. Optical textures. Indium tin oxide (ITO) coated planar cells (Instec Inc., USA) of thickness 5 μm were used for the experiments. The LC material was filled in the ITO cells via capillary action around 10 °C above the isotropic-nematic transition temperature. The temperature was maintained with a temperature controller (Instec. MK1000) attached to a hot-stage (Instec. HCS302). The optical textures of the LC compound were recorded between crossed polarizers using an OLYMPUS BX-51P POM. All the measurements were carried out while slowly cooling the sample from the isotropic phase.

2.2.2. Electro-optic measurements. The electro-optical measurements were carried out by using planar LC cells of thickness 5 μm and 3.2 μm with active electrode area 1 cm² and 0.25 cm², respectively. The polar switching was studied by analysing the current response across a 25 kΩ sample using a Tektronix AFG3021 function generator, a TPS 2024 digital oscilloscope and a homebuilt amplifier of gain 10, full response. For triangular-wave measurements, the background appears as an exponentially decaying function [34, 35]. Thus, after extraction of the polarization current contribution, the relation used to determine the polarization (P) is, P = \( \frac{\Delta V}{R_C} \) where Rs is the resistance (25 kΩ) connected in series with the cell, A is the cell’s active area and \( \Delta V \) is the excess voltage (current, \( I_P = \Delta V/R_S \)) due to the polarization reversal [27, 35, 36]. The factor 2 accounts for the double electrodes of the LC cell.

2.2.3. Dielectric measurements. For the dielectric spectroscopy measurements, an Agilent E4980A precision LCR meter was used in the frequency range 20 Hz–2 MHz with a measuring voltage of 0.1 V (VRMS). The frequency-dependent complex dielectric permittivity is given by, \( \varepsilon' (f) = \varepsilon' (f) - i \varepsilon'' (f) \), where \( \varepsilon' (f) \) and \( \varepsilon'' (f) \) represent the real and imaginary parts of the complex permittivity, respectively. The characteristic dielectric parameters such as the relaxation frequency (\( f_R \)) and the dielectric strength (\( \delta \varepsilon \)) were obtained by fitting the dielectric loss (\( \varepsilon'' \)) data to the imaginary part of the well-known Havriliak–Negami (H–N) fit function with an additional term (1st term on the right-hand side (RHS)) accounting for the low-frequency conductivity contribution [21, 37],

\[
\varepsilon'' = \frac{\sigma_0}{\varepsilon_0 (2 \pi f)^\alpha} + \sum_{k=1}^{N} \frac{\delta \varepsilon_k}{[1 + (2 \pi f / f_k)^\alpha]^{\beta_k}} = \frac{\sigma_0}{\varepsilon_0 (2 \pi f)^\alpha} + \sum_{k=1}^{N} \frac{\delta \varepsilon_k}{[1 + (2 \pi f / f_k)^\alpha]^{\beta_k}} \sin (\beta_k \theta) \left[ 1 + (2 \pi f / f_k)^\alpha \right]^{\beta_k/2} \]

where, \( \theta = \tan^{-1} \left[ \frac{(2 \pi f / f_k)^{\alpha/2} \sin (\alpha \pi / 2)}{1 + (2 \pi f / f_k)^{\alpha/2} \cos (\alpha \pi / 2)} \right] \), \( f \) is the frequency, \( \varepsilon_\infty \) is the high-frequency limit of permittivity (\( \varepsilon' \)). \( \delta \varepsilon_k \) is the dielectric strength, \( \sigma_0 \) is the dc conductivity, \( \varepsilon_0 \) is the free-space permittivity (8.854 × 10⁻¹² F m⁻¹), \( s \) is a fitting parameter responsible for the nonlinearity in dc conductivity part (for ohmic behaviour, \( s = 1 \)), \( k \) is the number of relaxation processes, \( \tau_k (\equiv 1/2 f_k) \) is the relaxation time for the kth relaxation process. \( \alpha_k \) and \( \beta_k \) are empirical fit parameters that describe symmetric and non-symmetric broadening, respectively, of the kth relaxation peak. The H–N fit model considers multiple relaxation scenarios while the conventional Debye model is based on single relaxation processes [38]. Also, the H–N model, unlike the Debye model, takes into account the asymmetry and broadening of dielectric relaxation modes encountered in practical scenarios. The H–N fit function is therefore versatile, and it reduces to (a) the Cole–Cole equation when \( \alpha \neq 1, \beta = 1 \), (b) the Cole–Davidson equation when \( \alpha = 1, \beta \neq 1 \), and (c) the Debye equation when \( \alpha = \beta = 1 \) [38]. Therefore, in LCs and polymers, one usually takes help of the H–N equations for the analysis of dielectric spectroscopy results [38]. For static dielectric measurements, planar LC cells of thickness 5 μm were used, and signals of amplitude 20 V and 0.1 V were applied to measure \( \varepsilon || \) and \( \varepsilon _\perp \), respectively. The dielectric anisotropy (\( \Delta \varepsilon \)) was computed using the relation, \( \Delta \varepsilon = \varepsilon || - \varepsilon _\perp \).
2.2.4. Preparation of LC nanocomposite. The TiO$_2$ NPs (particle size ~21 nm) were procured from Sigma-Aldrich, Merck (USA) for preparing the LC nanocomposite. To prepare the LC nanocomposite, TiO$_2$ NPs were taken at 1 wt% concentration and mixed with the LC CB7CB. To obtain a homogenous dispersion of the NPs in the LC matrix, chloroform was added to the mixture, and the mixture was ultrasonicated until a visibly homogeneous dispersion was achieved. The mixture was kept at ~60°C for 2–3 h, and it was then left overnight at room temperature for the slow evaporation of chloroform [39]. Once the chloroform was completely evaporated, 1 wt% TiO$_2$ NPs dispersed CB7CB LC nanocomposite was obtained.

3. Results and discussion

3.1. Optical textures

The characteristic LC textures of CB7CB, recorded between crossed polarizers are shown in figure 2. Sharp changes in colour were observed close to the isotropic-nematic (Iso-N) transition due to an increase in the birefringence. In the nematic (N) phase, a uniform marble-like texture appeared with a gradual, temperature-dependent change in the birefringent colour. These changes in colour indicate a significant change in birefringence and that highly ordered microstructures might be present in the N phase of the LC [3, 40]. The transition of the N phase to N$_{th}$ phase started near 103°C. A polygonal, rope-like, pseudo-focal-conic texture appeared below 103°C, typical of the N$_{th}$ phase [41, 42]. Transition to a crystalline state was realized after slowly cooling the sample for a sufficiently long time. It was noted that after a few months, the N$_{th}$ phase could be supercooled to room temperature via slow cooling.

3.2. Electro-optic measurements

Electro-optical measurements were carried out to investigate polarization behaviour of the LC compound. Planar LC cells of two different cell thicknesses 5 µm and 3.2 µm were used for the study. When a triangular input electric field of amplitude 12 V$_{pp}$ µm$^{-1}$ or higher was applied, a single delayed peak per half-cycle of the input field appeared (figure 3(a)). The peak can be clearly identified superimposed on the linear ohmic background [22–27, 43]. It was not centred about the zero-crossing of the applied field and persisted till frequencies up to ~150 Hz. The height and the time-scale position of the peak varied significantly with temperature. Such behaviour implies a long-lived ferroelectric state [23–25, 44]. The height of the current peak increased with increasing temperature and survived in the isotropic phase. It is similar to ferroelectric-like behaviour reported in a wide number of BLCs [21, 22, 26, 43]. The associated polarization (P) values were calculated from the obtained current response and its variation with temperature is shown in ESI figure S6(a). P increased with rising temperature, similar to several other BLCs [21, 22, 26, 43], but it continued to grow even after entering the isotropic phase. Therefore, it is possible that significant contributions from ionic impurities might be present in the obtained responses.

To check further, the sample was also probed with a square-wave electric field of amplitudes up to 16 V$_{pp}$ µm$^{-1}$ and frequencies till ~150 Hz. Similar to the triangular-wave measurements, a delayed, distinct polarization bump was obtained in the current response (figure 3(b)), appearing in each half-cycle. The calculated polarization values (P) from the square-wave responses, as a function of temperature, are shown in figure 4(a). These values are much smaller than those obtained from the triangular-wave responses (ESI figure S6(a)), and the obtained temperature-dependent variation is also different—P decreases on entering the isotropic phase. On cooling, in the N phase, P initially increases followed by a decrease with decreasing temperature. However, on entering the N$_{th}$ phase, P starts to increase and reaches a saturation value at even lower temperatures. It is important to mention that in the N phase, when a square-wave electric field was applied, the brightness of the texture decreased, and a frequency following switching was observed (ESI figures S7, S8, video 1). On field removal, the usual nematic texture reappeared. Under the same conditions, in the N$_{th}$ phase, an apparent deformation (or unwinding) of the twist-bend heliconical structure was observed, and a uniform dark texture was established (ESI figure S9, video 2). Deformation of the heliconical structure under external electric field was also confirmed using optical transmission measurements (ESI figure S10). The usual N$_{th}$ texture reappeared only very slowly once the field was turned off due to slow reorganization of the pseudolayered helical structure, which agrees well with the literature [16]. The field-induced dark texture does not represent a simple Fréedericksz-like transition because the dielectric anisotropy ($\Delta \varepsilon$) was found to be negative in this experimental frequency region (up to ~150 Hz), as presented later in the dielectric section. It also agrees well with the observations of dark textures under ferroelectric switching conditions for several other LCs [22, 23]. Therefore, an increase in polarization value in the N$_{th}$ phase is expected due to additional contributions from the unwound helices [17]. This is readily realized by looking at the polarization bumps obtained for the square-wave responses—an additional shoulder-like bump appears in the N$_{th}$ phase (ESI figure S6(b)). The striking difference between the variation of P in triangular and square-wave measurements is possibly because of the ramp-wise nature of the triangular input signal. Due to this ramp-wise nature, a timescale-based identification of the true polarization response could not be made for triangular inputs—the net response had significant contributions from ions. However, for a square-wave input, the polarization response appeared within ~1 ms of field-reversal, revealing its true polar nature, while the ionic contributions were buried under the saturation region of the response at higher time scales.

The polarization bump in figure 3(b) appeared within 1 ms of field reversal, especially in the N phase, due to switching of the bulk polarization (P) [28, 45]. The polarization switching times ($\tau_p$), evaluated from the time scale position of the polarization bumps, are shown in figure 4(b). The switching time ($\tau_p$) is in sub-millisecond range in the N phase, and it remains almost fixed (~500 µs). With decreasing temperature, $\tau_p$ showed an increase (in the N$_{th}$ phase) due to increasing...
Figure 2. The optical textures of different LC mesophases exhibited by CB7CB, recorded between crossed polarizers, using a POM at different temperatures. Figure (a) was captured with the LC sandwiched between an untreated glass slide and a coverslip; figures (b)–(f) were recorded in a 5 µm cell with planar alignment. The related scalebars are shown separately in each figure.

Figure 3. Time-dependent switching current responses of the LC, at different temperatures under an external electric field: (a) triangular input 18 V<sub>pp</sub> µm<sup>-1</sup> 10 Hz; (b) square-wave input 16 V<sub>pp</sub> µm<sup>-1</sup> 5 Hz. In (b), the arrows indicate position of the polarization bumps.

Figure 4. (a) Temperature dependent variation of the polarization values and (b) polarization switching time (τ<sub>p</sub>) of CB7CB under a square-wave electric field of frequency 5 Hz and amplitude 16 V<sub>pp</sub> µm<sup>-1</sup>, at different temperatures.
Paja et al have predicted that the twist-bend helices can unwind under a strong electric field, giving rise to splay-bend nematic (N_{SB}) and polar nematic (N_p) phases [11]. It was followed by Merkel et al, where they report experimental observations of a field-induced splay-bend nematic (N_{SB}) phase [46] and a large polar order [16] in the N_{tb} phase. This is analogous to field-induced deformation and consequent unwinding of helical structure in ferroelectric LCs (FLCs) [47]. Recently, a few other studies have also reported that a strong electric field, perpendicular to the helix axis, is expected to completely (or perhaps only partially) unwind, the helical structure of the N_{tb} phase [5, 11, 12, 16, 17, 29]. Again, the N_{tb} phase is expected to be locally polar [5–7, 11, 15], and our experimentally obtained threshold field values (∼12 V_{pp} μm^{−1}) for the polarization response are of the same order predicted in [11]. Therefore, unwinding of the helical structure is expected to give rise to a polar response, as obtained in our experiments. We further observed that at a fixed temperature, with increasing frequency, the polarization peak shifted to the right towards higher values in the time scale and with decreasing peak height (figure 5). It suggests that at higher frequencies the polar switching could not follow the input triangular field completely and as a result the value of P decreases at high frequencies [23]. There is a competition between the ferroelectric-like and the ionic contributions in the entire LC phase, which becomes dominantly ferroelectric-like at higher frequencies.

The polar response is persistent in the high-temperature N phase as well as the N_{tb} phase of the sample and its origin needs to be understood. In a recent study, Heist et al have discussed that the high-temperature N phase in CB7CB is a cybotactic nematic phase consisting of polar-twisted nematic clusters (N_{CtNPT}) [19]. It is in coherence with the prediction of clusters in the N phase of the bent flexible dimer CB7CB by Krishnamurthy et al [20]. In literature BLCs are known to form small aggregates/clusters (cybotactic clusters) with a higher internal symmetry (e.g. smectics) in their N phase [21, 25, 27]. These clusters are locally polar because of their layered internal structure and collective orientation of the dipoles inside each cluster [22, 25]. In the absence of an electric field, the clusters are randomly oriented in the LC bulk. When an external electric field above a certain threshold is applied, they align collectively giving rise to a net polar response [21–28]. The clusters can be present in the nematic as well as in the isotropic phases [21–26]. Therefore, the net polar response in the N phase of CB7CB can be attributed to the field-induced alignment of such clusters. We have explored the presence of these clusters in CB7CB using dielectric techniques later in the next sub-section. However, in the N_{tb} phase, based on our experimental results and the findings reported in literature [11, 19, 20, 46], we propose that the polarization has two contributing factors: (a) cybotactic clusters persisting in the N_{tb} phase and (b) deformation and consequent unwinding of the helical structure under a strong external electric field (>12 V_{pp} μm^{−1}). In the N phase, with decreasing temperature the value of P decreases due to increasing viscosity [25, 26]. In the N_{tb} phase, the polarization is predominantly due to the unwound helices with additional contributions from the clusters, which follows the power law equation in temperature [17].

The results till now indicate that the polar response has a ferroelectric-like origin but contributions from ionic impurities are also likely to be present. We discuss this possibility with reference to the results reported in the literature and a few additional experiments. For purely ionic cases, the polarization response only appears in the low-frequency regime and lacks in a strong temperature dependence [23–25]. Our results, in contrast, show a strong temperature dependence of the polarization and it persists at moderately high frequencies (up to viscosity [21, 28]. Recently, in a theoretical investigation viscosity [21, 28]. Recently, in a theoretical investigation
~150 Hz). Electroconvection patterns were not observed during the experiments, which indicates that the ionic impurities are less, and they hardly have any effect on the observed behaviour [25, 27]. If the polar contributions arise solely due to ions, the net polarization values would be proportional to the cell thickness [27, 28]. Therefore, to investigate this, we have compared the polarization values (triangular-wave) of two LC cells of different thickness—5 µm and 3.2 µm. The results are presented in figure 6. We found that with increasing frequency polarization values decreased, and eventually, at around 20 Hz the polarization profiles for both the cells merged together (figure 6(c)). Also, the polarization values decreased with increasing frequency, similar to several other BLCs [22, 24, 25]. It happened because at high frequencies the ionic contribution to net polarization goes down and only the contribution from a ferroelectric-like polar order remains. AC conductivity (σ_{ac}) measurements were also performed in the experimental frequency region (up to ~100 Hz) (figure 7). With increasing frequency, σ_{ac} increased which is opposite to the net polarization (decreased). Interestingly, on entering the isotropic phase σ_{ac} decreased (figure 7 inset), which is in contrast with the variation of triangular-wave polarization values (increased) but matches with the variation of square-wave polarization values (decreased). The crossover of σ_{ac} in the N_{gb} phase (green diamonds) with that of N (blue triangles) and Iso (red circles) phases in figure 7 could be readily adjudged by looking at the inset. The maximum (inset—figure 7) shifts to higher temperatures with increasing frequency, possibly due to larger viscosity in the N_{gb} phase which causes hindered movement of charges at higher frequencies. The values of σ_{ac} in our experimental frequency regime are nearly one order less than what is reported in the literature for CB7CB [48]. Further, the dc conductivity (σ_{dc}) value, obtained from dielectric fittings (discussed in the next sub-section), were found around ~10^{-9} S m^{-1} (matches with [46]) which is two orders of magnitude smaller than σ_{ac}. This is a strong indication that ionic impurities are not the principal reason behind the observed polar response. Also, the frequency range of existence of the polarization peak matches almost exactly with the range of collective mode (M_1) identified in our dielectric spectroscopy measurements (discussed later). Therefore, based on these experimental findings, we conjecture that the net polarization has a ferroelectric-like origin (cybotactic clusters and unwound helices in the N_{gb} phase) and it might have limited contributions from ionic charges at lower frequencies [22].

3.3. Dielectric measurements

Broadband dielectric spectroscopy was performed in the frequency range 20 Hz–2 MHz. The real and the imaginary (ε’ and ε’’) parts of the complex dielectric permittivity were measured at different temperatures (ESI figure S11). At smaller frequencies the value of ε’ is very large (~100), typical of ferroelectric substances [24, 25, 49]. The dielectric absorption spectra (ε’’') revealed two distinct relaxation modes: a low-frequency mode (M_1) and a high-frequency mode (M_2). The dielectric modes were further identified with certainty by analysing the differentiated profiles of ε’ (−dε'/dlogf0), which also revealed these two modes with identical properties (ESI figures S12 and S16) [46]. M_1 suggests collective relaxations, while M_2 represents reorientation of the LC molecular short-axis due to planar anchoring conditions [21, 49]. The dissipation factor tan δ (=ε’’/ε’), which is another measure of dielectric loss, was also analysed under an external DC bias voltage (ESI figure S13). The low-frequency tan δ loss-peak

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**Figure 6.** Temperature dependent variation of the polarization values (triangular-wave) using two cells of different thickness—3.2 µm and 5 µm, at various frequencies: (a) 5 Hz, (b) 10 Hz, and (c) 20 Hz. At 20 Hz (c), the polarization profiles overlap.

**Figure 7.** Frequency dependent variation of the ac conductivity (σ_{ac}) at different temperatures; the inset shows temperature dependent variation of σ_{ac} at different frequencies.
conductivity part. The three individual contributions extracted from the complete fit are shown in figure 8(a). The parameters $\alpha$ and $\beta$ (for both $M_1$ and $M_2$) vary between 0.98–0.99 and thus represent a near Debye-type relaxation. In the low-frequency regime (i.e. $M_1$), tilted smectic-like ferroelectric clusters are known to give rise to such Debye-type relaxations [53, 54]. The parameters dielectric strength ($\delta \varepsilon$) and relaxation frequency ($f_R$) of $M_1$, extracted from the fit of equation (1), are shown in figure 8(b). The range of $f_R$ matches well with the range of existence of the polarization responses (up to $\sim 150$ Hz). The dielectric strength of $M_1$ is large ($\delta \varepsilon_1 \sim 105–110$) and remains fairly constant with varying temperature, except for a small discontinuity near the $N$–$N_\theta$ transition [24, 25]. Such high values of $\delta \varepsilon_1$ indicates an associated polar order [16]. On the other hand, the relaxation frequency ($f_R$) decreases upon cooling, divulsing an Arrhenius-type behaviour ($f_R = f_0 \exp (-E_a/k_B T)$; $f_0$ is a temperature-independent constant, $E_a$ is the activation energy, $k_B$ is the Boltzmann’s constant and $T$ is the absolute temperature). The activation energy ($E_a$) of $M_1$ was evaluated from the slope of the linear fit of the Arrhenius plot (ESI figure S17). In the $N_\theta$ phase, $E_a$ has a value $\sim 71.34 \pm 1.24$ kJ mol$^{-1}$ which is nearly twice the value reported for mode $P_1$ ($\sim 10^5–10^6$ Hz) in [52]. In the $N$ phase, $E_a$ ($\sim 59.56$ kJ mol$^{-1}$) has values smaller than the $N_\theta$ phase (due to lesser viscosity at higher temperatures), but it is still quite large. Such high activation energy dictates that a large amount of energy is required to excite the collective mode ($M_1$). This is why it is rather hard to realize $M_1$ in a relatively thicker cell. It also explains the large threshold voltage required for a polar response, as found in our experiments. In case of $M_2$, the dielectric strength ($\delta \varepsilon_2$) is very small, and it decreases on cooling (ESI figure S15(b)). The dc conductivity ($\sigma_{dc}$) values extracted from the fitting data, were found around $\sim 10^{-9}$ S m$^{-1}$, which is of the same order reported in [46] (ESI figure S18).

Dielectric permittivity measurements (of $\varepsilon_\parallel$ and $\varepsilon_\perp$) at 1 kHz were performed to compare our results with the ones reported first by Cestari et al (ESI figure S19) [14]. The dielectric anisotropy ($\Delta \varepsilon$) values, as a function of temperature, were also evaluated (ESI figure S19-inset). Our results are in very good agreement, both quantitatively and qualitatively, with
the ones reported in the literature [14, 30]. These agreements particularly show the high purity of our sample under investigation. Additionally, we have also performed permittivity ($\varepsilon_\parallel$ and $\varepsilon_\perp$) and dielectric anisotropy ($\Delta \varepsilon$) measurements in the lower frequency region at 20 Hz and at 100 Hz (ESI figure S20). The $\Delta \varepsilon$ is a frequency dependent quantity and it has negative values for both N and N$_{th}$ phases at 20 Hz and 100 Hz. It indicates that a simple Fréedericksz transition is not possible in the low frequency region, and yet we have observed settling of a dark texture under an external electric field in the N$_{th}$ phase, as discussed in section 3.2. Therefore, it is established that the field-induced deformation of the twist-bend helical structure caused the dark texture to appear, accompanied by the polarization response. It is important to note that under the same conditions in the N phase, dark textures were not observed (hence, no Fréedericksz-like transition) and only a frequency following textural switching was present. It further establishes that the polar response observed in our experiments indeed has a ferroelectric origin, similar to experiments reported in a wide number of bent-core nematic LCs [21–28, 43].

3.4. 1 wt% TiO$_2$ NPs doped CB7CB

Next, we performed measurements on the 1 wt% TiO$_2$ NPs (∼21 nm) dispersed CB7CB by preparing an LC nanocomposite as described in section 2.2.4. It is known that TiO$_2$ NPs can act as ion releasing agents when the ion concentration in LC matrix is small and also as ion absorbing agents when the ion concentration of the host LC is large [55, 56]. Therefore, the idea is to explore the effects of this NP dispersion on the observed polar nature of CB7CB and to arrive at a conclusion regarding the extent of ion impurities in pristine CB7CB. We first observed that after doping both the isotropic-N and the N–N$_{th}$ phase transition temperatures were lowered by ∼4°C, compared to pure CB7CB (ESI table T3). It is a first indication that the impurity content has increased in the nanocomposite. The dielectric measurements revealed that the collective mode M$_1$ survives in the LC nanocomposite but with modified properties (ESI figure S22). The M$_1$ relaxation frequencies ($f_{R1}$) of the LC nanocomposite manifested a frequency upshift compared to pure CB7CB (ESI figure S23). Considering that the collective relaxations are associated with cybotactic clusters, it indicates a decrease in the size of the cybotactic clusters after doping [39]. Also, the activation energies were increased by ∼4 kJ mol$^{-1}$ in both the phases (N and N$_{th}$) after doping (ESI figure S24). Accordingly, the birefringence ($\Delta n$) and order parameter ($S$) values were reduced after doping due to the decrease in size of clusters (ESI figure S25). The birefringence measurements were performed in [39] and the order parameter values were evaluated by fitting the birefringence ($\Delta n$) data with the well-known Haller’s equation [31, 33].

The ac conductivity ($\sigma_{ac}$) values (∼10$^{-4}$ S m$^{-1}$) manifested nearly three orders of magnitude in increase after doping (ESI figure S26). The free ion concentration ($n$) and diffusion coefficient ($D$) values were evaluated by fitting the frequency-dependent dielectric spectrum with the modified Uemura equation (ESI equation (1)) proposed by Sawada et al [57]. Both the $n$ and $D$ values were found to increase after doping (ESI figure S27). Therefore, these results strongly suggest that the content of ionic impurities have increased after doping, and it also establishes that the impurity content of the host LC CB7CB was insignificant [55, 56]. Interestingly, no current peak (polarization response) could be observed in the re-polarization current measurements using a triangular input electric field (ESI figure S28). In the square-wave measurements, only an ionic bump was observed up to ∼5 Hz with switching times in the few tens of milliseconds (>10 ms) range (ESI figure S29). These ionic bumps ceased to exist at temperatures below 101°C. Therefore, doping resulted in an increased content of ionic impurities in the LC nanocomposite, but at a cost of extinction of the polar order. If the polarization response in pristine CB7CB was solely due to ionic impurities, doping with the NPs must have resulted in an enhancement of the net polarization in the LC nanocomposite. However, we observed the opposite—doping with NPs resulted in a reduction of the collective order, increase in the ionic impurity content and extinction of the polar order. These results strongly suggest that contributions from ionic impurities to the obtained polarization responses in pristine CB7CB are only finite and exist at lower frequencies. Therefore, we arrive at the conclusion that polarization in pristine CB7CB must have resulted from the field-induced collective reorientation of cybotactic clusters and additionally from the field-induced deformation of helical structures in the N$_{th}$ phase.

4. Summary and conclusion

A bent LC dimer CB7CB was investigated in the N and N$_{th}$ phases using various techniques. The formation of N and N$_{th}$ phases were confirmed by textural analysis using polarizing optical microscopy. The polarization response of the LC was analysed using both the triangular and square-wave input electric fields. In both cases, a single, delayed, polarization peak (not centred about the zero cross-over) was observed above a threshold electric field of ∼12 VPP $\mu$m$^{-1}$, which persisted till frequencies as high as ∼150 Hz. The values of polarization were calculated from the square-wave responses and analysed as a function of temperature. The polarization switching times were found ∼1 ms region, especially in the N phase. During these measurements, under the influence of external electric field, deformation of the twist-bend helical structure was observed in N$_{th}$ phase, while in the N phase a frequency following textural switching was observed. Dielectric anisotropy ($\Delta \varepsilon$) was found negative in the frequency region of these polarization measurements (up to ∼150 Hz). Dielectric measurements revealed the presence of cybotactic clusters via collective relaxation processes with large activation energies. The collective mode (M$_1$) relaxation frequencies ($f_{R1}$) match almost exactly with the range of frequency for which polarization ($P$) responses exist (∼150 Hz). We also observe that these collective modes are only obtained in relatively thin cells and have large activation energies [16, 46, 50]. Therefore, we conjecture that the net polarization resulted from the field-induced collective reorientation of cybotactic clusters.
and additionally from the field-induced deformation of helical structures in the N\_t phase. To check the contributions from external ionic impurities, if any, different experiments were designed and performed. If the polarization was solely due to ions, the polarization values must be proportional to the cell thickness. However, we found that the polarization values for two different cell thicknesses merged at around 20 Hz. In fact, in the triangular-wave measurements, at a fixed temperature, with increasing frequency, the polarization peak shifted to the right towards higher values in the time scale and with decreasing peak height. These observations reveal the true ferroelectric-like nature of the obtained polar responses at higher frequencies.

To further explore the possibility of the ionic contributions, we prepared 1 wt\% TiO\_2 NPs dispersed CB7CB LC nanocomposite and performed experimental measurements. It mimics the situation for externally added impurities. The doping with TiO\_2 NPs resulted in a reduction of the collective order, an increase in the ionic impurity content and conductivity, but it caused an extinction of the polarization response. Therefore, it establishes with certainty that contributions from ionic impurities to the obtained polarization responses in pristine CB7CB are finite and only exist at lower frequencies. The net polarization has competing contributions from both ferroelectric-like and ionic origin, but it becomes dominantly ferroelectric-like at higher frequencies. Hence, we arrive at the conclusion that polarization in the pristine CB7CB has ferroelectric-like contributions from the field-induced collective reorientation of cybotactic clusters and additionally from the field-induced deformation of helical structures in the N\_t phase.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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