The Twist Bend Nematic phase in Cyanobiphenyl and Difluoroterphenyl based Bimesogens

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Abstract: The paper reviews assignment of the observed low temperature nematic phase in simple bimesogenic or dimeric systems based on cyanobiphenyls and difluoroterfluorophenyls to the twist-bend nematic phase, N_{TB}, using a range of experimental techniques. These include DSC, X-rays, Polarising Microscopy, electro-optics, birefringence and measurements of the electroclinic effect arising from flexoelectricity. An emphasis is laid on the observations of the chiral domains of opposite handedness at zero field in an otherwise achiral liquid crystalline system in this phase. These observations are a direct consequence of the structure of the twist-bend phase predicted by Ivan Dozov for achiral bent core molecules. The paper reviews the electro-optic phenomena and the observed electroclinic effect and how these observations assign it as the N_{TB} phase. Results of the nano-scale helical pitch measurements using freeze-fracture microscopy are reviewed and discussed briefly. Results of the measurements of elastic constants especially close to the N-N_{TB} transition are also reviewed.

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Introduction:

Liquid crystals (LCs) in their typical nematic (N) phase are used predominantly in the current multibillion dollar display technology. However non-display applications of liquid crystals are gaining increasing importance in the study of biological systems. Their use in biological sensors as well as in photonics not only offers promise for the future but other applications are also on a significant upward trend in the recent years. Liquid crystals are considered to be one of the prime examples of self-organised systems as building blocks for supra-molecular systems with wide use in nano-science and technology. In the nematic phase, the orientational order exists but the long range positional order is absent. In 1888, Reinitzer [1] observed what turned out to be two liquid crystalline phases in cholesteryl benzoate: the cholesteric phase and the blue phase. As per the text of the paper in the literature, Reinitzer 'noticed that the cloudy sample became bluish before going into the isotropic state while heating'. This would imply that blue phase was observed over a very narrow range of temperatures which is generally true to this date unless extra procedures are introduced to stabilize it. There is no Brownian motion of molecules in the blue phase. Such observations of liquid crystalline phases at an early stage led to the discovery of the fourth state of matter in addition to the known states of matter: gases, liquids and solids at the time. The fourth state was established only after significant controversy in the literature was resolved in favour of this state being different from liquids and crystalline solids [2]. In 1890, Gattermann [3] synthesized para-azoxyanisole in which he observed a nematic liquid crystalline phase now regarded as one of the two most commonly used in the devices. The other very commonly used LC phase is the cholesteric phase e which could be classed as the third nematic phase. Such observations of nematic phases were made without realizing that such findings one day would have far reaching positive impact on almost every human-being on this planet. The most profound use of liquid crystals in display technology is in portable devices such as the screens of mobile phones, tablets, lap-top computers and the flat-wall TVs. These displays were extensively developed during the latter parts of the 20th and at the beginnings of the 21st century. Gray's discovery [4] of a stable nematic phase at room temperature observed in 4-cyano-4'-pentylbiphenyl (5CB) provided a breakthrough which enabled its wide use in displays in the 1980's and 1990's. The latter finding gave enormous incentive and boosted interests of scientists involved and attracted many young minds to the field of LC research. Several display modes in the nematic phase were invented in the latter parts of the 20th century [5-8]. These innovations had a major impact on the operation of liquid crystal devices. Liquid crystalline materials such as cyanobiphenyls, fluorobiphenyl and difluoroterphenyl based mesogens and mixtures of these mesogens with other materials were engineered to broaden the useful temperature range and the electro-optical properties of mixtures for their successful use in devices. For example, the E7 mixture with 5CB as the major component was developed by Merck UK for LC displays.

Friedel in 1922 [9] realized that the key distinction between liquid crystals with different textures was thermodynamic and due to the molecular organisations rather than due to viscosity of the medium. He identified and named the nematic and smectic phases and correctly identified the key features of their molecular structures. Vorländer [10] and his group of researchers synthesized over 1000 liquid crystalline compounds - from early 1900's up to 1935. Vorländer's main thesis was that liquid crystalline properties were exhibited better by the long-rod-shaped molecules: longer and better molecules are the rod-likes, better would be 'a liquid crystal' composed of these molecules. In the light of recent advances in new classes of liquid crystals such as discotics, bent-core and bimesogens, it would seem that Vorländer conclusion was overly simplistic. .

While extending the Maier-Saupe theory to include the asymmetrical molecules in the nematic phase of thermotropic liquid crystals, Freiser [11] predicted the existence of a biaxial nematic phase with two optical axes. This phase was suggested to arise from a second-order uniaxial to biaxial (N_U to N_B) phase transition at a temperature lower than isotropic to uniaxial nematic (I-N_U) phase transition. In 1980, Yu and Saupe [12] experimentally observed a biaxial nematic phase (the 4th in the series of the nematics) in a lyotropic liquid crystal and this discovery was extended to those in thermotropic liquid crystals in 2004 for the bent-core systems and tetrapodes [13-15]. These and other findings were recently illustrated by Luckhurst and Sluckin [16].

Following the work on an EU project focused on biaxial nematic device (BIND), bimesogens where the two mesogens linked by an odd number of methylene units were investigated by the Hull and Dublin groups. Clear evidence was given [17] for a nematic-nematic first order transition that occurred below the high temperature N phase. The low temperature phase initially called Nx, though proven not to be biaxial, had been found to exhibit special properties. A detailed set of investigations led to the observation of fascinating characteristics both for the high temperature nematic and the Nx phases in bimesogens and the other similar dimeric liquid crystals. For example, this new nematic phase, Nx, below the high temperature nematic phase, showed spontaneously formed beautiful stripes of the type never observed before when using a planarly aligned rubbed cell. This cell showed large chiral domains even in the absence of the chiral centres of the molecules of cyanobiphenyl and difluoroterphenyl based dimers [17-19] having being present. In 2011, Cestari et al [20] suggested that the splitting in the deuterium NMR spectra of deuterated CB7CB on its entry to the X phase (as denoted by Cestari et al) could arise from the bend of the director stabilized by its twist. The authors termed this phase as the twist-bend N_{TB}. Though they were the first to suggest the existence of such a nematic phase in bimesogens, Cestari et al [20] did not give a proof and the conclusion that 'the optical periodicity associated with a twist-bend nematic liquid crystal could be in the optical region' did not turn out to be correct. They based their interpretation on their observations of focal conic textures in CB7CB. No value for the helicoidal angle (the angle which the director made with the optical axis), was given. Their observation of alternate stripes being of opposite chirality was at variance with the observations of stripes for zero external field, by Panov et al [18]. Panov et al found that the neighbouring stripes were of the same handedness. Chiral domains of opposite handedness were separated by domain boundaries. Only at high fields, the adjacent stripes were of the opposite handedness [19]. Panov et al reported the fast electroclinic switching arising from flexoelectricity and suggested this 'to correspond to the presence of a very short uniform lying helical pitch (ULH)'. However, the presence or absence of such a short pitch was 'impossible to confirm by optical methods', [18].

During 2013, three groups gave experimental evidence of the existence of the 5th nematic phase [21-23], the twist-bend nematic phase found in dimers in terms of being characterized by a nano metric helical pitch and provided estimations of the values and range of the helicoidal angle. This phase had been proposed by R. B. Meyer while considering chiral systems where the homogeneous bend and the twist allowed the director to be confined on to a cone rather than it being restricted to lying in a plane [24]. The phase was independently predicted later by Dozov [25] for achiral banana-shaped molecules. This was supported by Memmer's computer simulations [26] of the bent-core achiral liquid crystalline molecules. It was predicted that the resulting phase would exhibit conglomerates of chiral domains of opposite handedness arising from the symmetry breaking of achiral molecules. These domains were experimentally observed the first time in the low temperature phase in dimeric systems by Panov et al [18, 19].

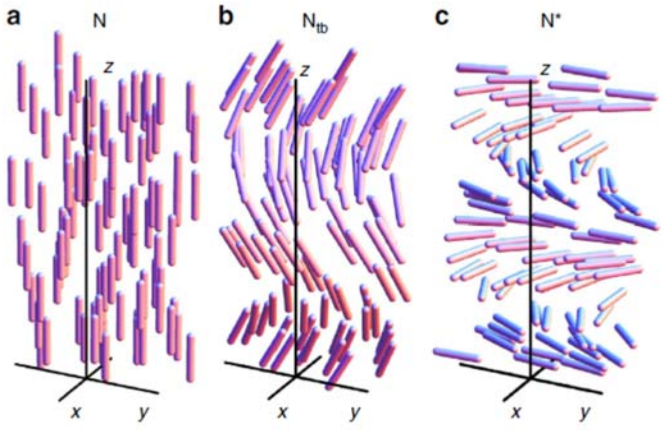

Figure 1 Schematics of local director arrangements in nematics. (a) Nematic N phase, uniaxial alignment with the angle the director makes with the helicoidal axis θ_0=0, (b) N_{TB}, with oblique helicoid $0<\theta<\pi/2$ and (c) chiral nematic N* phase $\theta_0=\pi/2$ [drawn with permission from reference 22]

The dimeric systems initially studied were characterized by large permanent dipole moments, the dipoles were either parallel to the mesogenic long axes as in cyanobiphenyls or directed at right angles to the long molecular axes such as in individual difluoroterphenyl based mesogens. These liquid crystalline materials are thus characterized by either positive or negative dielectric anisotropies, which also depended on the distribution of the various conformers in the structure. In bimesogens, the two mesogens are separated by a flexible spacer of methylene groups with an odd number of carbon atoms, in most cases C =7, 9 to 11. Apart from practical applications, the discovery alone is scientifically noteworthy and intriguing in that it represents a breakthrough in finding a new nematic phase, the 5th in a series of nematics [, after 125 years of the discovery of the first nematic by Reinitzer [1]. The twist-bend nematic phase represents a missing link between the conventional nematic where no helicoid is present and the cholesteric phase where the helicoidal axis is directed normal to the optical axis or the main director. Here the oblique helicoid angle θ_0 lies in between zero and $\pi/2$ radians (Figure 1 from [22]) and the magnitude of the angle depends on the temperature and the material.

We note that early work on liquid crystal main chain polymers had resulted in the detection of two nematic phases by Ungar et. al. [27], however the structure of the second nematic phase was not investigated at the time. Schröder et. al. [28] detected two nematic phases for a set of bent core molecules. The low temperature phase was identified provisionally as the nematic columnar. Lesac et. al. [29] observed quite similar textures for nematic phases for a different type of bent core system and assigned the low temperature nematic phase preliminarily to the nematic columnar. In dimers with an odd number of methylene units containing Schiff bases, Sepelj et. al. [30] detected a second monotropic nematic phase at higher temperatures which was assigned preliminarily to be N_{Col} phase. Interestingly Kimura *et al* [31] may have already realized that the low temperature nematic phase in cyanobiphenyl based dimers with an odd carbon numbered spacer was not a columnar nematic phase. The low temperature phase in such cyanobiphenyl dimers with an odd numbered methylene spacer was identified as smectic by Barnes et. al. [31] based on the observed focal conic textures and this was reviewed by Imrie and Henderson [32]. It is now known that these focal conic textures can also arise from the N_{TB} phase of a dimer for large cell thicknesses. The major difference however lies in the texture of a thin cell being similar to that of the high temperature nematic phase but more importantly the absence of X-ray reflections for the lamellar structure of smectic phase is the indicator for this phase to be a nematic type. The field of liquid crystalline dimers thus lay almost dormant until it was realized that odd membered methylene units linked directly to mesogenic groups could easily form a second nematic phase at low temperatures. It may be noted that none of the early investigators reported any special characteristics of the low temperature and the higher temperature nematic phases. This is the crucial point to make here, an additional nematic phase was reported which had special characteristics [17].

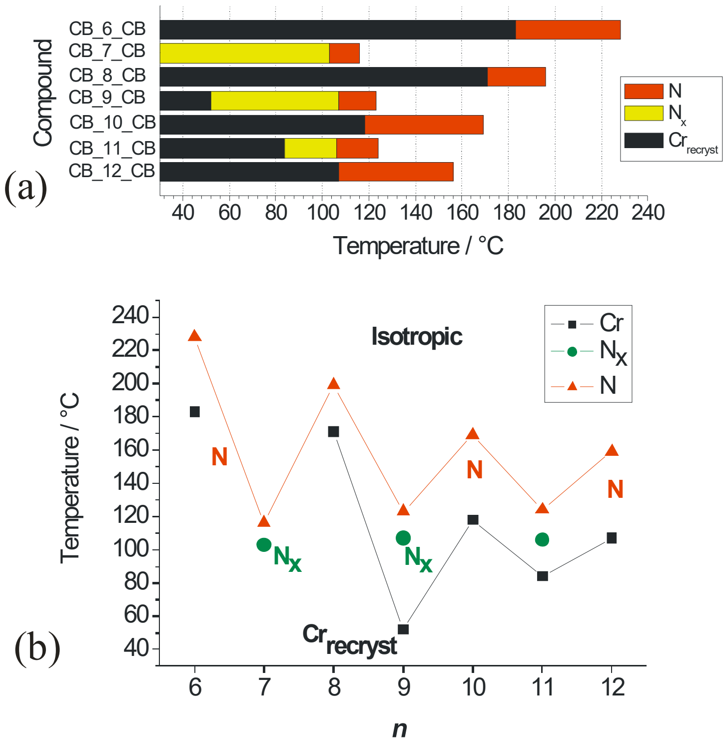

Figure 2. Odd-Even effect in cyano-biphenyl based dimers; (a) the temperature ranges for the N and Nx phases. (b) The transition temperatures plotted as a function of the integer n. The temperature range of the Nx phase is much wider for CBC7CB than for CBC11CB.

A series of bimesogens, where initially cyanobiphenyl groups were linked by alkyl spacers (Cn, where n varies from 6 to 12) with the general formula of YCnY [Y stands for the mesogenic groups] were synthesized in Hull by Mehl and his group. The resulting bimesogenic liquid crystals were characterized by using DSC, OPM textures and X-diffraction studies. The molecular architectures were systematically explored by extending it initially to mesogens with strong lateral dipoles forming a nematic phase, such as difluoroterphenyls [34]. It was initially considered that the nitrile group in the cyanobiphenyl systems might form anti-parallel co-ordination assemblies. These materials are arguably the first clearly designed systems that systematically explored the structure of this new low temperature nematic phase. For all these sets of materials, it was found that when the integer *n* in the spacer is an odd number, an additional nematic phase is observed in the temperature range below the conventional nematic one (Figure 2).

Table 1 shows the transition temperatures and the transition enthalpies for transitions. The transition enthalpy for the N_{TB} is larger for CBC7CB (1.12 kJ/mol) than for CBC9CB (0.86 kJ/mol), and it is much larger for (1.12 kJ/mol) than CBC11CB (0.14 kJ/mol); these are calculated during the cooling processes. Figure 2 shows that the temperature range of the N_{TB} phase for CBC7CB is much wider than for CBC9CB or CBC11CB. For CBC11CB, temperature range for N_{TB} phase is very narrow and it shows only a weak first order transition (0.14 kJ/mol).

Table 1: Transition temperatures, transition enthalpies during cooling and heating for CBCnCB, n varies from 6 to 12. Heating/Cooling rate 10 ^{0}K per minute.

Compound CBCnCB	Transition temperatures [°C]/ transition enthalpy ΔH[kJ/mol] on cooling (heating)		
	T_{Cr-NTB} ΔH/$_l$	T_{Ntb-N}/ ΔH/ $ΔH_{cool}$	T_{N-Iso}/ ΔH/ $ΔH_{cool}$
CBC6CB	191°C	N/A	231°C
CBC7CB	102°C / 21.23	103°C / 1.12 (104.4°C / 1.09)	115.6°C / 1.1 (116.7°C / 1.07)
CBC8CB	178°C	N/A	199°C
CBC9CB	40.5°C / 23.65 (85.2°C / 35.83)	107.3°C /0.86 (104.9°C / 1.15)	122.4°C / 2.19 (124.2°C / 2.1)
CBC10CB	140°C	N/A	172°C
CBC11CB	85.2°C /33.04 (105.8°C / 36.06)	108.6°C / 0.14 (106.2°C / 0.25)	123.6°C / 2.46 (125°C / 2.59)
CBC12CB	139°C	N/A	157°C

X-ray Diffraction of C9CB and 15% 5CB:

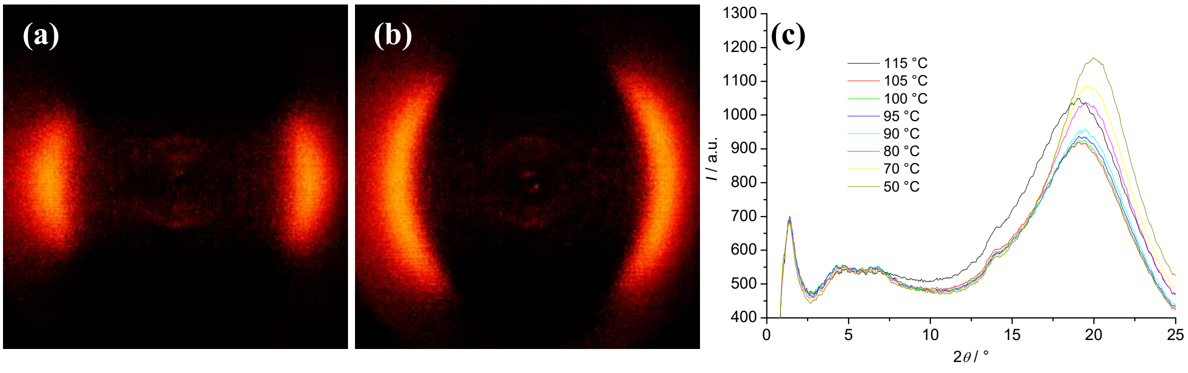

Fig 3. XRD patterns of a magnetically aligned sample of compound of a mixture of 5CB and CBC9CB (15/85 w/w %) on cooling: (a) N phase at 100 °C; (b) $N_{X/TB}$ at 50 °C; (c) Θ-scan of the diffraction pattern in the N and N_x phases

Since x-ray diffraction peaks as signatures of the lamellar or layered structure could not be observed, the XRD data unambiguously showed absence of smectic ordering. These peaks if present would have represented modulation of the electron density associated with this periodic structure. It was found that x-ray diffraction experiment incorporating both small and large angles for the low temperature phase gave rise to similar results to those as observed for the high temperature nematic phase. The results showed only a small narrowing of the wide angle reflection peaks on the transition from N to N_{TB}. These intensities are related to the lateral distances of molecules but no increased intensity associated with asmectic layering at small scattering angles was detected. When n was an even number, such a low temperature nematic phase was found to be absent. This effect termed 'odd –even' had been computer simulated by Luckhurst and Romano [35]. One should note that the N_{TB} phase in some compounds of the series YCnY occurs at room temperature, and the phase is stable over a range of temperatures and concentrations of mixtures of bimesogens and their monomers. Hence the temperature range and the other properties of the N_{TB} phase needed for applications can be easily tailored to meet the practical requirements.

An example of the typical X-ray diffraction data is shown in Figure 3 for a composition of 5CB and CBC9CB (15/85 w/w %) which on heating shows the phase sequence, Cr 76.3 N_{TB} 87.2 N 108.4 Iso (°C) and on cooling: Iso 106.7 N 85.5 N_{TB} -9.2 T_g (T_g = glass transition temperature in °C). The subtle changes in the diffraction patterns are clearly visible. On cooling the sample from the nematic at 100 °C (Fig 3 a) to 50 °C to the N_{TB} phase (Fig 3b), loss of the macroscopic orientation is detected. Fig 3c shows a pseudo 1D plot (Θ-scan) of the diffraction patterns for this composition. A narrowing of the wide angle reflection is clearly detected; notable too are the very low distributions in the small angle intensities. A detailed thermal analysis of the various compositions has been carried out and described [36].

Dozov model and the Stripes:

In 2001 Dozov [25] had theoretically considered the possibility of a phase being formed by bent-core (banana shaped) molecules by assuming negative bend elastic constant K_{33}. He predicted the possibility of having two periodic helical structures formed by achiral molecules: twist-bend and splay-bend. The twist-bend leads to chiral domains of opposite handedness whereas the splay-bend does not. The simplest possible deformation of the uniform nematic director field [17] $\boldsymbol{n} = (\cos\theta cos\varphi\,, cos\theta sin\varphi, sin\theta)$, in a planar cell produced similar patterns to that observed in such a rubbed cell by polarizing microscopy. This can be described as a harmonic distortion of azimuthal and polar angles $\varphi = \Phi\cos\left(\frac{\pi z}{d}\right)\sin\left(\frac{\pi y}{d}\right)$, $\theta = \Theta\cos\left(\frac{\pi z}{d}\right)\cos\left(\frac{\pi y}{d}\right)$, where d is the cell gap, φ and θ are the azimuthal and polar angles of the deviation from the uniform state; *y* is parallel the rubbing direction; z is normal to the cell plane. Φ and Θ are the amplitudes of modulations for deviation angles. It has been shown that spontaneous formation of the director field as expressed by these equations would require a necessary condition that $(K_{11}+K_{22}) < 0$, where K_{11} and K_{22} correspondingly are the splay and the twist elastic constants [17]. The demonstrated requirement of introducing negative elastic constant in explaining the striped patterns in the Nx phase is of major interest to pursue. The known striped patterns formed by helical structures (such as the cholesteric fingerprints or Grandjean-Cano textures) are significantly different from the self-deformed stripes both in appearance and experimental conditions under which these have been observed. Though, the twist-bend model of Dozov is now widely accepted for reasons of the observed chirality [18, 19], electroclinic effect arising from flexoelectric polarisation [17], fast switching [18, 21] and recent observations from the Resonant Carbon K-edge soft x-ray scattering of lattice-free heliconical molecular ordering [37]. No adequate model though as yet is available to link the helicoidal periodicity of 8 nm with the periodic striped pattern observed for bimesogens at the μm scale in the N_{TB} phase of the investigated bimesogens.

The Switching properties

Further intriguing discovery was made with the observation of a fast (4μs or less) optical response in the N_{TB} phase [19]. Such a fast response surprisingly coexists with the ordinary Freedericksz transition (which takes over a minute to occur) close to the N_{TB}-N transition where the viscosity is pretty large.

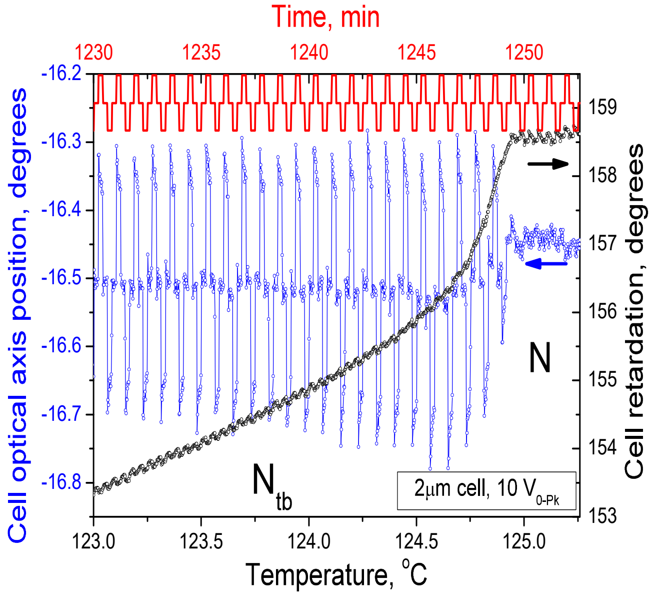

FIG. 4. Optical axis position and retardation obtained with PEM on applying of an alternating electric field (waveform shown by the red line, top of this figure) to the cell during a temperature ramp. (Applied voltage: amplitude 10 $V_{0\text{-}Pk}$, Period 50 s, heating rate 0.1 °C/min). Optical Retardation is marked to the right, and the azimuthal angle is marked to the left. Drawn from reference [18] .

An important aspect of this finding was that the deviation of the optical axis depended on the sign of the applied electric field. Figure 4 shows data obtained using Photo-elastic modulator (PEM) from a difluoroterphenyl-based dimer with negative dielectric anisotropy. On can see clear differences in the behaviour of the conventional nematic from the N_{TB} phase: While the response in the N phase to the electric field is below the resolution of the experiment, the cell in N_{TB} phase shows an in-plane deviation of the optical axis corresponding to the electroclinic coefficient of 0.04°/(V/μm). It may be pointed out that such a phenomenon cannot be due to ionic impurity in the sample since the switching is angular and follows the polarity of the field. Dipolar impurity if any should have given similar response both in N and NTB phases, which is not the case here.

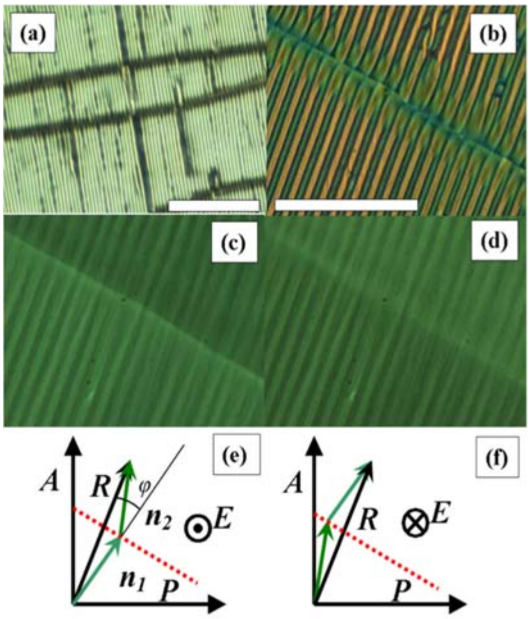

Figure. 5. Textures of in planar cells of 2 μm (a) and 5 μm (b,c,d) thickness. Domain boundary at 0 V(a,b), +200 VDC (c,e), and −200 VDC (d,f). White bar length is 100 μm. In (e,f), $\boldsymbol{n_1}$ and $\boldsymbol{n_2}$ are the optical axes of the neighbouring domains deviated in the opposite directions and the dotted red line corresponds to the domain boundary.[20]

Since the molecules of the system are achiral, such a response is possible only for the case of chiral segregated domains of the left or right handedness. These could arise from the breaking of the chiral symmetry as was predicted by Dozov [25]. Such domains are experimentally observed (Figure 5) and the domain boundaries between these are found to cross the self-deformation stripes in the absence of the external electric field (Figure 5(a), 5(b)). A possible explanation of the electro-optic response had been suggested to be a uniformly lying helical (ULH) [18, 21] structure. For the ULH switching, the tangent of the deviation angle, ϕ is given by $\tan\phi = \frac{eEp}{2\pi K}$ where e/K is the effective flexoelectric coefficient, p is the pitch, K is the effective elastic constant and E is the magnitude of the electric field. The switching time is given by. $\tau = \frac{\gamma p^2}{4\pi^2 K \sin^2\theta_0}$. γ is the viscosity of the nematic phase, θ_0 is the oblique angle also called the heliconical angle that the director makes with the helicoidal axis. If $\theta_0 = 90°$, $\sin\theta_0 = 1$, the formula reduces to that for the cholesteric phase. Based on these two equations for ϕ and τ, and by using the observed fast switching time of 4 μs and a relatively small switching angle ($\phi \sim 0.1$ to 1° at fields of approx. 10-20 V/μm), the pitch is calculated to be short and << 100 nm. Based on these calculations of the measured results, the helical pitch was suggested by Panov et al [18] to be *shor*t less than 100 nm. Though not all the material constants were available at the time, hence the exact value of the pitch could not be calculated but Meyer et al [21] estimated it to be ~ 8 nm based on using values available for similar materials. However if $\theta = 0°$, as suggested by Hoffmann *et. al.* [38] then $\tau \rightarrow \infty$. The system obviously is not switchable contrary to the observations of fast switching [18].The phase would also have been akin to the usual nematic phase. Results of the switching experiment can only be explained by the chiral domains of both handedness being present; as well as to having a large domain of single handedness appearing over the field of view of a polarizing microscope. It has also been shown that when the applied field is higher than a certain threshold value (usually rather large field), the domains of opposite chirality appear side by side. Domain boundaries are rather sharp and these appear normal to the rubbing direction [19]. The periodicity of the pattern is of the order of several μm and depends on the magnitude and the frequency of the applied field. The periodicity is comparable or larger than the cell gap. Though the observed decrease in the periodicity of the stripes with an increase in the strength of the field and frequency can intuitively be explained, yet its exact theory has not so far been developed.

Freeze-Fracture Microscopy:

The prediction of a short helical pitch well below the optical wavelengths [18] led us to plan as to how a short pitch is to measured. Subsequent work carried out in Kent State University measured the pitch using Freeze-Fracture Transmission Electron Microscopy (FF TEM) (Figure 6) and reported by Borshch et al [22]. The appearance of the Bouligand arches was a convincing argument in favour of the helicoidal structure with an oblique helicoidal angle. At the same time, Chen et al [23] obtained similar results for the same dimer and their results were also supported by atomistic molecular dynamic simulation. Results for the nanoscale helicoidal modulation agreed with each other [22,23]. A helical pitch of the order of few nanometre found in the N_{TB} phase has aided us in resolving the mismatch between the Dozov's theoretical prediction based on the negative bend constant K_{33} and the need to have $(K_{11}+K_{22}) < 0$ based on the observed spontaneous self-deformation pattern from a rubbed planar cell. The analysis was based on the assumption of having a small molecular distortion in the N_{TB} phase from a uniform nematic phase.

It is now clear that pitch of the helicoid at the nano-scale level could not have been investigated using the conventional optical polarizing microscopy. Hence these stripes could not have been caused directly by such a short pitch but instead the local chirality may lead to a hierarchy of structures having helices of different pitch values under different experimental conditions [39 to 41]. It was pointed out by Goodby [42] that parabolic defects such as those seen as fish-like pictures in Fig. 7, are reminiscent of the helicoidal structure in chiral smectic C* phase where the pitch bands and the dechiralization lines appear around a parabolic defect [43]. A striped structure seen normal to the rubbing direction could be due to the parabolic defects appearing in a plane normal to the plane of the texture where these defects appear as straight lines. These defects are reminiscent of the helical structures in ferroelectrics. Results thus provide us with a platform for a further analysis and for arriving at an understanding of the striped patterns to advancing the practical applications of this phase. This observation confirms the local chirality in a domain and this in turn leads to the helcoidal structures in the N_{TB} phase formed from achiral molecules.

Here Figs. 6 and 7

Flexoelectric Polarisation and flexoelectric coefficients:

The flexoelectric polarisation was measured using the pyroelectric effect. The source of modulation of temperature is He-Ne laser used in conjunction with a mechanical chopper, the shining of the modulated laser beam on the sample modulates its temperature. This gives rise to a pyroelectric signal which is detected by the electronic-hardware given here. The signal is integrated to give rise to the flexoelectric polarisation, P_f. The measured polarisation is calibrated with reference to the known polarisation of a ferroelectric liquid crystal material. Details of the measurements are given in the paper by Balachandran et al [45]. Some of the results are being reviewed here.

Fig. 8a The pyroelectric coefficient and the flexoelectric polarisation of CBC11CB. There is an observed increase in the P_f at the I-N and the N-N_{TB} transitions. [Reproduced with permission from reference 45].

Fig. 8b Flexoelectric coefficients

The main outcome is that P_f in both the nematic and the twist-bend nematic phases is greater than in 5CB by a factor ranging between2 and 3. The effective flexoelectric coefficient in the temperature range of the N phase of CBC11CB above N_{TB} is higher by a factor of at least 2 compared to that observed for bimesogens that do not form N_{TB} phase [44]. Using this technique, the splay and the bend flexoelectric coefficients in the N_{TB} phase cannot be measured due to problems realted to the hybrid alignment in the N_{TB} phase.

Twist-Bend Nematic phase and the elastic constants:

Dozov [25] predicted that the twist-bend nematic phase can be spontaneously formed when K33<0 and K11/K22>2. Balachandran et al. [45] reported K_{11} and K_{33} of a bimesogen, CB11CB. They found K_{33} first increased at the I-N transition overtaking K_{11} but then it decreased with a reduction in temperature to a small value of 6 pN, then stayed at that level almost independent of temperature. K_{11} increased with a reduction in temperature and continued to increase; K_{22} was not independently measured. To verify whether Dozov's hypothesis is correct, Yun et al [46] made precise measurements for the temperature dependencies of the three elastic constants of CB7CB. Yun et al measured K_{22} independently of the other two elastic constants. Measurements were made in the entire temperature range of the nematic phase and close to the N-N_{TB} transition temperature in the twist-bend nematic phase. Results were obtained by combing the Freedericksz threshold methods (i) for a twisted nematic and (ii) for the in-plane switching cells. Anomalous changes in K_{22} and K_{33} are observed across the phase transition temperature of the N-N_{TB} phases. The elastic constants estimated through extrapolation of the data in the higher temperature region of the nematic phase fully satisfied Dozov's hypothesis, whereas the data obtained for the elastic constants in the vicinity of the phase transition temperature exhibited the opposite trend. Dozov considered the theoretical basis of both models (splay-bend and the twist-bend) and suggested that a helical structure could be formed through either splay-bend deformations or through conical twist-bend if the bend elastic constant (K_{33}) became negative. Dozov also determined that the twist-bend phase was much more stable than the splay-bend especially when the twist elastic constant (K_{22}) is less than half of the splay elastic constant (K_{11}). After extrapolation of the experimental results, of the nematic phase (??correct??) there was no indication that K_{33} would turn negative in the N_{TB} phase. Adlem et al. [47] confirmed tendencies of elastic constants for a mixture of dimers. They showed that , K_{33} tended to be closer to zero and then apparently increased as the temperature approached the N-N_{TB} phase transition temperature. In their results too, K_{33} could not be extrapolated to a negative value through a temperature reduction. Yun et al [46] with their extensive measurements and analysing techniques proceeded to answer the important question, as to how the elastic constants behave close to the N-N_{TB} phase, especially in the N_{TB} phase? Some of their experimental results are given in Figs. 9 and 10 will be discussed below . To some extend they are at variance to those reported by Cestari et al [20] for the same material. None of these results in [44] show that extrapolated value of K_{33} is negative . The experimental results are also at variance with their simulated results. They (who ?) predict K_{11}, going first up and then going down with a reduction in temperature. Comment; the last 3 lines need to be clearer; I am not sure what you want to say.

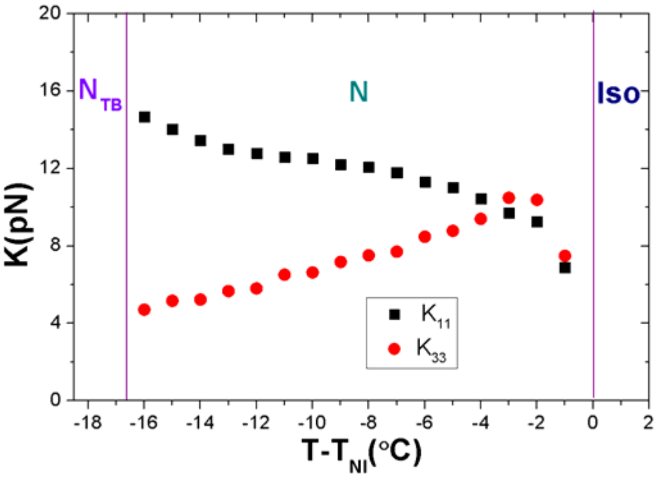

Fig. 9 K_{11} and K_{33} as function of reduced temperature T -T_{NI} for CBC11CB. Reproduced with permission from Balachandran et al reference [45].

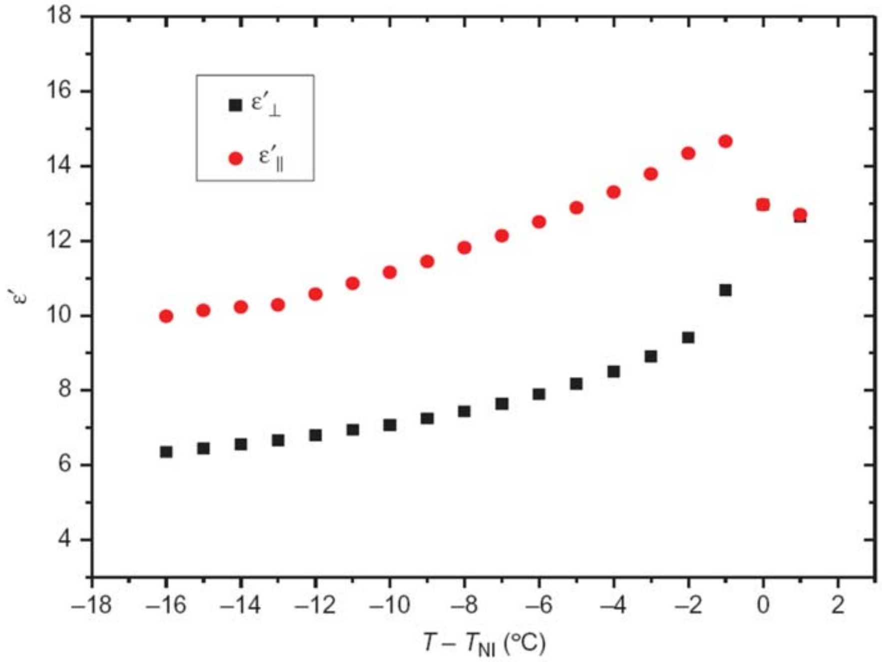

Fig. 10 Dielectric permittivity, $\varepsilon'_\perp$, $\varepsilon'_\parallel$ of CBC11CB as a function of the reduced temperature. Note that the dielectric anisotropy $\varepsilon'_\parallel - \varepsilon'_\perp$ only slightly reduces in going from N towards the N_{TB} phase.

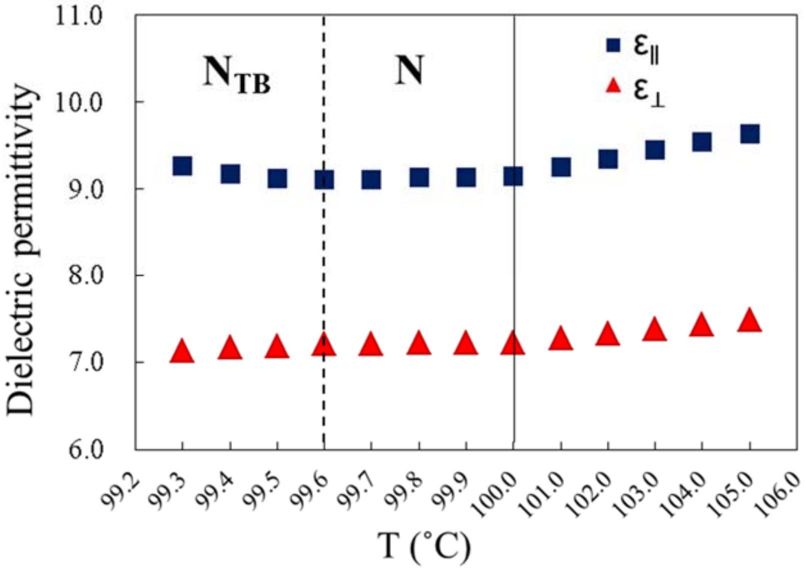

Fig 11. Dielectric permittivity for N and N_{TB} phases of CBC7CB. Reproduced with permission from Yun et al [46]. See the dielectric anisotropy, $\varepsilon_{\parallel} - \varepsilon_{\perp}$, is positive and the change from the N to the N_{TB} phase is insignificant in both N and N_{TB} phases as for CBC11CB in Fig. 10.

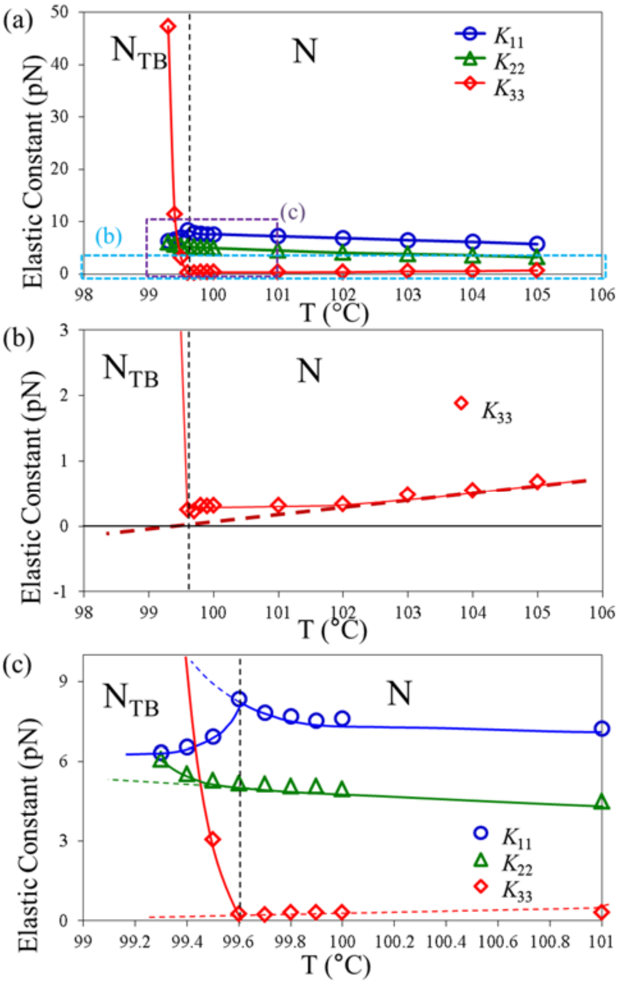

Fig. 12. The elastic constants as a function of temperature for CBC7CB. Reproduced with permission from Yun et al [46].

The important outcome of this work is that Dozov's hypothesis is satisfied in the high temperature nematic phase. An interesting implication would be that T that the twist-bend structure is already forming in the N phase close to the N-N_{TB} as a pre-transitional phenomenon. This could explain the first order character of the N-N_{TB} transition. It is noted that for CBC11CB, K_{33} does not approach zero and a low transition enthalpy is observed , this could be rationalized as associated with a weak first-order transition for the N – NTB transition.

Dielectric anisotropy:
One of the surprising outcomes of the experimental results is that the dielectric anisotropy in the N_{TB} phase is positive and only slightly lower than in the N phase. For CBC7CB it is ~2.2 than in the N phase and for CBC11CB it is 3.3 times the value observed of that in the N phase ; the precise values depending on the temperature. These results imply that the distribution of conformers does not change significantly in going from the N to the N_{TB} phase. These results need to be revisited in greater detail in the future.

N_{TB} phase in other systems:
The N_{TB} phase has also been observed in many other systems recently: asymmetrical bent core [48], a bent-core liquid crystal trimer [49], in dimers with and without chiral dopant [50], in asymmetrical phenyl-benzoate bimesogens ranging from diemrs to trimers and oligomers.[51]. The chemical structures have recently been reviewed. [52] .

Conclusion

A brief account is given of the recent discovery of the twist bend nematic phase. The low temperature phase in bimesogens of cyanobiphenyls and difluoroterphenyls has been assigned to the twist-bend nematic phase using texture, DSC and X-rays. Periodic stripes parallel to the rubbing direction, with a periodicity of 2 times the cell thickness, have been observed from a planar rubbed cell containing these bimesogens. Chiral domains of relatively large size of opposite handedness were observed in this phase at zero external field, the structures made up of achiral liquid crystalline molecules. On applying a rather large electric field across a planarly aligned cell, chiral domains of opposite handedness are observed lying side by side and normal to the rubbing direction. Periodicity of these stripes is greater than the cell thickness. The electroclinic effect arising from flexoelectricity leads to faster switching which has experimentally been observed. The texture gives the signature of helicoidal structures. Freeze-fracture electron microscopy has found the helical pitch to be ~8 -10 nm.
These observations indicate that this phase is consistent with the model proposed by Dozov far a 'twist-bend nematic', structure in 2001. Quite surprisingly it has been found also that Dozov's hypothesis for the $K_{22} < K_{11}/2$ is satisfied in the high temperature nematic phase and for CBC7CB it was found that $K_{33} \rightarrow 0$ in the nematic phase. . This would suggest that the twist bend-nematic like assemblies are formed a pre-transitional phenomenon which persists in the N_{TB} phase..

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fig. 6 freeze fracture microscopy

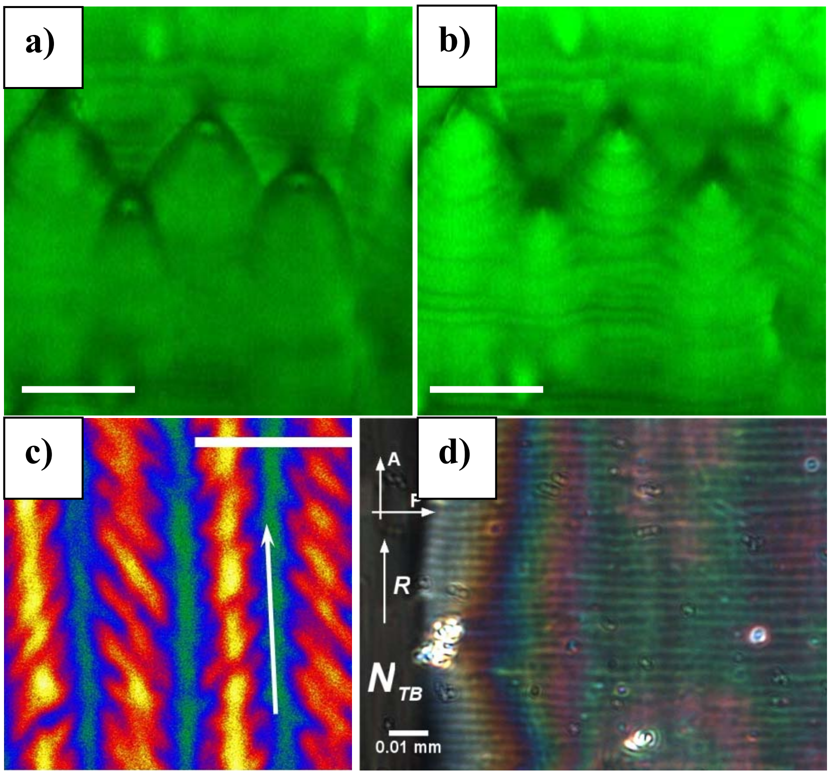

Figure 7. Patterns observed in planar cells. Rubbing direction vertical and parallel to the incident polarization. Scale bars are 0.01mm. a-b) Three-photon excitation fluorescence polarizing microscopy (3PEF-PM) images of focal-conic domains in 10 μm thick planar cell. Note pseudo-layered pattern formed normal to the rubbing direction.[26] c) Fluorescent confocal polarizing microscopy (FCPM) image of a 6 μm cell showing “rope-like” pattern intermediate in the hierarchy between the 8-nanometer twist-bend pitch and the self-deformation stripes determined by the cell gap. [39] d) Periodic texture at the N_{tb}-N interface in a 25 μm cell [41].

fig. 8pyroelectric coefficient

Figs 9 and 10 are given
Fig 11 Dielectric anisotropy
Fig12 Elastic constants.