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IN KRAKÓW

DOCTORAL THESIS

**Models of nematic phases formed
by bent-shaped molecules**

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Faculty of Physics, Astronomy and Applied Computer Science

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Oświadczenie

Ja niżej podpisany Wojciech Tomczyk (nr indeksu: 1053232) doktorant Wydziału Fizyki, Astronomii i Informatyki Stosowanej Uniwersytetu Jagiellońskiego oświadczam, że przedłożona przeze mnie rozprawa doktorska pt. „Models of nematic phases formed by bent-shaped molecules” jest oryginalna i przedstawia wyniki badań wykonanych przeze mnie osobiście, pod kierunkiem prof. dr hab. Lecha Longi. Pracę napisałem samodzielnie.

Oświadczam, że moja rozprawa doktorska została opracowana zgodnie z Ustawą o prawie autorskim i prawach pokrewnych z dnia 4 lutego 1994 r. (Dziennik Ustaw 1994 nr 24 poz. 83 wraz z późniejszymi zmianami).

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Kraków, dnia 12 sierpnia 2020 r.

podpis doktoranta

The most exciting phrase to hear in science, the one that heralds new discoveries, is not “Eureka!” (I found it!) but “That’s funny. . . ”

– Isaac Asimov

“Quote of the day”, source code of the “Fortune” computer program (June 1987)

Geometry, which should only obey Physics, when united with it sometimes commands it.

– Jean le Rond d’Alembert

Essai d’une nouvelle théorie de la résistance des fluides (1752)

JAGIELLONIAN UNIVERSITY IN KRAKÓW

Abstract

Faculty of Physics, Astronomy and Applied Computer Science
Department of Statistical Physics

Doctor of Philosophy

Models of nematic phases formed by bent-shaped molecules

by Wojciech TOMCZYK

The research topic undertaken within the framework of this PhD thesis, concerns the theoretical description of the newly discovered twist-bend nematic phase (N_{TB}), which chiral (heliconical) structure is formed by achiral molecules. It is a unique example of spontaneous chiral symmetry breaking in a liquid state with no support from long-range spatial ordering. Additionally, N_{TB} is distinguished by one of the shortest helix periods of all chiral liquid crystal structures, just a few nanometers. Based on the theories of Maier-Saupe and Landau-de Gennes, generalized models were built with the use of tensorial order parameter $\mathbf{Q}$ in a classical form and by means of the so-called “helicity modes” expansion. Thanks to these generalized models, it was possible to answer a number of questions about the nature of the formation of N_{TB} . Namely, i.a. how does the symmetry of the arms and the opening angle of the molecules forming N_{TB} its stability, what will happen when chiral molecules are added to the system with stable N_{TB} , and is flexopolarization a legitimate mechanism to explain experimental results obtained for N_{TB} ?

JAGIELLONIAN UNIVERSITY IN KRAKÓW

Abstrakt

Faculty of Physics, Astronomy and Applied Computer Science
Department of Statistical Physics

Doctor of Philosophy

**Models of nematic phases formed
by bent-shaped molecules**

by Wojciech TOMCZYK

Podjęta tematyka badawcza, w ramach niniejszej pracy doktorskiej, dotyczy opisu teoretycznego nowo odkrytej fazy nematycznej “twist-bend” (N_{TB}), której chiralna (helikonikalna) struktura formowana jest przez achiralne molekuły. Jest to unikatowy przykład spontanicznego łamania symetrii chiralnej w fazie ciekłej bez wsparcia dalekozasięgowego porządku. Dodatkowo, N_{TB} wyróżnia się jednym z najkrótszych okresów helisy ze wszystkich chiralnych struktur ciekłokrystalicznych, zaledwie kilka nanometrów. W oparciu o teorie Maiera-Saupe i Landau’a-de Gennesa zbudowano uogólnione modele z zastosowaniem tensorowego parameteru porządku $\mathbf{Q}$ w ujęciu klasycznym oraz w rozwinięciu w tzw. “helicity modes”. Dzięki tym uogólnionym modelom możliwe było udzielenie odpowiedzi na szereg pytań dotyczących istoty formowania się N_{TB} . Mianowicie, m.in. jaki wpływ ma symetria ramion i kąt rozwarcia molekuł tworzących fazę N_{TB} na jej stabilność, co się stanie gdy do układu ze stabilną fazą N_{TB} doda się molekuły chiralne, oraz czy fleksopolaryzacja jest mechanizmem za pomocą którego można wytłumaczyć wyniki eksperymentalne uzyskane dla N_{TB} ?

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First and foremost I would like to thank my supervisor **Prof. Lech Longa** for being my mentor and support, to whom I owe many things that I have learned and accomplished during my PhD studies. Countless hours spent on resolving problems during group meetings and afterward, thousands of exchanged emails, dozens of phone calls regardless of time and location, marked path to the place where I am now. I am boundlessly grateful for his patience and his belief in me. It is an honor and privilege to learn from him and grasp even a little bit from his vast scientific knowledge, alongside his insightful thoughts about life. Thanks to his efforts and guidance I could see what does it take to be a “full-blooded” theoretical physicist.

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Dedicated to my Family

Preface

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1.1 Thesis objectives

From the very beginning the collection of liquid crystalline phases expands by a wealth of unique phases. Year before this PhD project was initiated, the existence of a novel nematic phase has been unequivocally confirmed. That latest addition to nematic family is the so-called “twist-bend” nematic (N_{TB}) phase, which forms through the unique phenomenon of spontaneous chiral symmetry breaking in a system of achiral bent-core molecules. To the set of uncommon properties of this phase, one can add: heliconal structure of a nanoscale pitch without long-range positional order of molecules and a degenerate sign of the chirality (ambidextrous chirality).

In spite of its importance, the mechanisms correlating chirality at molecular-, nanoscale- and macroscopic levels are not yet understood. Therefore, there is a need for new concepts and theoretical strategies, which will enhance the comprehension of chiral self-assembly being one of the greatest challenges in the modern physics of liquid crystals. This thesis is a contribution to tackle this issue by investigating the relationship between molecular structure, symmetry and local self-assembly that can stabilize macroscopically organized chiral fluids. In particular we give answers to the following three major questions:

- How can a change in molecular structure affect the relative stability and structural properties of the twist-bend nematic phase?
- How structural chirality of the twist-bend nematic phase can respond to the presence of molecular chirality, with later being introduced through chiral centers incorporated in the molecules or chiral dopants?
- Is the flexopolarization mechanism, claimed to be responsible for the emergence of twist-bend nematic phase, capable of accounting quantitatively for experimental data known to date?

1.2 Thesis outline

This PhD thesis consists of five chapters. Chapter 1 presents scope of the thesis and its composition. Chapter 2 provides compact knowledge about liquid crystals and relevant structures with reference to this thesis. Chapter 3 introduces essential theoretical framework for studying liquid crystalline systems. Chapter 4 starts with a synopsis encompassing results presented in the following original, peer-reviewed contributions:

1. W. Tomczyk, G. Pająk and L. Longa
“Twist-bend nematic phases of bent-shaped biaxial molecules”
Soft Matter 12, 7445 (2016)
2. L. Longa and W. Tomczyk
“Twist-bend nematic phase in the presence of molecular chirality”
Liquid Crystals 45, 2074 (2018)
3. W. Tomczyk and L. Longa
“Role of molecular bend angle and biaxiality in the stabilization of the twist-bend nematic phase”
Soft Matter 16, 4350 (2020)
4. L. Longa and W. Tomczyk
“Twist-bend nematic phase from Landau-de Gennes perspective”
The Journal of Physical Chemistry C - under review
ArXiv: 2005.02455

Chapter 5 briefly summarizes the conclusions drawn from the study and provides perspectives for future works.

Liquid crystals

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2.1 Introduction

Soft matter physics encompass materials that are easily deformed by thermal fluctuations and external forces, like for example liquid crystals [1]. Undoubtedly the terms “crystal” and “liquid” are mutually exclusive, but it turns out that their merge perfectly reflects the uniqueness of the material to which it refers.

The name “liquid crystal” (LC) was coined in the late 1880s by Lehmann [2] in the wake of the experimental observations made by Reinitzer [3] regarding the thermal behavior of cholesteryl benzoate. Namely, Reinitzer noticed a peculiar phenomenon based on the occurrence of “two melting points”, which separated three phases. The lower temperature was the boundary between the solid and the new phase, which was a cloudy and viscous liquid and the higher one determined the moment in which the new phase changed into the isotropic liquid. In no time, it turned out that this new intermediate phase (mesophase¹) binds properties of both: solids and liquids. It manifests through that LCs can flow like liquids (they retain ordinary rheological properties), which is the result of no restrictions on translational degrees of freedom of molecules, and exhibit the crystal-specific anisotropy of physical properties, which arises from the long-range orientational ordering of the molecules. For comparison, in a crystalline solid the molecules are uniformly arranged in a lattice structure (translational order) and their orientations are fixed throughout the sample (orientational order). On the other hand, we have isotropic liquid where neither translational nor orientational order is retained: the molecules are randomly distributed in sample and have random orientations.

One of the key factors driving the formation of liquid crystalline mesophases is the anisotropic² structure of constituent molecules (mesogens). This structural condition can be realized on many ways, i.a. through

¹ *Meso* comes from the Greek word μέσος which means “middle”.

² It is not a general rule as there are anisotropic molecules, which do not form liquid crystals (see e.g. [4]).

conventional shapes like rods, bricks or discs and also non-conventional like pyramids, cones or bananas (Fig. 2.1). Nevertheless, those shapes still do not empty the pool of possibilities. Anyhow, we will focus our attention on the bent-core and dimeric molecules.

Generally “bent-core”³ (BC) molecules are made up of a rigid core unit, like phenyl or oxadiazole, that is terminated by long, flexible chains on both sides of the core (Fig. 2.2). The history of BC mesogens dates back to 1930s, where the first compounds were synthesized by Vorländer and Apel [5]. However, at that time, they have not attracted much attention. This changed after the works by Matsunaga *et al.* [6, 7] and Niori *et al.* [8] in the 90s of the XX-th century. BC molecules kindled a worldwide interest due to the number of unique properties arising from the combination of polarity and chirality. Among them can be distinguished the ability to form polar mesophases, emergence of supramolecular chirality out of achiral molecules and astonishing optical, ferroelectric and antiferroelectric responses [9]. BC molecules can form mesophases associated with calamitic (rod-like) LCs, like nematic or chiral nematic phase [10]. Although, what is interesting, there is a set of mesophases that are exclusively formed by BC mesogens and they are called “B” phases [11]. In the context of BC mesogens, it is also worth mentioning their “reverse” counterpart, in the sense of molecular structure, a dimer (bimesogen). It consists of two rigid units, commonly built of cyclic groups, which are connected via a flexible spacer (e.g. methylene or ether units), Fig. 2.2.

Liquid crystals can be classified, according to the source behind the formation of the mesophases, into lyotropic and thermotropic [12]. First group, lyotropic liquid crystals, emerge when amphiphilic mesogens, composed of a flexible hydrophobic chain and a polar head group (ionic or nonionic), are dissolved in a suitable solvent at an appropriate temperature, pressure, and concentration. The second group are thermotropic liquid crystals, where the existence of mesophase is exclusively controlled by temperature and the composition of the forming material is not changing with temperature. Interestingly, we can also distinguish materials that show both thermotropic and lyotropic liquid crystalline behavior and they are called amphotropic [13].

Nowadays, many distinct liquid crystalline phases are known and their distinguishability is based on the symmetry arguments concerning the dimensionality of positional order and the orientational number of axes. Interested Readers are referred to [14–16] as here we will narrow the discussion to the solely relevant (thermotropic) liquid crystalline phases with respect to the scope of thesis, namely: nematic, cholesteric and twist-bend nematic. Their structural features will be explored in the following Subsections.

³ In the literature bent-core molecules are alternately described by different terms, i.a. banana-shaped, bent-shaped, bow-shaped or V-shaped. Thus, for the sake of clarity, through this thesis, phrases like “bent-shaped”, “V-shaped” and “bent-core” will be used jointly for molecules having bent-molecular structure, which applies also to dimeric mesogens.

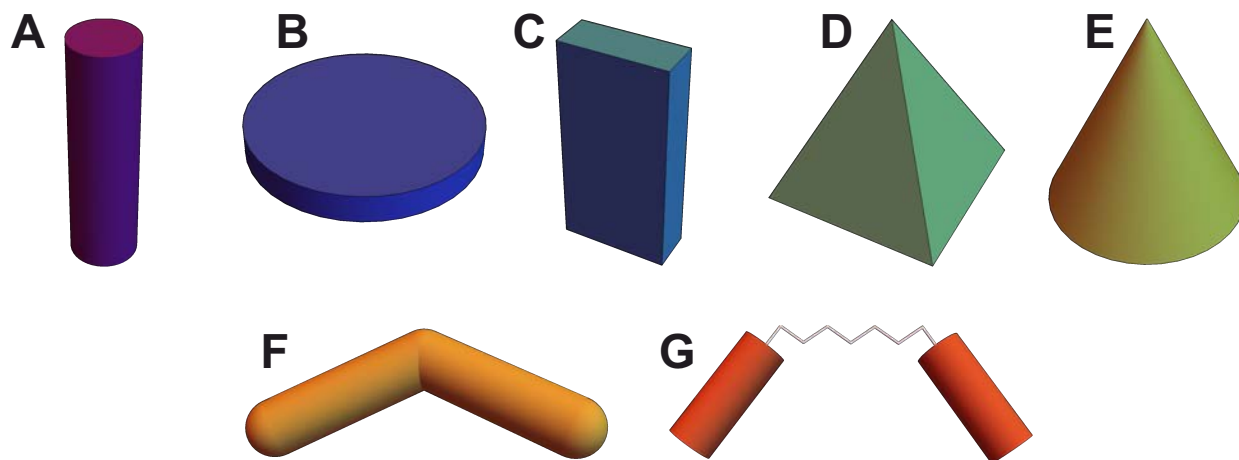


FIGURE 2.1: Exemplary shapes of mesogens that are conducive to exhibit a liquid crystalline phase: (A) rod-like (calamitic), (B) disc-like (discotic), (C) brick-like, (D) pyramid-like, (E) cone-like, (F) banana-like (bent-core) and (G) dimeric. For relevant molecular structures see [17].

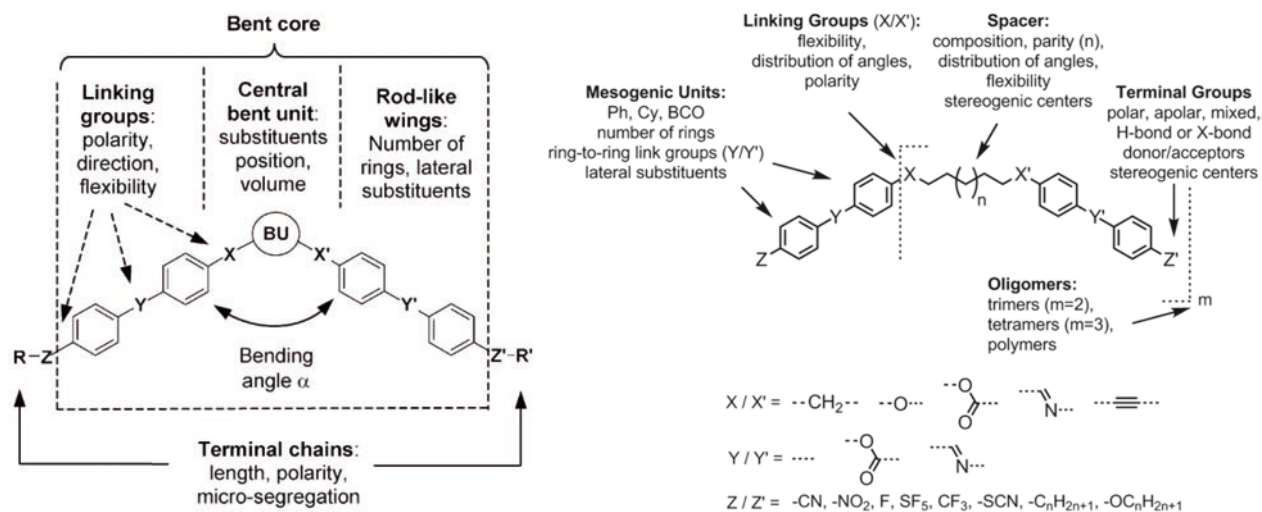


FIGURE 2.2: (Left panel) General structure of bent-core molecule. (Right panel) General structure of dimeric molecule. Left panel: reprinted with permission from [11] - Published by The Royal Society of Chemistry. Right panel: reprinted with permission from [18] - Published by The Royal Society of Chemistry.

2.1.1 Nematic

The nematic phase (N) is one of the most common and the simplest among liquid crystalline phases. It is characterized by its long range orientational order and absence of translational order. The molecules prefer to orient with their longest axes approximately parallel as shown in Fig. 2.3, which results in a uniaxial and cylindrically symmetric mesophase (point group $D_{\infty h}$). The direction, on average, in which the molecules point is the salient aspect of liquid crystalline phase and is a result of spontaneous orientational symmetry breaking upon cooling from the isotropic phase. For this moment, let us state that aforementioned, statistically preferred orientation is specified by a headless unit vector $\hat{n}$ ($|\hat{n}| = 1$), with head-tail symmetry⁴, called the director. Its fundamental meaning will be explained in detail in Section 3.1.

Two types of uniaxial nematics can be distinguished [19]: one of them is formed from prolate-like molecules (N_{U+}). In this case global symmetry axis ($\hat{n}$) is associated with the long axis of the molecule. Molecules that are oblate (disc) in shape yield the N_{U-} phase. Here, the molecular axis of symmetry is perpendicular to the face of the disc. Both, N_{U+} and N_{U-} are of the $D_{\infty h}$ point group symmetry.

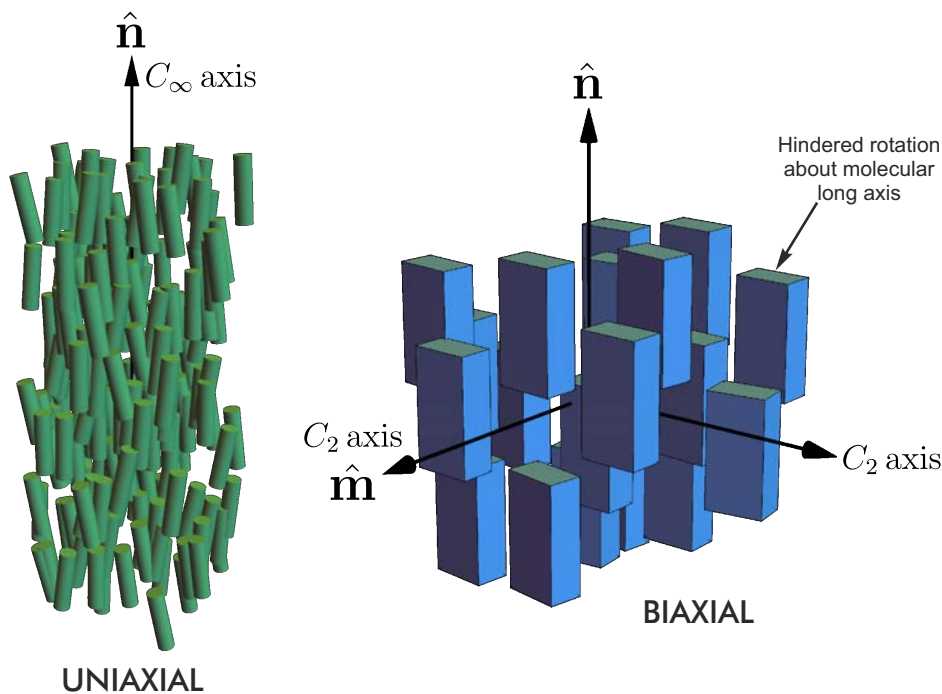


FIGURE 2.3: Schematic representation of uniaxial and biaxial nematic phases.

Nematic phase can also possess a biaxial symmetry (point group D_{2h}), which is characterized by two axes of symmetry, one main axis of symmetry $\hat{n}$ and second symmetry axis $\hat{m} \perp \hat{n}$ ($|\hat{m}| = 1$), locally invariant and with head-tail symmetry (Fig. 2.3). Thus, the parallel alignment tendency can be attributed to molecular brick-shaped (matchbox) or bent-shaped symmetries⁵, where all the molecules tend to align along both the long and short axes. Due to overall lack of polarity of the biaxial nematic (N_B) one can find that $\hat{l} = -\hat{l}$

⁴ The head-tail symmetry of $\hat{n}$ reflects the apolar nature of the nematic liquid crystal.

⁵ It is worth noting that phase symmetry does not have to be a direct result of the symmetry of individual molecules.

($\hat{\mathbf{l}} = \hat{\mathbf{n}} \times \hat{\mathbf{m}}$), $\hat{\mathbf{m}} = -\hat{\mathbf{m}}$ and $\hat{\mathbf{n}} = -\hat{\mathbf{n}}$. Up to now the biaxial nematic phase has been identified unequivocally in lyotropic LC systems [20]. On the other hand it is possible to artificially induce biaxiality by breaking the cylindrical and head-tail symmetry. It can be done for example by subjecting uniaxial nematic phase to external factors, like surface or electric field [21]. Breaking one (or more) of the symmetries of the N phase (e.g. mirror symmetry, uniaxiality, a-polarity) can lead to a variety of other nematic phases, like chiral nematic or twist-bend nematic.

2.1.2 Chiral nematic (cholesteric)

Chirality (gr.: $\chi\epsilon\iota\rho$ (cheir), hand), which means handedness, is a notion inherently bonded with symmetry [22]. In 1884 Sir William Thomson, Lord Kelvin of Largs defined the chirality as:

“I call any geometrical figure, or group of points, *chiral*, and say it has chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself [23].”

In other words, any chiral object, ranging from nano- to macro-scale item, cannot be transformed into its mirror image by proper rotations and/or translations, as it lacks an internal plane of symmetry and inversion center. If it is otherwise, then we call such object achiral (Fig. 2.4). Some organic compounds are chiral on the molecular level, because they contain i.e. a carbon atom that has four different functional groups attached to it in a quasi-tetrahedral structure (Fig. 2.5). Chiral molecules can be identified as having either left-handed (denoted by S for “Sinister”) or right-handed (denoted by R for “Rectus”) cores, and it is very common for one molecule to form either handedness [24]. The manifestation of left and right-handedness is also present on a macro scale i.a. in creeping plants (Fig. 2.6). Molecules that are mirror images but are not superimposable are called enantiomers, whereas the molecules that have the same molecular arrangement but differ in spatial orientation are known as stereoisomers.

Chirality is an universal property that spans through many length scales [25, 26] and its presence or lack has tremendous impact on materials (see i.e. [27]) and life itself (see i.e. [28]). Especially, chirality plays a key role in formation of many unique liquid crystalline phases [29], among which is a chiral analogue of nematic phase.



FIGURE 2.4: Simple and intuitive grasp of difference between achiral (non-chiral) and chiral objects in two dimensions. The mirror image of “A” requires no rotation to be superimposed on its original (achiral), whereas the mirror image of “Z” can never be superimposed over its original. Although, in three dimensions “Z” is non-chiral.

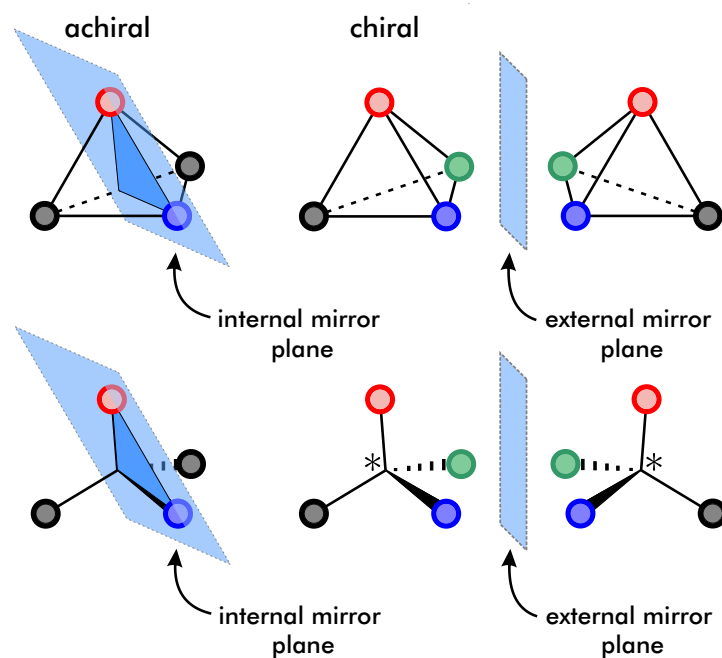


FIGURE 2.5: Chirality in 3-D with a regular tetrahedron (top) and tetrahedral atoms (bottom). Each atom that carries four different substituents in a tetrahedral arrangement is a chirality center (denoted by an asterisk). Adapted with permission from [30]. Copyright 2020 American Chemical Society.



FIGURE 2.6: Example of handedness in nature: Chinese wisteria (A) ascends up to the right (clockwise from the ground, right-handed), whereas Japanese wisteria (B) ascends up to the left (counter-clockwise from the ground, left-handed). Photo: (A) Chris Evans, University of Illinois, Bugwood.org; (B) Michael Ellis, M-NCPPC.

The chiral nematic phase (N^*), also known as cholesteric⁶ (Ch), is formed by chiral molecules or in mixtures of the latter with ordinary nematogenic compounds [31, 32]. This phase is locally equivalent to nematic⁷ but not globally, because chiral intermolecular interaction leads to the emergence of supramolecular helicoidal structure. Therefore, chiral nematic can be perceived as a pile of nematic “quasi-layers” with director $\hat{n}$ slightly rotated between consecutive adjacent layers along the helical axis (Fig. 2.7). Assuming that helical axis coincides with z -axis then, the director in chiral nematic phase is given by:

$$\hat{n} = [\cos(kz), \sin(kz), 0], \quad (2.1)$$

where $k = 2\pi/p$ is the helical wave vector and p is pitch⁸. For a positive p , the pitch of the helix is right-handed, and a negative p gives a left-handed helical pitch. Another effect resulting from inclusion of chirality into nematic structure is lowering nematic’s point group symmetry from $D_{\infty h}$ to D_{∞} (symmetry of a twisted cylinder). What is more, the magnitude of chirality in the nematic system can be controlled [38, 39], meaning that it is possible to amplify or weaken it. The first scenario (amplification) can give rise to the frustration in the system, which over some threshold point results in i.a. the emergence of so-called blue phases (BP) [40]. The second scenario (weakening) can lead to the macroscopic removal of chirality, whereas mesogens are still chiral. For example, it can be done by mixing two enantiomers (racemic mixture), each forming a chiral nematic phase, and as an outcome, a conventional nematic phase with no twist is acquired. It happens so because opposite chiralities cancel out [41].

For many years it was a well-established paradigm that macroscopic chirality is a consequence of molecules being chiral (for review see [42, 43]). However, it was meant to change, when it turned out that achiral molecules can also organize into chiral liquid crystalline phases [9, 44]. As a result novel liquid crystalline phases were discovered and among them was a twist-bend nematic, which is a leitmotif of this thesis.

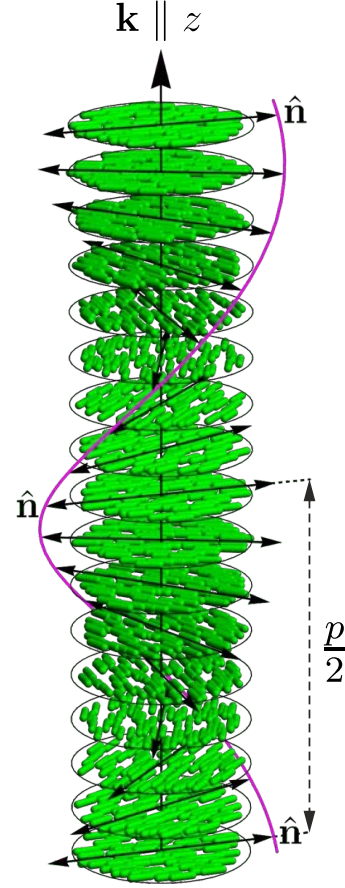


FIGURE 2.7: Schematic representation of chiral nematic phase. Due to the condition $\hat{n} = -\hat{n}$ the “proper” periodicity of the structure is $p/2$, which is equivalent to 180° rotation of $\hat{n}$ around z .

⁶ The first observations of chirality in liquid crystals were in cholesteryl derivatives.

⁷ If we consider the chiralization of a uniaxial nematic, it has to be emphasized that the formation of a helix induces small local biaxiality [33]. However, far more profound conclusions can be drawn, i.a. emergence of heliconical structures (“progenitors” of twist-bend nematic phase), when the chiralization of biaxial nematic is considered [34–36].

⁸ The typical value of chiral nematic’s pitch length is in the range of hundreds of nanometers, although it can be altered accordingly [37].

2.1.3 Twist–bend nematic

Spontaneous symmetry breaking (SSB) is a phenomenon that occurs when physical system in an initially symmetric state ends up in an asymmetric state, despite that the underlying dynamic equations are still invariant under a symmetry transformation [45]. SSB is one of the cornerstones of modern physics with broad domain of application [46].

At the theoretical level a possibility of spontaneous chiral symmetry breaking (SCSB) in bent-shaped mesogens has been suggested by Meyer in 1973 [47]. He pointed out that bend deformations, which should be favored by bent-shaped molecules, might lead to flexopolarization–induced chiral structures. This idea was later on retaken by Dozov [48], where he considered the Oseen-Zocher-Frank⁹ free energy of the director field $\hat{\mathbf{n}}$. He correlated a possibility of SCSB in nematics with the sign change of the bend elastic constant (K_{33}). In this latter case, in order to guarantee the existence of a stable ground state, some higher order elastic terms had to be added to the free energy expansion. Limiting to defect-free structures, Dozov predicted competition between a twist-bend nematic phase, where the director simultaneously twists and bends in space by precessing on the side of either a right or left circular cone and a planar splay-bend phase with alternating domains of splay and bend, both shown in Fig. 2.8. If we take into account temperature dependence of the Frank elastic constants then the uniaxial nematic phase becomes unstable relative to the formation of modulated structures at $K_{33} = 0$, which is the critical point of the model. The behavior of the system depends on the relationship between the splay (K_{11}) and twist (K_{22}) elastic constants. As it turns out the twist-bend ordering prevails if $K_{11} > 2K_{22}$, while the splay-bend phase is more stable if $K_{11} < 2K_{22}$.

Assuming that the wave vector $\mathbf{k}$ of N_{TB} stays parallel to the z -axis of the laboratory reference frame ($\mathbf{k} = k\hat{\mathbf{z}}$), the symmetry-dictated, features of the heliconical N_{TB} structure are essentially accounted for by the uniform director modulation

$$\hat{\mathbf{n}}(\tilde{z}) = \mathcal{R}_{\hat{\mathbf{z}}}(\phi)\hat{\mathbf{n}}(0) = [\cos(\phi)\sin(\theta), \sin(\phi)\sin(\theta), \cos(\theta)], \quad (2.2)$$

where $\hat{\mathbf{n}}(0) = [\sin(\theta), 0, \cos(\theta)]$ and where $\mathcal{R}_{\hat{\mathbf{z}}}(\phi) \equiv \mathcal{R}_{\hat{\mathbf{z}}}(\phi(z))$ is the homogeneous rotation about $\hat{\mathbf{z}}$ through the azimuthal angle $\phi(z) = \pm kz = \pm 2\pi z/p$ and where p is the pitch. The $\pm$ sign indicates that both left- and right-handed chiral domains should form with the same probability (ambidextrous chirality), which is the direct manifestation of a SCSB in the bulk. Note that the molecules in N_{TB} are inclined, on the average, from $\mathbf{k}$ by the conical angle θ - the angle between $\hat{\mathbf{n}}$ and the wave vector $\mathbf{k}$ (Fig. 2.8). One should notice that Eq. (2.2) describes also nematic phase under assumption $k = 0 \wedge \theta = 0$ and chiral nematic phase for $k \neq 0 \wedge \theta = \pi/2$.

The symmetry of N_{TB} implies that the structure must be locally polar with the polarization vector $\mathbf{P}$ staying perpendicular both to the director and the wave vector

$$\mathbf{P}(z) = \mathcal{R}_{\hat{\mathbf{z}}}(\phi)\mathbf{P}(0) = \tilde{p}_0 [\sin(\phi), -\cos(\phi), 0], \quad (2.3)$$

⁹ This issue will be discussed more broadly in Subsection 3.4.2.

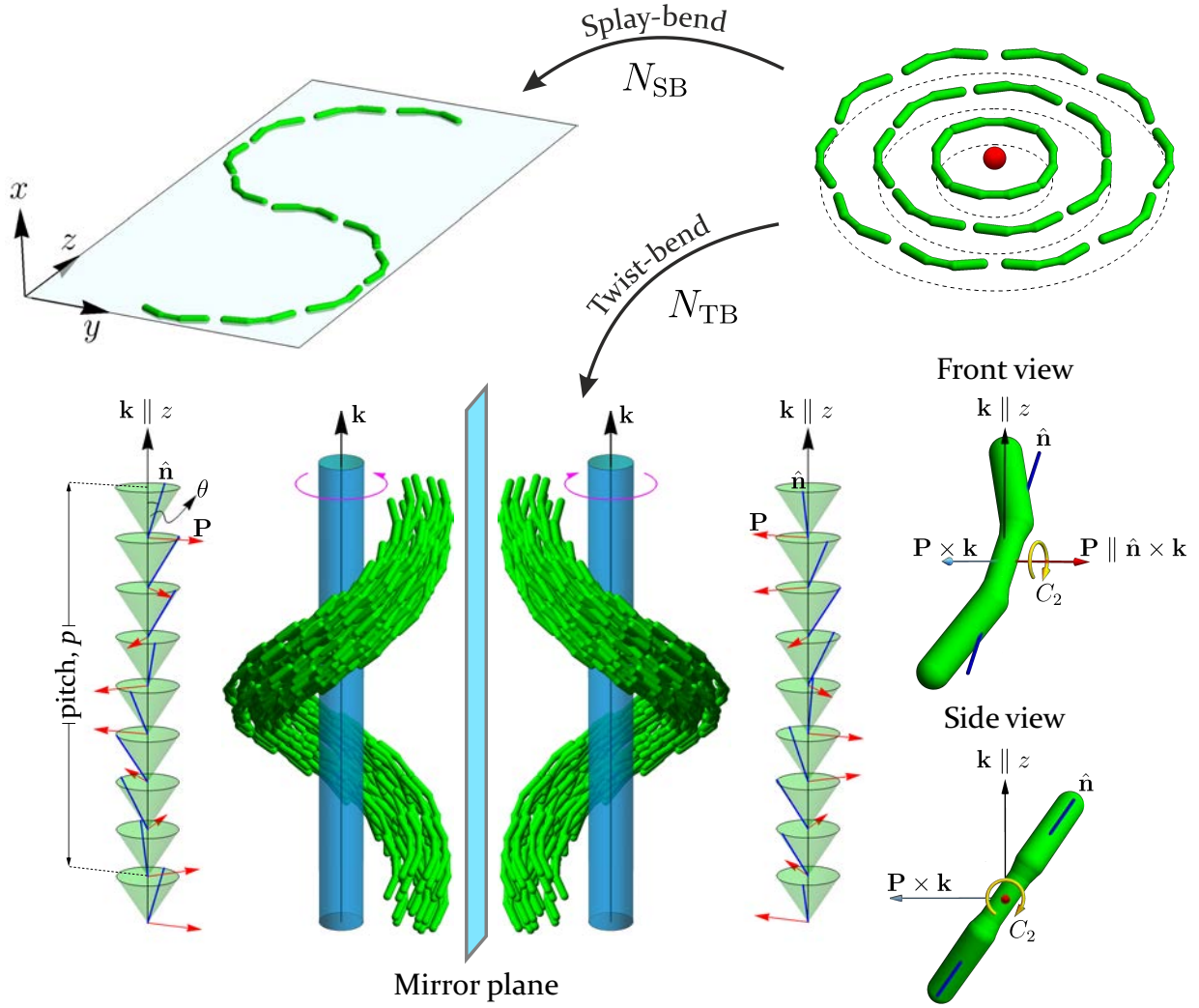


FIGURE 2.8: Pure bend distortion in 2D leads to the emergence of defects (red sphere). Their appearance can be circumvented by alternating the bend direction periodically or allowing nonzero twist by lifting bend into the third dimension. These possibilities, respectively, give rise to the two alternative nematic ground states: splay-bend (N_{SB}) and twist-bend (N_{TB}). Schematic representation of molecular organization in the N_{TB} with right and left handedness (ambidextrous chirality) has been depicted at the bottom of the image. Right/left circular cone of conical angle θ shows the tilt between the director $\hat{n}$ and the helical symmetry axis, parallel to the wave vector $\mathbf{k}$. Red arrow represents polarization $\mathbf{P}$, where $\mathbf{P} \parallel \hat{n} \times \mathbf{k}$. Note that N_{TB} has a local C_2 symmetry with a two-fold symmetry axis around $\mathbf{P}$.

where $\mathbf{P}(0) = [0, -1, 0]$. Hence, in the nematic twist-bend phase, both $\hat{\mathbf{n}}$ and $\mathbf{P}$ rotate along the helix direction $\mathbf{k}$ giving rise to a phase with constant bend and twist deformation of no mass density modulation (Fig. 2.8).

The important message that arose from Meyer's and Dozov's considerations was that the properly "bent" structures can facilitate the formation of novel liquid crystalline structures (Fig. 2.9). This concept perfectly matched at the time with the renewed interest with bent-shaped mesogens. As it was outlined in Section 2.1 bent-shaped molecules have attracted considerable attention not only for technological reasons [49] but also due to their unique mesogenic properties. A top of that, they were supposed to be perfect candidates to investigate in search for the elusive thermotropic biaxial nematic [9, 50], which for the scientists involved into research of liquid crystals become a "Holy Grail" of liquid crystalline science [51].

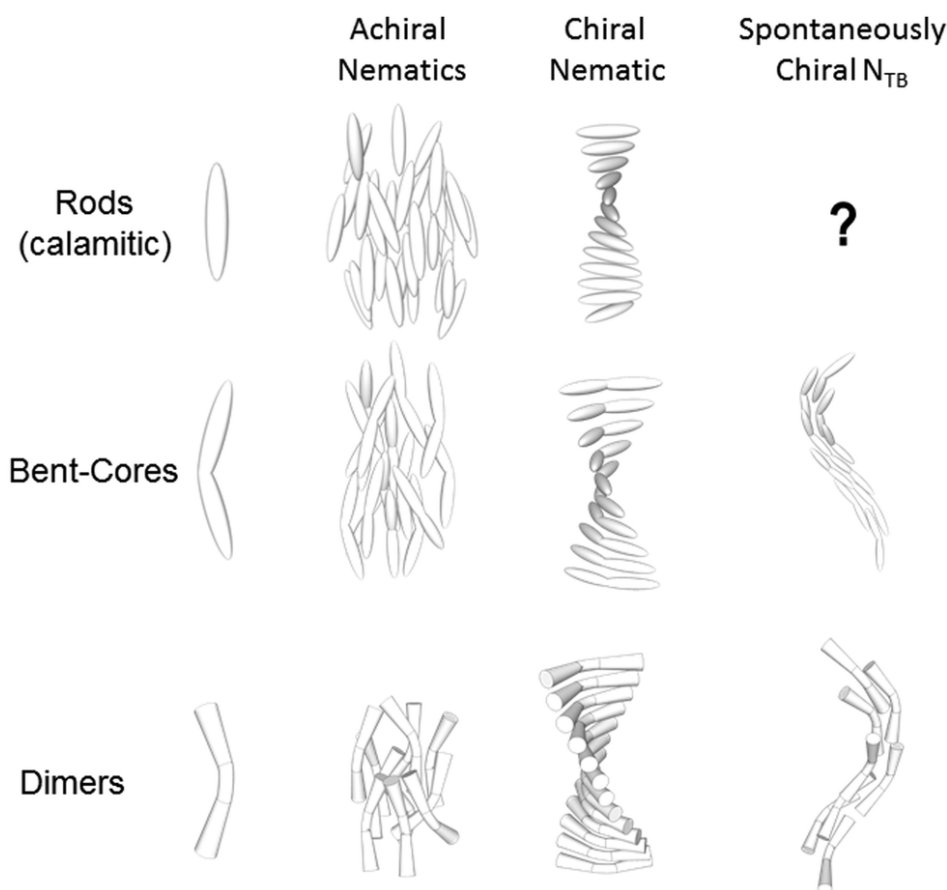


FIGURE 2.9: Comparison between general molecular structures of rod-like, bent-core and dimer liquid crystals along with a schematic depictions of the achiral nematic (N), chiral nematic (N^*) and spontaneously chiral N_{TB} mesophases formed by these general structures. Reprinted with permission from [18] - Published by The Royal Society of Chemistry.

In no time, it appeared that for one of dimeric compounds a nematic-nematic phase transition occurs [52]. The higher temperature nematic phase was attributed as uniaxial nematic, whereas the lower temperature was denoted as N_x . A milestone was set when for the first time the N_x in CB7CB compound was assigned to

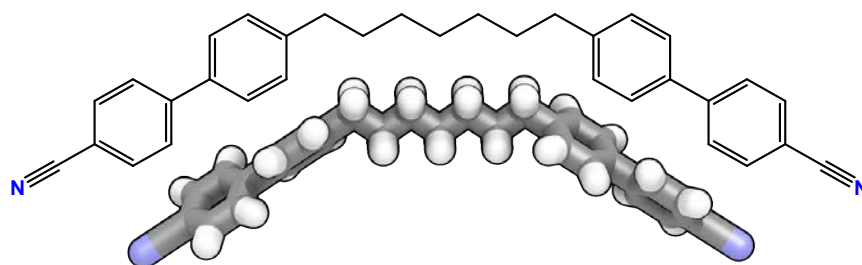


FIGURE 2.10: Chemical structure of CB7CB (1'',7''-bis(4-cyanobiphenyl-4'-yl)heptane) forming twist-bend nematic phase.

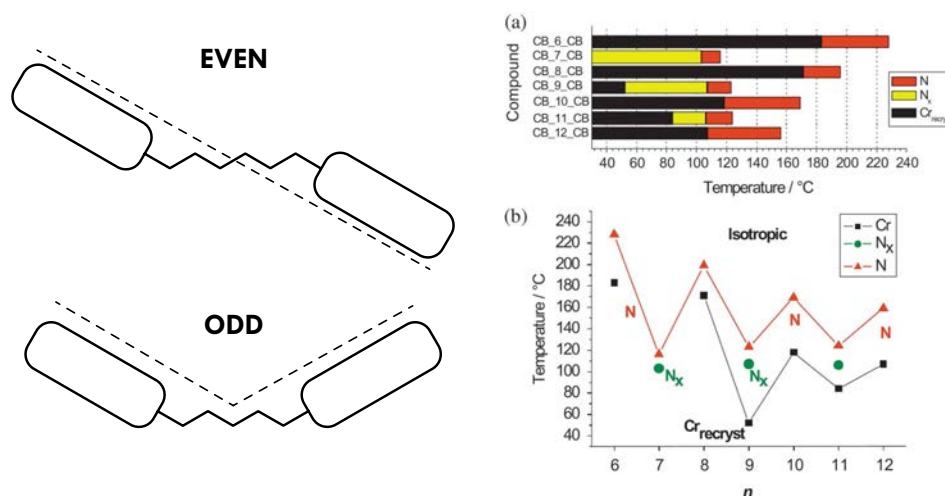


FIGURE 2.11: (Left panel) Schematic depiction of “odd-even” effect in dimers. (Right panel) The temperature ranges and phase sequences for CB_nCB series (top), along with the transition temperatures plotted as a function of the number of methylene units (n) in the flexible spacer (bottom). Right panel was reprinted with permission from [60] - Published by the Taylor & Francis.

be a twist-bend nematic phase [53], according to Dozov’s nomenclature. It was dictated by the observation of anomalous behavior of bend elastic constant and no density modulation (ergo no smectic layers). Onward, CB7CB was examined independently by Chen *et al.* [54] and Borshch *et al.* [55]. Their results established that indeed N_x formed by CB7CB molecules is a twist-bend nematic phase with a heliconal structure and nanoscale pitch. Nevertheless, what is interesting, the CB7CB compound was not novel at that period.

CB7CB is an abbreviation for 1'',7''-bis(4-cyanobiphenyl-4'-yl)heptane. This compound belongs to the 1, ω -bis(4-cyanobiphenyl-4'-yl) alkane homologous series, which is denoted by the acronym CB_nCB, where n refers to the number of methylene (CH₂) units in the flexible spacer. In other words, the CB7CB molecule consists of two 4-cyanobiphenyls (CB), which are linked by an alkylene spacer C₇H₁₄ (Fig. 2.10). Primarily the phase that preceded the nematic phase in many cyanobiphenyl-based [56–58] dimers was attributed to be a smectic phase. This probably arose from the ambiguity in the identification based on the texture observations under the polarizing optical microscope. As many bimesogenic compounds CB_nCB series exhibits the so-called “odd-even” effect (Fig. 2.11) [59].

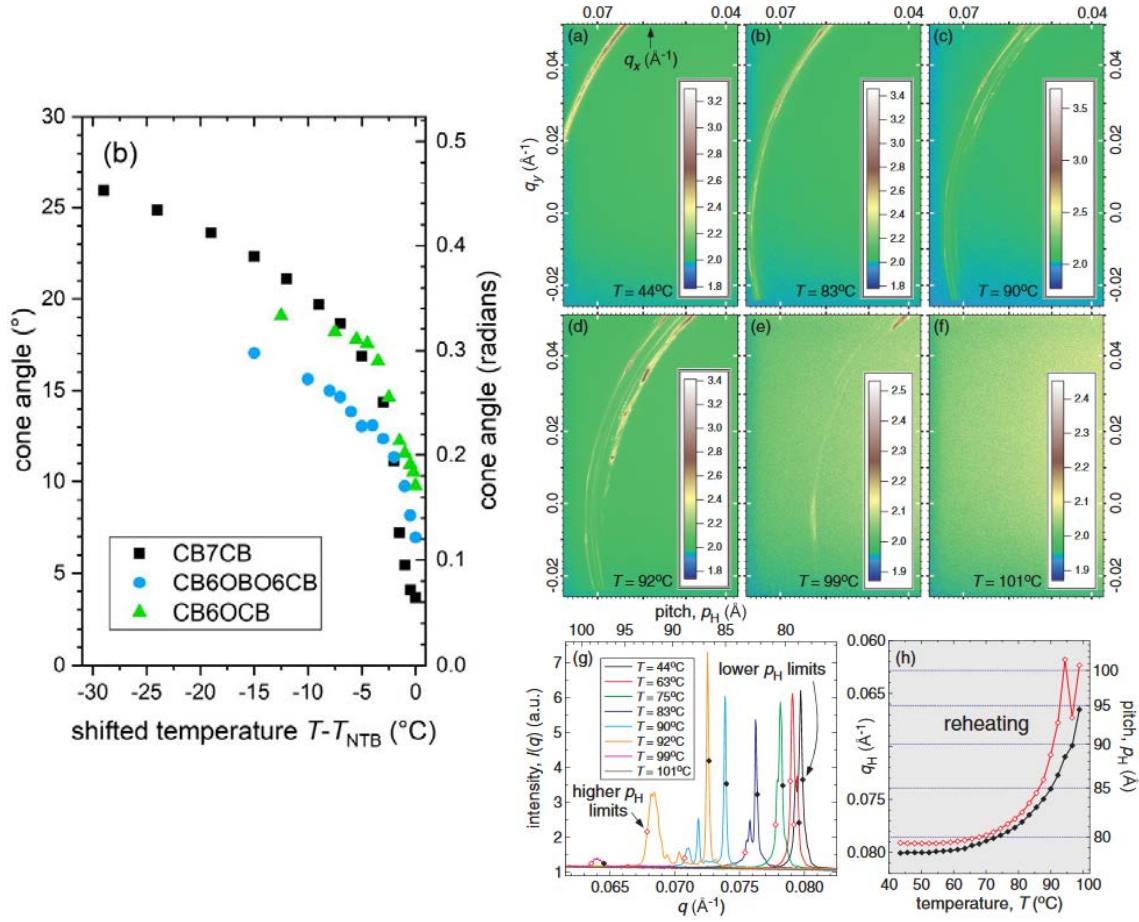


FIGURE 2.12: (Left panel) Based on the procedure developed by Meyer *et al.* [65], temperature behavior of calculated cone (tilt) angle θ from the birefringence measurements for CB6OCB, CB6OBO6CB and CB7CB. (Right panel) Temperature behavior of pitch (on reheating) in twist-bend nematic phase of CB7CB. Measurements were done by the means of resonant soft x-ray scattering (RSoXS) with incident x-ray photon energy at the carbon K edge ($E = 283.5\text{ eV}$). Left panel: reprinted with permission from [69] - Published by National Academy of Sciences. Right panel: reprinted with permission from [70] - Published by American Physical Society.

Since the discovery of the N_{TB} phase, there were made significant advances in understanding the nature of this structure [44, 61, 62]. It is now a well documented that the helix of N_{TB} is very short, only a few nanometers [54, 55, 63, 64], and the conical angle predominantly reaches the value between 20° and 40° [65–69], Fig. 2.12.

Nowadays, there are many classes of compounds, which are known to form the N_{TB} phase, e.g. bent-core LC [71], dimers [59], hybrid bent-core LC dimers [72] and trimers [73, 74], hydrogen-bonded oligomers [75], a duplexed hexamer [76], oligomers [77, 78] and polymers [79]. Moreover, many mixtures involving the compounds with N_{TB} have already found technological applications [80–82].

In the most common scenario N_{TB} is preceded (upon cooling) by nematic phase, however there are cases where N_{TB} can form directly from isotropic phase [83, 84]. Furthermore, both of those phase transitions are

weakly first order. It has been also found that a chiral analogue¹⁰ of twist-bend nematic phase (N_{TB}^*) can be formed by chiral molecules [85, 86] and in mixtures of achiral N_{TB} forming molecules with chiral additives [87–90]. The pitch of N_{TB}^* seems to be either slightly longer¹¹ [85] or comparable [90] to the pitch of its achiral counterpart (N_{TB}). Also astonishing is the fact that there are mixtures, where the N_{TB}^* is preceded (upon cooling) by blue phase [87, 89]. Further, on a wave of new data about N_{TB} , novel twist-bend-like phases were discovered, namely twist-bend smectic C (SmC_{TB}) [91] and twist-grain-boundary-twist-bend (TGB_{TB}) [92].

¹⁰ Miscibility studies [85] suggest that N_{TB}^* and N_{TB} are thermodynamically the same. Although, in N_{TB}^* the double degeneracy of the chiral domains (ambidextrous chirality) is removed and the favoured handedness (left or right) becomes more stable [86].

¹¹ In [85] the pitch of the N_{TB}^* was measured by atomic force microscope (AFM) and estimated to be 50 nm (10–15 molecular lengths), whereas for N_{TB} , formed by e.g. CB7CB molecules, the pitch is ca. 8 nm (3–4 molecular lengths) [54].

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Theoretical background

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3.1 Order parameter

Combination of a molecule's shape and way that molecules self-assemble leads to a vast range of distinct types of liquid crystals. Nevertheless, their common feature is the tendency of molecules to align along preferred direction represented by a unit vector $\hat{n}$ called the director. The degree of molecular order around $\hat{n}$ can be quantified by constructing microscopic (Section 3.1.1) and/or macroscopic (Section 3.1.2) order parameters.

3.1.1 Microscopic approach

Assuming a rigid-body models for LC molecules, a comprehensive information about the orientational order in the mesophase can be obtained from singlet distribution function $f(\Omega)$ [93], where Ω denotes the Euler angles (α, β, γ) that defines the molecular orientation of a rigid molecule through rotation $\mathbb{F}_{\text{LAB}} \xrightarrow{\Omega} \mathbb{F}_{\text{MOL}}$ from the laboratory frame $\mathbb{F}_{\text{LAB}}$ to the molecular frame $\mathbb{F}_{\text{MOL}}$. Additionally, for any single molecule property $X(\Omega)$ averaged over the orientations of all molecules we have [93]:

$$\langle X \rangle = \int_0^{2\pi} d\alpha \int_0^\pi \sin(\beta) d\beta \int_0^{2\pi} d\gamma X(\Omega) f(\Omega). \quad (3.1)$$

One of the commonly used approaches is based on expanding $f(\alpha, \beta, \gamma)$ in terms of basis set of Wigner rotation matrices¹, $D_{m,n}^L$, that are orthogonal² when integrated over $d\alpha \sin(\beta) d\beta d\gamma$, as follows [93, 95]:

$$f(\Omega) = \sum_{L=0}^{\infty} \sum_{m=-L}^L \sum_{n=-L}^L f_{m,n}^L D_{m,n}^L(\Omega) \quad (3.2)$$

where L, m, n are integers. By multiplying both sides of Eq. (3.2) by $D_{m,n}^{L*}(\Omega)$ and integrating we acquire the following equation from which the coefficients $f_{m,n}^L$ can be obtained using the orthogonality properties of the basis set of functions:

$$\iiint_{\Omega} f(\Omega) D_{m,n}^{L*}(\Omega) d\alpha \sin(\beta) d\beta d\gamma = \sum_{L=0}^{\infty} \sum_{m=-L}^L \sum_{n=-L}^L f_{m,n}^L \iiint_{\Omega} f(\Omega) D_{m,n}^L(\Omega) D_{m,n}^{L*}(\Omega) d\alpha \sin(\beta) d\beta d\gamma. \quad (3.3)$$

Substitution of these coefficients gives, for the case of a rigid molecule of arbitrary shape:

$$f(\alpha, \beta, \gamma) = \sum_{L=0}^{\infty} \sum_{m=-L}^L \sum_{n=-L}^L \frac{2L+1}{8\pi^2} \langle D_{m,n}^{L*}(\alpha, \beta, \gamma) \rangle D_{m,n}^L(\alpha, \beta, \gamma), \quad (3.4)$$

in which the coefficients $\langle D_{m,n}^{L*} \rangle$ represent the full set of the microscopic orientational order parameters.

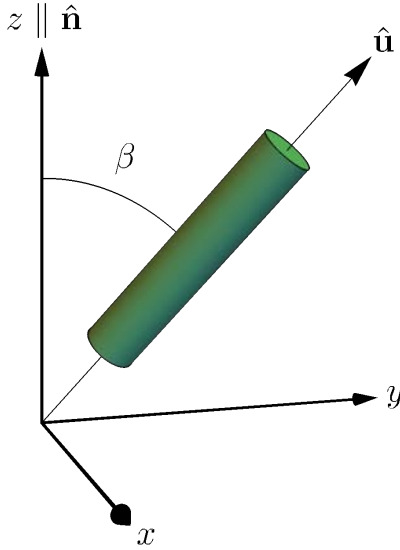


FIGURE 3.1: Relevant Euler angle that describe the orientational order of a uniaxial molecule in a uniaxial phase.

Eq. (3.4) can be simplified accordingly depending on the considered symmetry of both the mesophase and the molecules themselves. For example, if we take into account a uniaxial nematic phase composed of cylindrically symmetric molecules (Fig. 3.1) with the nematic director parallel to the z -axis, then $m = 0$, $n = 0$, and f depends solely on the angle β between the director and the long axis of molecule. Due to the symmetry in the plane perpendicular to the nematic director, only terms with even L can appear. As a result, it yields Eq. (3.4) in form

$$f(\beta) = \sum_{L \text{ even}}^{\infty} \frac{2L+1}{2} \langle D_{0,0}^{L*}(\beta) \rangle D_{0,0}^L(\beta). \quad (3.5)$$

The D -matrix elements where $n = 0$ are proportional to spherical harmonics and associated Legendre polynomials, thus Eq. (3.5) can be alternatively written as:

$$f(\beta) = \sum_{L \text{ even}}^{\infty} \frac{2L+1}{2} \langle P_L(\cos(\beta)) \rangle P_L(\cos(\beta)). \quad (3.6)$$

¹ These are irreducible representations of the rotation group $SO(3)$, which are called spherical tensors [94].

² Orthogonality: $\iiint_{\Omega} D_{m,n}^{L*}(\alpha, \beta, \gamma) D_{m',n'}^L(\alpha, \beta, \gamma) d\alpha \sin(\beta) d\beta d\gamma = \frac{8\pi^2}{2L+1} \delta_{L,L'} \delta_{m,m'} \delta_{n,n'}$, where δ is Kronecker delta.

Eq. (3.5) in its explicit form, up to $L = 4$, reads:

$$f(\beta) = \frac{1}{2} + \frac{5}{2} \langle D_{0,0}^2 \rangle D_{0,0}^2 + \frac{9}{2} \langle D_{0,0}^4 \rangle D_{0,0}^4 + \dots, \quad (3.7)$$

where the first three expansion coefficients are:

$$\begin{aligned} D_{0,0}^0(\beta) &= \langle D_{0,0}^0(\beta) \rangle = 1, \\ \langle D_{0,0}^2(\beta) \rangle &= \frac{1}{2} \langle 3 \cos^2(\beta) - 1 \rangle, \\ \langle D_{0,0}^4(\beta) \rangle &= \frac{1}{8} \langle 35 \cos^4(\beta) - 30 \cos^2(\beta) + 3 \rangle. \end{aligned} \quad (3.8)$$

On the basis of Eq. (3.7) and Eq. (3.8) one can see that the second coefficient is the first relevant term in the expansion. Thus, it can be used as the leading order parameter, often denoted as S , describing the degree of orientational order of the molecules around the average orientation:

$$S \equiv \langle D_{0,0}^2(\beta) \rangle = \langle P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}) \rangle = \langle P_2(\cos(\beta)) \rangle = \frac{1}{2} \langle 3 \cos^2(\beta) - 1 \rangle. \quad (3.9)$$

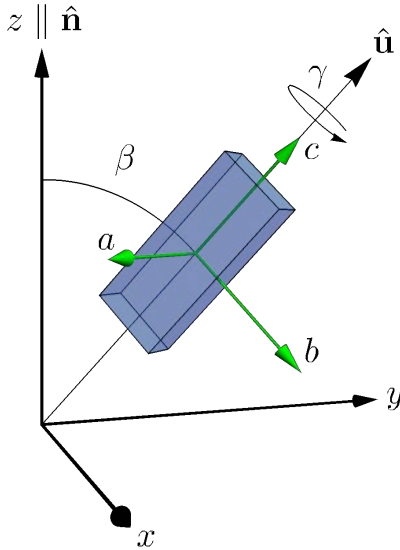


FIGURE 3.2: Relevant Euler angles that describe the orientational order of a biaxial molecule in a uniaxial phase.

From Eq. (3.9) it can be directly observed that $S \in [-1/2, 1]$ for $\beta \in [0, \pi/2]$. Perfect nematic alignment occurs when $S = 1$ ($\beta = 0$), $S = 0$ indicates the isotropic phase, whereas $S = -1/2$ characterizes the system where molecules lie (on average) perpendicular to the director ($\hat{\mathbf{u}} \perp \hat{\mathbf{n}}$). Such defined quantity can be measured by various experimental techniques [96–99] and as one would expect S is temperature-dependent (it increases with decreasing temperature). In case of a nematic phase the order parameter S lies in the range between 0.3 - 0.7 [12].

Up to this point, we have briefly discussed the example of uniaxial molecules in uniaxial phase, but to put things in a broader perspective, let us consider a different scenario. Assume that now the uniaxial phase is composed of non-cylindrical rigid molecules (e.g. prolate ellipsoid). Now, it is possible that other axes (short) of the molecules may exhibit the tendency to mutually align along with the molecule's long axis. Thus, the molecules can be perceived as systems with the D_{2h} point group symmetry (Fig. 3.2). As it was aforementioned, the phase is uniaxial, therefore the resulting orientational distribution function is independent of angle α :

$$f(\beta, \gamma) = \sum_{L=0}^{\infty} \sum_{n=-L}^L \frac{2L+1}{4\pi} \langle D_{0,n}^{L*}(\beta, \gamma) \rangle D_{0,n}^L(\beta, \gamma). \quad (3.10)$$

Molecule's D_{2h} symmetry [100] implies that a , b and c -axis, each respectively, coincide with the twofold rotational symmetry axis (C_2). As a result, we have additionally a system of three mutually perpendicular mirror planes indicated as $\sigma_{(ab)}$, $\sigma_{(ac)}$ and $\sigma_{(bc)}$, where the subscript shows which axes constitute the given plane [100]. Now, by taking into account these symmetry conditions and useful feature that spherical harmonics, under the same operation, are multiplied by $(-1)^L$ [93] we can limit ourselves to the sole analysis of Wigner matrices of even rank L . For brevity, we will write out exclusively a couple of them:

$$\begin{aligned} D_{0,0}^0 &= \langle D_{0,0}^0(\beta, \gamma) \rangle = 1, \\ \langle D_{0,0}^2(\beta, \gamma) \rangle &= \frac{1}{2} \langle 3 \cos^2(\beta) - 1 \rangle, \\ \langle D_{0,\pm 2}^2(\beta, \gamma) \rangle &= \sqrt{\frac{3}{8}} \sin^2(\beta) \exp(\mp i 2\gamma). \end{aligned} \quad (3.11)$$

As before, we have S order parameter as the first non-trivial term of the expansion with the difference that here we have an extra non-trivial contribution in the form of $\text{Re} \langle D_{0,2}^2(\beta, \gamma) \rangle$. This additional order parameter is conventionally denoted as D and it is a biaxiality parameter, which measures the ordering of minor molecular axes with respect to the major phase axis. In an identical manner, as in previous examples, one can expand the considerations on the situation when both the molecules and phase are biaxial or when the phase is biaxial and molecules are uniaxial [101].

Alternative approach, convenient i.a. in the description of biaxial systems [102–105], relies on the expansion of orientational distribution function into the set of D_{2h} symmetry-adapted functions $\Delta_{m,n}^L(\Omega)$ introduced by Mulder [106] and defined as:

$$\Delta_{m,n}^L(\Omega) = \left(\frac{\sqrt{2}}{2} \right)^{2+\delta_{m,0}+\delta_{n,0}} \sum_{\sigma, \sigma'=\{-1,1\}} D_{\sigma m, \sigma' n}^L(\Omega), \quad (3.12)$$

with L even, $0 \leq m, n \leq l$, even or, with L odd, $2 \leq m, n \leq l$, even,

where $D_{m,n}^L(\Omega)$ is Wigner rotation matrix and δ denotes the Kronecker delta. For the record, here we list all relevant $\Delta_{m,n}^L(\Omega)$ functions of $L = 2$ [107]:

$$\begin{aligned} \Delta_{0,0}^2(\Omega) &= \frac{1}{2} (3 \cos^2(\beta) - 1), \\ \Delta_{0,2}^2(\Omega) &= \frac{\sqrt{3}}{2} \sin^2(\beta) \cos(2\gamma), \\ \Delta_{2,0}^2(\Omega) &= \frac{\sqrt{3}}{2} \sin^2(\beta) \cos(2\alpha), \\ \Delta_{2,2}^2(\Omega) &= \frac{1}{2} (1 + \cos^2(\beta)) \cos(2\alpha) \cos(2\gamma) - \cos(\beta) \sin(2\alpha) \sin(2\gamma). \end{aligned} \quad (3.13)$$

3.1.2 Macroscopic approach

In previous Subsection the microscopic order parameters were derived under the assumption of molecule's rigidity, which as we know is up to some extent valid. An alternative approach, which sets aside the molecular features, is based on the introduction of the macroscopic order parameter. Within this framework, the key idea is to focus on symmetry considerations.

In order to construct the macroscopic order parameter, one should refer to an appropriate response function. This quantity describes the reaction of a medium to an applied external stimuli, for example, diamagnetic susceptibility tensor χ or dielectric tensor ϵ . What should be outlined all response functions of the bulk material are anisotropic [108]. Following de Gennes [109, 110], we will derive a macroscopic order using the diamagnetic susceptibility.

Most organic materials are diamagnetic, i.a. nematic liquid crystals [111], meaning that in those materials the magnetization $\mathbf{M}$ is proportional to the external magnetic field $\mathbf{H}$:

$$M_\alpha = \chi_{\alpha\beta} H_\beta, \quad (3.14)$$

where $\alpha, \beta = x, y, z$, $\chi_{\alpha\beta}$ is an element of the diamagnetic susceptibility tensor χ and the summation convention over repeated indices is used. When the field $\mathbf{H}$ is static, then the tensor $\chi_{\alpha\beta}$ has symmetric form, i.e. $\chi_{\alpha\beta} = \chi_{\beta\alpha}$. In the isotropic phase we have

$$\chi_{\alpha\beta} = \chi \delta_{\alpha\beta}, \quad (3.15)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta.

For a uniaxial phase with the symmetry axis along z -axis, all properties along x and y are identical and $\chi_{11} = \chi_{22} \neq \chi_{33}$ [108]. The corresponding matrix has form

$$\chi_{\alpha\beta} = \begin{bmatrix} \chi_{11} & 0 & 0 \\ 0 & \chi_{22} & 0 \\ 0 & 0 & \chi_{33} \end{bmatrix} = \begin{bmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{bmatrix}, \quad (3.16)$$

where $\chi_\perp$ and $\chi_\parallel$ are the susceptibilities perpendicular and parallel to the symmetry axis, respectively. The average susceptibility is given by

$$\bar{\chi} = \frac{1}{3}(2\chi_\perp + \chi_\parallel), \quad (3.17)$$

and the anisotropy is defined by

$$\Delta\chi = \chi_\parallel - \chi_\perp. \quad (3.18)$$

The anisotropic part of tensor $\chi_{\alpha\beta}$ is

$$\chi_{\alpha\beta}^a = \chi_{\alpha\beta} - \bar{\chi} \delta_{\alpha\beta}, \quad (3.19)$$

Hence, the anisotropy tensor is traceless, has dimension of the χ value and becomes zero in the isotropic phase:

$$\chi_{\alpha\beta}^a = \begin{bmatrix} \chi_{\perp} & 0 & 0 \\ 0 & \chi_{\perp} & 0 \\ 0 & 0 & \chi_{\parallel} \end{bmatrix} - \begin{bmatrix} \bar{\chi} & 0 & 0 \\ 0 & \bar{\chi} & 0 \\ 0 & 0 & \bar{\chi} \end{bmatrix} = \Delta\chi \begin{bmatrix} -\frac{1}{3} & 0 & 0 \\ 0 & -\frac{1}{3} & 0 \\ 0 & 0 & \frac{2}{3} \end{bmatrix}, \quad (3.20)$$

although it is not bounded from above in the ordered phase. In order to eliminate this inconvenience, we normalize diamagnetic anisotropy $\Delta\chi$ to the maximum possible anisotropy corresponding to the perfectly ordered nematic phase [110], which yields

$$Q_{\alpha\beta} = \frac{\Delta\chi}{\Delta\chi_{\max}} \begin{bmatrix} -\frac{1}{3} & 0 & 0 \\ 0 & -\frac{1}{3} & 0 \\ 0 & 0 & \frac{2}{3} \end{bmatrix}. \quad (3.21)$$

The factor $\Delta\chi/\Delta\chi_{\max}$ measures the deviation of $\Delta\chi$ from $\Delta\chi_{\max}$, which is directly associated with the skewed orientation of molecules with respect to the director. In other words, $\Delta\chi/\Delta\chi_{\max}$ is a scalar modulus of the order parameter dependent on the degree of molecular order. Thus, such factor can be tied with microscopic order parameter S as follows:

$$S = \frac{\Delta\chi}{\Delta\chi_{\max}} = \langle P_2(\cos(\theta)) \rangle = \frac{1}{2} \langle 3 \cos^2(\theta) - 1 \rangle. \quad (3.22)$$

It should be reminded that Eq. (3.21) corresponds to a state where $\hat{\mathbf{n}} \parallel z$. For an arbitrary orientation of the director with respect to the reference frame, the tensor order parameter can be written using the director components

$$Q_{\alpha\beta} = S \begin{bmatrix} n_x n_x - \frac{1}{3} & n_x n_y & n_x n_z \\ n_y n_x & n_y n_y - \frac{1}{3} & n_y n_z \\ n_z n_x & n_z n_y & n_z n_z - \frac{1}{3} \end{bmatrix} = S \left(n_{\alpha} n_{\beta} - \frac{1}{3} \delta_{\alpha\beta} \right). \quad (3.23)$$

Eq. (3.23) is commonly referred in literature as $\mathbf{Q}$ tensor or alignment tensor [109, 112].

The tensor order parameter can be used also for description of different symmetries. For example, if we were to consider biaxial system, where $\chi_{11} \neq \chi_{22} \neq \chi_{33}$ [108], it is possible to define the degree of biaxial order by including a second scalar order parameter T in the tensor $\mathbf{Q}$. Through the same way of reasoning as before we get

$$Q_{\alpha\beta} = S \left(n_{\alpha} n_{\beta} - \frac{1}{3} \delta_{\alpha\beta} \right) + \frac{1}{3} T (l_{\alpha} l_{\beta} - m_{\alpha} m_{\beta}), \quad (3.24)$$

where $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$ and $\hat{\mathbf{l}}$ are the orthonormal eigenvectors of $\mathbf{Q}$ corresponding to eigenvalues $\{(2/3)S, (-1/3)(S+T), (-1/3)(S-T)\}$ [113], respectively. The local director of the system is defined by the eigenvector of $\mathbf{Q}$ corresponding to the maximal modulus of a nondegenerate eigenvalue. Coefficient S is the familiar uniaxial order parameter, as defined in Eq. (3.22), while T coefficient is the biaxial order parameter. Upon inspection of Eq. (3.24) one can see that isotropic phase is represented by $S = 0$ and $T = 0$, uniaxial phase by $S \neq 0$ and $T = 0$ (or $S \neq 0$ and $T = \pm 3S$), and biaxial phase by $S \neq 0$ and $T \neq 0$. For nonchiral systems the $\mathbf{Q}$

tensor accounts for three possible states of local symmetries $O(3)$, $D_{\infty h}$ and D_{2h} . On other hand, in chiral systems (broken mirror symmetry) the corresponding symmetries are $SO(3)$, D_{∞} and D_2 .

Full form of the $\mathbf{Q}$ tensor, Eq. (3.24), comprises the information about the orientation of the directors $\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}\}$ along with the magnitude of the scalar order parameters S and T . Hence, it is widely incorporated in many microscopic and macroscopic theories [114].

3.2 Maier-Saupe mean-field theory

One of the most successful theories elucidating the phenomenon of nematic-isotropic phase transition is a microscopic one formulated by Maier and Saupe (MS) [115–117]. In its assumptions it concerns a system of cylindrically (uniaxial) symmetric molecules interacting via van der Waals dispersion forces. Additionally, the considerations are conducted within the mean-field paradigm, which roughly means that a molecule is “submerged in the sea” of many molecules and each one experiences the same forces. The effective mean-field interaction potential is given by

$$V_{\text{eff}}(S, \theta) = -\varepsilon S \left(\frac{3}{2} \cos^2(\theta) - \frac{1}{2} \right) = -\varepsilon S P_2(\cos(\theta)), \quad (3.25)$$

where ε is the orientational interaction parameter (in units of energy), S is the order parameter (see Subsection 3.1.1, Eq. (3.9)), $P_2(\dots)$ is the Legendre polynomial of second order and θ is the angle between the long molecular axis and the liquid crystal director. The equilibrium orientational distribution function (ODF) of the molecule orienting along the director with polar angle θ is described by the Boltzmann distribution:

$$p(S, \theta, T) = \frac{1}{Z} \exp \left[\frac{-V_{\text{eff}}(S, \theta)}{k_B T} \right], \quad (3.26)$$

where

$$Z = \int_0^\pi \exp \left[\frac{-V_{\text{eff}}(S, \theta)}{k_B T} \right] \sin(\theta) d\theta \quad (3.27)$$

is the orientational single-molecule partition function, k_B is the Boltzmann constant and T is the absolute temperature. Onward, we can calculate the order parameter from the ODF:

$$\begin{aligned} S &= \frac{1}{Z} \int_0^\pi P_2(\cos(\theta)) \exp \left[\frac{-V_{\text{eff}}(S, \theta)}{k_B T} \right] \sin(\theta) d\theta \\ &= \frac{1}{Z} \int_0^\pi P_2(\cos(\theta)) \exp \left[\frac{S P_2(\cos(\theta))}{t^*} \right] \sin(\theta) d\theta, \end{aligned} \quad (3.28)$$

where $k_B T / \varepsilon \equiv t^*$ is the reduced (dimensionless) temperature. As one can see, both sides of Eq. (3.28) contain S , which means that it is a self-consistent equation for S . For the record, without going into details, Eq. (3.28) can be solved by numerical methods.

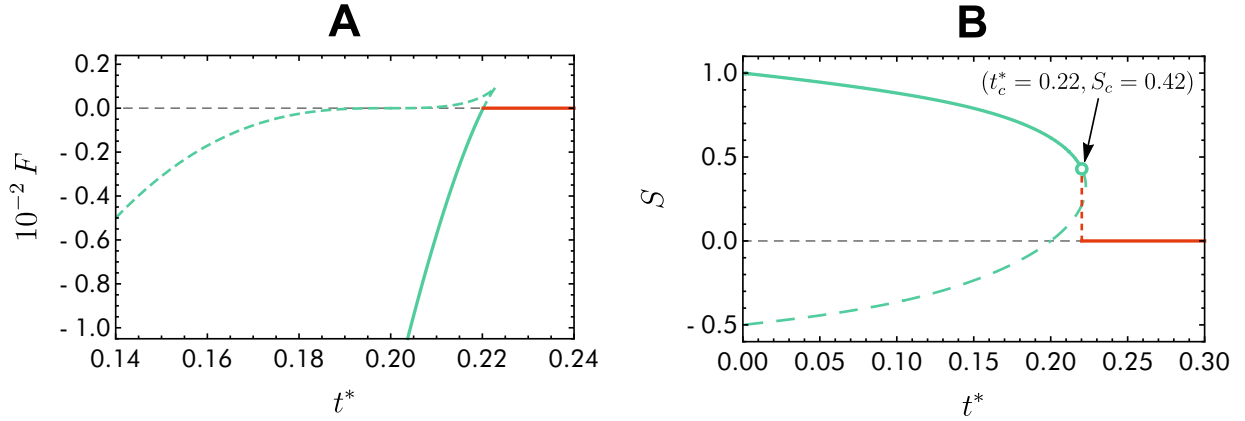


FIGURE 3.3: (A) Free energy F and (B) order parameter S as a function of the reduced temperature t^* in the MS theory. Continuous lines represent the physical branches of solutions.

The dimensionless free energy (per molecule) for Maier-Saupe theory reads:

$$F = U - TS = \frac{1}{2}S^2 - t^* \ln(Z), \quad (3.29)$$

where U is the internal energy and S is entropy. The plots of free energy and order parameter as a function of the reduced temperature t^* are illustrated in Fig. 3.3. Components of Eq. (3.29) were determined as follows. The internal energy (per molecule) is given by

$$U = \frac{1}{2} \langle V_{\text{eff}}(S, \theta) \rangle = \frac{1}{2Z} \int_0^\pi V_{\text{eff}}(S, \theta) \exp \left[\frac{-V_{\text{eff}}(S, \theta)}{k_B T} \right] \sin(\theta) d\theta, \quad (3.30)$$

where the factor $1/2$ avoids counting the interactions twice. From Eq. (3.25) we have:

$$\langle V_{\text{eff}}(S, \theta) \rangle = -\varepsilon S^2. \quad (3.31)$$

Therefore, inserting Eq. (3.31) into Eq. (3.30) gives:

$$U = -\frac{1}{2}\varepsilon S^2. \quad (3.32)$$

The entropy (per molecule) of a system at constant temperature can be calculated as:

$$S = -k_B \langle \ln(p(S, \theta, T)) \rangle = -\frac{k_B}{Z} \int_0^\pi \ln(p(S, \theta, T)) \exp \left[\frac{-V_{\text{eff}}(S, \theta)}{k_B T} \right] \sin(\theta) d\theta. \quad (3.33)$$

From Eq. (3.26) we have

$$\ln(p(S, \theta, T)) = \frac{-V_{\text{eff}}(S, \theta)}{k_B T} - \ln(Z). \quad (3.34)$$

Thus, upon inserting Eq. (3.31) and Eq. (3.34) into Eq. (3.33) we acquire:

$$\mathcal{S} = \frac{1}{T} \langle V_{\text{eff}}(S, \theta) \rangle + k_B \ln(Z) = -\frac{1}{T} \varepsilon S^2 + k_B \ln(Z). \quad (3.35)$$

The Maier-Saupe theory predicts that nematic-isotropic phase transition is of first-order³ at $t^* = 0.22 \equiv t_c^*$ with the order parameter $S(t_c^*) = 0.42 \equiv S_c$. In the limit $t^* \rightarrow 0$, S approaches unity associated with perfect order in the system.

In the course of further developments and findings MS theory was extended in many ways (see e.g. [118, 119]). One of the most studied extensions, is the biaxial generalization of the attractive, SO(3)-invariant Lebwohl–Lasher (LL) potential [120, 121], which we will briefly discuss.

LL potential involves second-rank quadrupolar tensor $\mathbf{Q}$ with uniaxial $\left(\mathbf{T}_0^{(2)}(\Omega)\right)$ and biaxial $\left(\mathbf{T}_2^{(2)}(\Omega)\right)$ component, which are built out of the orthonormal tripod Ω_k ($k = i, j$) of vectors $\{\hat{\mathbf{a}}_k, \hat{\mathbf{b}}_k, \hat{\mathbf{c}}_k\}$ defining the orientation degrees of freedom. Following these assumptions we have [122]:

$$H(\Omega_i, \Omega_j) = -\varepsilon \text{Tr}[\mathbf{Q}(\Omega_i)\mathbf{Q}(\Omega_j)] = -\varepsilon \text{Tr} \left[\left(\mathbf{T}_0^{(2)}(\Omega_i) + \sqrt{2}\lambda \mathbf{T}_2^{(2)}(\Omega_i) \right) \left(\mathbf{T}_0^{(2)}(\Omega_j) + \sqrt{2}\lambda \mathbf{T}_2^{(2)}(\Omega_j) \right) \right], \quad (3.36)$$

where

$$\begin{aligned} \mathbf{T}_0^{(2)}(\Omega) &\equiv \mathbf{T}_0^{(2)}(\hat{\mathbf{c}}_k) = \sqrt{\frac{3}{2}} \left(\hat{\mathbf{c}}_k \otimes \hat{\mathbf{c}}_k - \frac{1}{3} \mathbb{1} \right) \Rightarrow D_{\text{och}} \text{ symmetric}, \\ \mathbf{T}_2^{(2)}(\Omega) &\equiv \mathbf{T}_2^{(2)}(\hat{\mathbf{a}}_k, \hat{\mathbf{b}}_k) = \frac{1}{\sqrt{2}} \left(\hat{\mathbf{a}}_k \otimes \hat{\mathbf{a}}_k - \hat{\mathbf{b}}_k \otimes \hat{\mathbf{b}}_k \right) \Rightarrow D_{2h} \text{ symmetric}. \end{aligned} \quad (3.37)$$

Parameter λ is a measure of the deviation from cylindrical symmetry⁴ [121] (for $\lambda = 0$ MS theory is recovered), $\otimes$ denotes the tensor product and $\mathbb{1}$ is the identity matrix. The next step is the decomposition of the tensor $\mathbf{Q}$ in the basis of symmetrized irreducible tensors in the director basis:

$$\begin{aligned} \mathbf{T}_0^{(2)}(\hat{\mathbf{n}}) &= \sqrt{\frac{3}{2}} \left(\hat{\mathbf{n}} \otimes \hat{\mathbf{n}} - \frac{1}{3} \mathbb{1} \right), \\ \mathbf{T}_2^{(2)}(\hat{\mathbf{m}}, \hat{\mathbf{l}}) &= \frac{1}{\sqrt{2}} \left(\hat{\mathbf{l}} \otimes \hat{\mathbf{l}} - \hat{\mathbf{m}} \otimes \hat{\mathbf{m}} \right). \end{aligned} \quad (3.38)$$

In order to do so, we have to use D_{2h} -symmetrized identity operator for $L = 2$ constructed in the director basis [102, 123]. Afterwards, we substitute the director basis for $\Omega_i \equiv \{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}\}$ and the molecular basis for molecule for $\Omega_j \equiv \{\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3\}$, which leads us to the following form of Eq. (3.36):

$$H = -\varepsilon \left[\left(q_0 \mathbf{T}_0^{(2)}(\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}) + q_2 \mathbf{T}_2^{(2)}(\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}) \right) \left(\mathbf{T}_0^{(2)}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3) + \sqrt{2}\lambda \mathbf{T}_2^{(2)}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3) \right) \right], \quad (3.39)$$

³ This notion will be explained later in the text.

⁴ In [104, 105] this parameter governs the molecule's arms biaxiality.

where q_0 and q_2 are uniaxial and biaxial order parameters, respectively. Onward, explicit form of Eq. (3.39) reads:

$$H = -\varepsilon \left[\underbrace{q_0 \mathbf{T}_0^{(2)}(\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}) \mathbf{T}_0^{(2)}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3)}_{\Delta_{00}^{(2)}(\Omega)} + \underbrace{q_0 \sqrt{2} \lambda \mathbf{T}_0^{(2)}(\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}) \mathbf{T}_2^{(2)}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3)}_{\Delta_{02}^{(2)}(\Omega)} + \underbrace{q_2 \mathbf{T}_2^{(2)}(\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}) \mathbf{T}_0^{(2)}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3)}_{\Delta_{20}^{(2)}(\Omega)} + \underbrace{q_2 \sqrt{2} \lambda \mathbf{T}_2^{(2)}(\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}) \mathbf{T}_2^{(2)}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3)}_{\Delta_{22}^{(2)}(\Omega)} \right] \quad (3.40)$$

In a final step, we can simplify Eq. (3.40) by using $\mathbf{T}_m^{(2)}(\Omega_i) \mathbf{T}_{m'}^{(2)}(\Omega_j) = \Delta_{mm'}^{(2)}$ [102], where $\Delta_{mm'}^{(2)}$ is the D_{2h} symmetry-adapted function introduced in Subsection 3.1.1:

$$H = -\varepsilon \left[q_0 \left(\Delta_{00}^{(2)}(\Omega) + \sqrt{2} \lambda \Delta_{02}^{(2)}(\Omega) \right) + q_2 \left(\Delta_{20}^{(2)}(\Omega) + \sqrt{2} \lambda \Delta_{22}^{(2)}(\Omega) \right) \right] = -\varepsilon \mathcal{H}. \quad (3.41)$$

The corresponding dimensionless free energy per molecule is given by:

$$F = \frac{1}{2} (q_0^2 + q_2^2) - t^* \log Z, \quad (3.42)$$

where

$$Z = \iiint_{\Omega} \exp \left[\frac{\mathcal{H}(q_0, q_2, \Omega)}{t^*} \right] d\Omega. \quad (3.43)$$

All features arising from the application of Eq. (3.41), in different scenarios, were thoroughly discussed i.a. in [102, 104, 105, 122, 124–129].

3.3 Landau theory of phase transitions

Landau theory of phase transitions belongs to the pantheon of the most successful theories of twentieth century. In its foundations, it is a phenomenological theory, which neglects the microscopic details, and relies solely on the considerations about the symmetry of the system.

One of the assumptions of this theory is the existence of a primary order parameter, let us tentatively call it Ψ , which is non-zero in low-temperature phase ($\Psi \neq 0, T < T_c$) of symmetry G_1 and zero in the high-temperature phase ($\Psi = 0, T \geq T_c$) of symmetry G_0 . Moreover, it is assumed that near the phase transition temperature (T_c) ψ is small and non-equilibrium Gibbs (or Helmholtz) free energy per unit volume, can be constructed as an analytical function that is a power series of the primary order parameter Ψ :

$$\mathcal{F}(\psi, T, P) = \mathcal{F}_0 + \alpha \psi + \frac{A}{2} \psi^2 + \frac{B}{3} \psi^3 + \frac{C}{4} \psi^4 + \dots, \quad (3.44)$$

where the coefficients $\alpha, A, B, C, \dots$ depend on the temperature T and the pressure P of the system, while $\mathcal{F}_0$ is the free energy of the disordered state⁵. Simultaneously, it is required for free energy to be invariant

⁵ In the literature the low-temperature phase is commonly referred to as ordered phase, while the high-temperature phase as a disordered one.

with respect to the symmetry operations of the disordered state.

Phase transition, associated with symmetry change of the system⁶, can occur through:

- abrupt structural change (first order phase transition), where order parameter changes in discontinuous manner at the transition temperature (Fig. 3.4A);
- an infinitesimal change that causes the disappearance (appearance) of some element of symmetry (second order phase transition), where order parameter changes in continuous manner at the transition temperature (Fig. 3.4B).

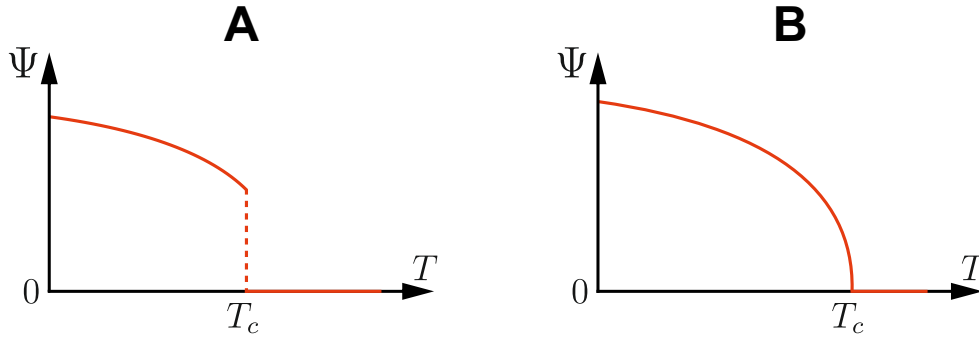


FIGURE 3.4: Temperature dependence of the order parameter Ψ for (A) discontinuous (first order) and (B) continuous (second order) phase transition.

In what follows, we will describe all insights that arise from Landau's theory based on the example of the nematic-isotropic (N - I) phase transition.

3.4 Landau-de Gennes theory of nematics

Initially, the Landau theory was formulated to describe second order phase transitions [131]. Although, it can be also customized for analysis of discontinuous (i.e., first-order) phase transitions [132]. The best example is the famous Landau-de Gennes (LdG) theory of nematics, which was formulated by de Gennes [133], in order to characterize fluctuations of the order parameter in the isotropic phase close to the nematic (cholesteric) phase transition.

In general, the LdG theory contains $O(3)$ (or $SO(3)$ for cholesteric) symmetric invariants, which can be constructed from the tensor order parameter $\mathbf{Q}$ and its derivatives. Without losing the brevity, the total LdG free energy $\mathcal{F}_{\text{LdG}}$ can be depicted through two major components⁷:

$$\mathcal{F}_{\text{LdG}} = \mathcal{F}_{\text{bulk}} + \mathcal{F}_{\text{elastic}} = \frac{1}{V} \int_V (f_{\text{bulk}} + f_{\text{elastic}}) dV, \quad (3.45)$$

⁶ It can be shown that if the phase transition undergoes between two systems that possess different symmetries, the linear term in Eq. (3.44) vanishes, i.e. $\alpha \equiv 0$ [130].

⁷ It should be noted that LdG can be further extended to incorporate influence of external stimuli like i.a. electric/magnetic field, or anchoring (surface) [109]. But yet, those fall out of the scope of the thesis, thus they will not be discussed.

where V is the volume, $\mathcal{F}_{\text{bulk}}$ is the “bulk” part describing the nematic-isotropic phase transition in the spirit of Landau’s theory (Subsection 3.4.1) and $\mathcal{F}_{\text{elastic}}$ is the “elastic” part, which is a contribution that penalizes distortions from the preferred alignment (Subsection 3.4.2).

3.4.1 Bulk free energy

De Gennes’ pioneering approach toward the description of the nematic-isotropic (N - I) phase transition consisted in the introduction of the tensorial order parameter $\mathbf{Q}$ and constructing on its basis the Landau-type free-energy expansion [133].

From Section 3.3 we know that free energy has to be invariant with respect to the symmetry operations of the disordered state. Since $\mathbf{Q}$ transforms like a tensor under the rotation group, the terms in the expansion allowed by the symmetry, must be scalar invariants⁸ of $\mathbf{Q}$. Therefore, the free energy has to be expanded in terms of $\text{Tr}(\mathbf{Q}^n)$, where $n = 1, 2, 3, \dots$ denotes the subsequent power order in the expansion. First term is trivial, as for $n = 1$, by the virtue of $\mathbf{Q}$ definition (see Subsection 3.1.2), we have $\text{Tr}(\mathbf{Q}^1) \stackrel{\text{def}}{=} 0$. Further analysis leads to a conclusion that all invariants of order $n \geq 4$ can be expressed by $\text{Tr}(\mathbf{Q}^2)$ and $\text{Tr}(\mathbf{Q}^3)$ [110]. What is more, $\text{Tr}(\mathbf{Q}^2)$ and $\text{Tr}(\mathbf{Q}^3)$ fulfill (coordinate-independent) relation [110]:

$$\frac{1}{6} \text{Tr}(\mathbf{Q}^2)^3 \geq \text{Tr}(\mathbf{Q}^3)^2, \quad (3.46)$$

which can be rewritten in more compact form by introducing w parameter that obeys $w^2 \leq 1$:

$$w = \sqrt{6} \frac{\text{Tr}(\mathbf{Q}^3)}{\text{Tr}(\mathbf{Q}^2)^{3/2}}. \quad (3.47)$$

Parameter w is a scalar measure of how strongly (locally) is the uniaxial/biaxial order. Uniaxial nematic states are set out by $w = 1$ (prolate) and $w = -1$ (oblate), whereas biaxial nematic state by $w \in (-1, 1)$, Fig. 3.5.

The general expansion of bulk free energy density up to the fourth order, which is equivalent to free energy per volume, reads [109]:

$$f_{\text{bulk}} = f_0 + \frac{1}{2}a \text{Tr}(\mathbf{Q}^2) - \frac{1}{3}b \text{Tr}(\mathbf{Q}^3) + \frac{1}{4}c \text{Tr}(\mathbf{Q}^2)^2, \quad (3.48)$$

where

$$\text{Tr}(\mathbf{Q}^2) = \sum_{\alpha, \beta=1}^3 Q_{\alpha\beta} Q_{\beta\alpha}, \quad \text{Tr}(\mathbf{Q}^3) = \sum_{\alpha, \beta, \gamma=1}^3 Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha}, \quad \text{and} \quad c > 0.$$

Term f_0 stands for the free energy density of the isotropic phase and constants a , b and c are phenomenological coefficients, whereas the negative sign of b was chosen for the reason of convenience. Stability conditions implies that $c > 0$, which ensures that free energy is well-conditioned and bounded from below.

⁸ There are two types of $O(3)$ invariants that can be constructed out of $\mathbf{Q}$, namely traces and determinants of powers of $\mathbf{Q}$. However, determinants can be expressed in terms of traces (see [134]).

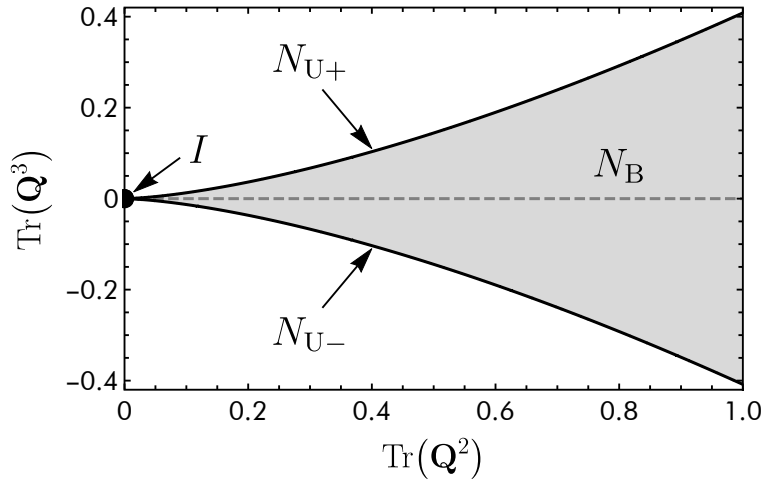


FIGURE 3.5: Identification of the corresponding phases in the $\{\text{Tr}(\mathbf{Q}^2), \text{Tr}(\mathbf{Q}^3)\}$ space. Continuous black curves depict uniaxial phases and everything between these lines relates to biaxial states, while the isotropic phase is a point with the coordinates $(0, 0)$. The dashed line where $\text{Tr}(\mathbf{Q}^3) = 0$ depicts the nematic structures with maximum biaxiality.

Furthermore, Eq. (3.48) as whole cannot be truncated at an odd-term, as it would lead to an ill-conditioned free energy.

As it was already mentioned, the cause behind the lack of linear term in $\text{Tr}(\mathbf{Q})$ in the expansion is straightforward. Moreover, its absence is in accordance with the existence of the stable high temperature disordered phase. Although, in a different scenario, where we permit the influence of external electric/magnetic field, then a term proportional to $\text{Tr}(\mathbf{Q})$ should be incorporated [110].

In principle, the coefficients a , b , and c are temperature and pressure dependent. However, in practice, it is assumed that pressure is fixed and a is the only coefficient associated with temperature dependence:

$$a = a_0(T - T^*), \quad (3.49)$$

where $a_0 > 0$ is a constant⁹, T is the absolute temperature and T^* is the maximal supercooling temperature of the isotropic phase. Thus this term governs the nematic to isotropic phase transition. The remaining coefficients b and c are supposed to be essentially constant with temperature and represented by their actual value at the temperature T^* .

From the symmetry requirements the presence of term $b \text{Tr}(\mathbf{Q}^3)$ is mandatory¹⁰ (see e.g. [133]). Additionally, the presence of this term distinguishes between different states of $\mathbf{Q}$ (prolate or oblate). In the case of $b > 0$, the minimization of f_{bulk} would predict N_{U+} - I phase transition, on contrary to $b < 0$ where we

⁹ The f_{bulk} is expressed in units of J/m^3 , hence knowing that $\text{Tr}(\mathbf{Q}^2)$ and $\text{Tr}(\mathbf{Q}^3)$ are dimensionless, it follows that coefficient a_0 has the dimension $\text{J}/(\text{m}^3 \text{K})$, whereas remaining coefficients are expressed in J/m^3 .

¹⁰ When the cubic invariant is forbidden by the symmetry ($b = 0$) then the Eq. (3.48) describes the second order phase transition (see e.g. [131]). On the other hand, if the cubic invariant is not forbidden by the symmetry ($b \neq 0$) then the Eq. (3.48) describes the first order phase transition.

would have $N_{U-}-I$ phase transition. Nevertheless, it is possible to alter between those states, as the free energy is invariant with respect to the transformation: $\{b, \mathbf{Q}\} \rightarrow \{-b, -\mathbf{Q}\}$, which makes all thermodynamic functions, including phase diagrams, symmetric with respect to the $b = 0$ line, followed by a subsequent change of $N_{U\pm}$ into $N_{U\mp}$ [134].

Assuming a uniaxial nematic, Eq. (3.23), the trace invariants of the order parameter tensor simplify to

$$\text{Tr}(\mathbf{Q}^2) = \frac{2}{3}S^2, \quad (3.50)$$

$$\text{Tr}(\mathbf{Q}^3) = \frac{2}{9}S^3. \quad (3.51)$$

By using Eq. (3.49), Eq. (3.50) and Eq. (3.51) one can rewrite Eq. (3.48) as a function of the scalar order parameter S :

$$f_{\text{bulk}} = f_0 + \frac{1}{3}a_0(T - T^*)S^2 - \frac{2}{27}bS^3 + \frac{1}{9}cS^4. \quad (3.52)$$

The equilibrium value of S is obtained by minimizing the free energy density (Eq. 3.52) with respect to S , which yields:

$$\frac{\partial f_{\text{bulk}}}{\partial S} = a_0(T - T^*)S - \frac{1}{3}bS^2 + \frac{2}{3}cS^3 = 0. \quad (3.53)$$

Eq. (3.53) is a cubic equation, whose solutions are (Fig. 3.6A):

$$S = 0, \quad (3.54a)$$

$$S_{\pm} = \frac{b}{4c} \left(1 \pm \sqrt{1 - \frac{24a_0c(T - T^*)}{b^2}} \right). \quad (3.54b)$$

First solution is straightforward as it refers to the isotropic phase. Now out of remaining two solutions (S_- and S_+) we have to pinpoint the right one describing the temperature dependence of the order parameter in the nematic phase. To do so, we have to calculate the transition temperature T_{NI} by using the condition:

$$f_{\text{bulk}} = f_0 \quad \Rightarrow \quad a_0(T_{NI} - T^*)S_{NI}^2 - \frac{2}{9}bS_{NI}^3 + \frac{1}{3}cS_{NI}^4 = 0, \quad (3.55)$$

and the relation between S_{NI} and T_{NI} given by Eq. (3.53):

$$a_0(T_{NI} - T^*)S_{NI} - \frac{1}{3}bS_{NI}^2 + \frac{2}{3}cS_{NI}^3 = 0. \quad (3.56)$$

Combining Eq. (3.55) and Eq. (3.56) we acquire:

$$\frac{1}{9}bS_{NI}^3 = \frac{1}{3}cS_{NI}^4. \quad (3.57)$$

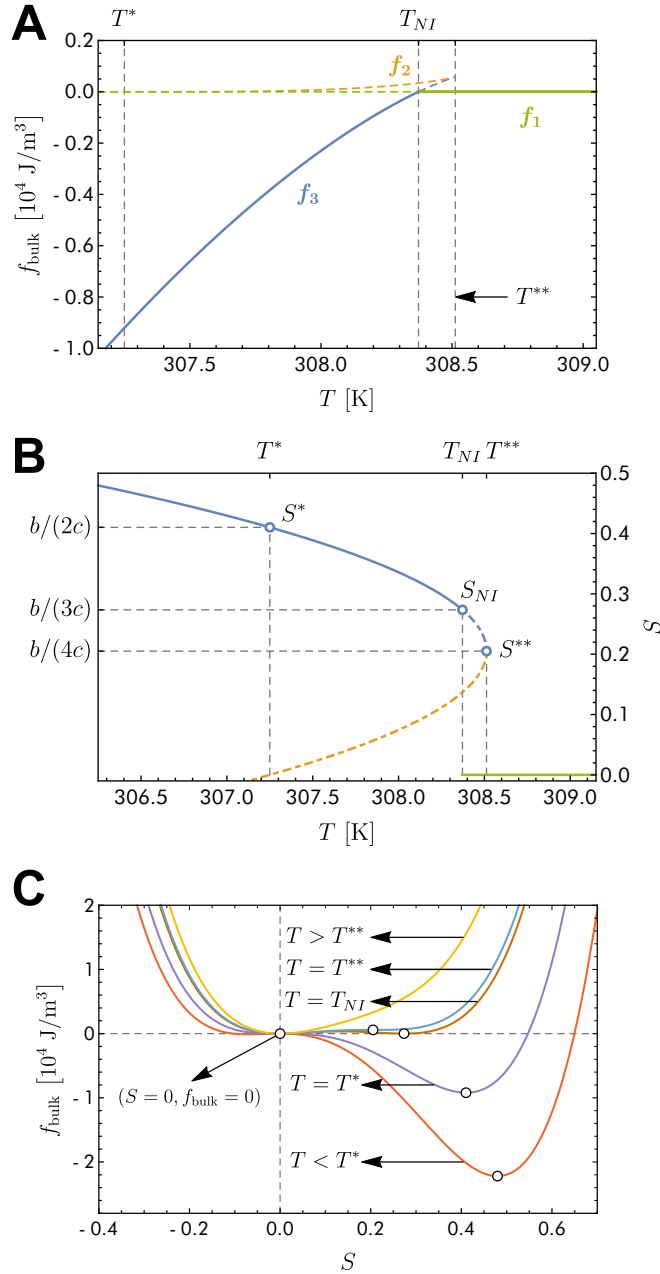


FIGURE 3.6: (A) Bulk free energy density as a function of temperature for three roots of Eq. (3.53), where f_1 is associated with $S = 0$, f_2 with S_- and f_3 with S_+ . Continuous lines (f_1 and f_3) indicate the global minimum values of f_{bulk} , orange dashed line corresponds to either local minimum values of f_{bulk} for S_- (f_2) or the local maximum values of f_{bulk} and dashed green line depicts the local minimum values (but not the global ones) of f_{bulk} . (B) Temperature dependence of the order parameter S within the LdG theory. Characteristic temperature points: T^* , T_{NI} and T^{**} are depicted along with corresponding order parameters: S^* , S_{NI} and S^{**} , respectively. (C) Plots of the bulk free energy density for the generic model, Eq. (3.52), as a function of order parameter for different T s. Hollow points denote (meta-) stable states (local minima) or unstable states (local maxima). Temperature T^* represents the maximal supercooling temperature of the isotropic, wherein T^{**} is the maximal superheating temperature of the uniaxial nematic phase. Plots (A), (B) and (C) were constructed based on the data from Ref. [135] for 5CB compound with assumption that $T^* = 307.25$ K.

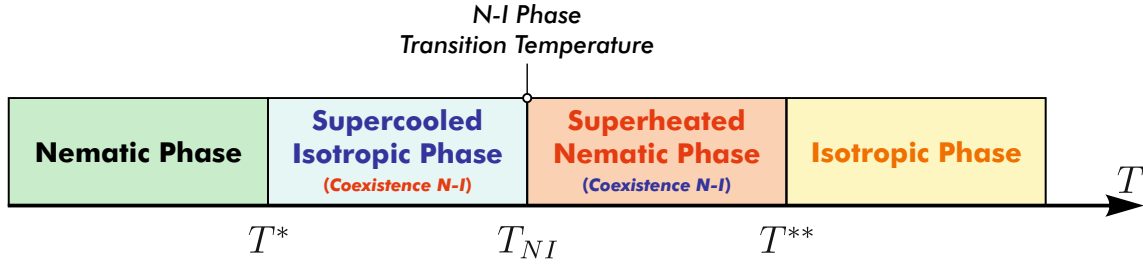


FIGURE 3.7: Graphical illustration of important temperature spans, along with related phase stability. Distances between characteristic temperatures are not to scale.

Eq. (3.57) gives two possible solutions (Fig. 3.6B):

$$S_{NI} = 0, \quad T_{NI} = T^*, \quad (3.58a)$$

$$S_{NI} = \frac{b}{3c}, \quad T_{NI} = T^* + \frac{b^2}{27a_0c}. \quad (3.58b)$$

Upon inspection we notice that S_- solution gives the result $S_{NI} = 0$ at $T = T^*$, whereas the S_+ solution gives $S_{NI} = b/(3c)$ at the higher temperature $T_{NI} = T^* + b^2/(27a_0c)$. From Eq. (3.54b) we retrieve information about third relevant temperature T^{**} :

$$T^{**} = T^* + \frac{b^2}{24a_0c}. \quad (3.59)$$

Referring to Eq. (3.54b), one can see that $S_{\pm} \in \mathbb{R}$ for $T \leq T^{**}$ and $S_{\pm} \in \mathbb{C}$ for $T > T^{**}$.

In the light of foregoing analysis, it follows that there are four crucial temperature regimes (Fig. 3.6C and Fig. 3.7):

- 1) $T > T^{**}$: the isotropic phase is stable.
- 2) $T_{NI} < T < T^{**}$: the isotropic phase is stable and the nematic phase is metastable.
- 3) $T^* < T < T_{NI}$: the nematic phase is stable and the isotropic phase is metastable.
- 4) $T < T^*$: the nematic phase is stable.

The entropy density change between N and I at T_{NI} is given by

$$\Delta S = -\left. \frac{\partial(f_{\text{bulk}} - f_0)}{\partial T} \right|_{T_{NI}} = \frac{1}{3}a_0S_{NI}^2 = \frac{a_0b^2}{27c^2}. \quad (3.60)$$

Correspondingly, the entropy jump in a first-order transition is connected with the latent heat (per unit volume) as follows

$$\Delta H = \Delta S T_{NI} = \frac{a_0b^2}{27c^2} T_{NI}. \quad (3.61)$$

The knowledge about the bulk expansion coefficients a_0 , b and c can be gathered from different experimental techniques, like adiabatic calorimetry (T_{NI} , T^* , T^{**} and ΔH) [136], along with nuclear magnetic resonance ($S(T)$ and S_{NI}) [137]. In practice, it is done e.g. by fitting expression $S_+(T)$ (3.54b) to experimentally obtained data of order parameter variation with respect to temperature.

Mostly, it is sufficient to truncate the expansion of bulk free energy density at the fourth order. However to account for biaxial nematic, along with isotropic phase and experimental data for uniaxial nematic, the bulk free energy has to be extended up to the sixth order [138]:

$$f_{\text{bulk}} = \frac{1}{2}a_0(T - T^*)I_2 - \frac{1}{3}bI_3 + \frac{1}{4}cI_2^2 + \frac{1}{5}dI_2I_3 + \frac{1}{6}eI_2^3 + \frac{1}{6}(f - e)I_3^2, \quad (3.62)$$

where $I_2 = \text{Tr}(\mathbf{Q}^2)$ and $I_3 = \text{Tr}(\mathbf{Q}^3)$. Properties of Eq. (3.62) have been broadly and thoroughly discussed in [138].

3.4.2 Elastic free energy

The ground state of a nematic liquid crystal is a spatially uniform director field. Upon the exposure to external stimuli like electric and magnetic fields, shear or mechanical stress, the director field becomes distorted. This induces an elastic restoring force, which onward increases the free energy of the system. Oseen [139], Zocher [140] and Frank [141], basing on the symmetry arguments of uniaxial nematic, derived the following formula¹¹ of the bulk elastic free energy density:

$$f_{\text{elastic}}(\hat{\mathbf{n}}, \nabla \hat{\mathbf{n}}) = \frac{1}{2}K_{11}(\nabla \cdot \hat{\mathbf{n}})^2 + \frac{1}{2}K_{22}(\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}})^2 + \frac{1}{2}K_{33}(\hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}})^2, \quad (3.63)$$

where K_{11} , K_{22} and K_{33} are the Frank elastic constants for the elementary deformations of splay, twist, and bend, respectively (Fig. 3.8). Those constants quantify the proportionality between deformation and the corresponding restoring force, which is typically the order of pN.

OZF free energy density obeys following requirements [144]:

$$\begin{aligned} f_{\text{elastic}}(\hat{\mathbf{n}}, \nabla \hat{\mathbf{n}}) &= f_{\text{elastic}}(-\hat{\mathbf{n}}, -\nabla \hat{\mathbf{n}}) \\ f_{\text{elastic}}(\hat{\mathbf{n}}, \nabla \hat{\mathbf{n}}) &= f_{\text{elastic}}(R\hat{\mathbf{n}}, R\nabla \hat{\mathbf{n}}R^T) \end{aligned} \quad (3.64)$$

where R is any proper orthogonal matrix ($\det(R) = 1$) and R^T is its transpose. The first requirement arises from the a-polarity of nematic phase and the second one imposes that the energy of a given configuration is invariant upon rigid body rotation. What is more, all three Frank elastic constants have to obey Ericksen inequalities [145]:

$$K_{11} \geq 0, \quad K_{22} \geq 0, \quad K_{33} \geq 0, \quad (3.65)$$

¹¹ Commonly it is referred to as Oseen-Zocher-Frank (OZF) free energy density. Herein, it is assumed that director distortions are small [142]: $|\nabla \hat{\mathbf{n}}| \ll a^{-1}$, where a is a typical molecular length and the bulk to surface ratio is high enough to exclude the surface terms [143].

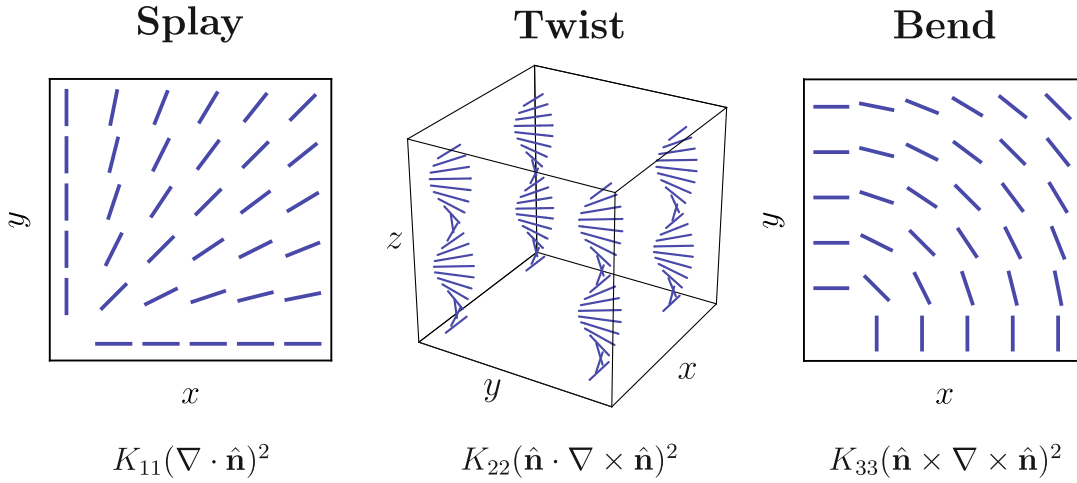


FIGURE 3.8: Schematic illustration of elementary elastic deformations in nematic liquid crystals: splay, twist and bend.

because otherwise perfect alignment (homogeneous nematic) would not correspond to a state of minimum energy.

Up to this point we have only considered the scenario of distortions in the nematic phase, but Eq. (3.63) can be also adapted to describe deformations in chiral nematic. To do so we need to incorporate a term, which is not invariant against inversion in order to properly account for the symmetry of a chiral structure. Such term, linear in gradients, would be:

$$K_{22}q_0[\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}})]. \quad (3.66)$$

By introducing Eq. (3.66) into Eq. (3.63) we acquire the OZF free energy density for the chiral nematic (cholesteric) [146]:

$$f_{\text{elastic}}^{\text{Ch}}(\hat{\mathbf{n}}, \nabla \hat{\mathbf{n}}) = \frac{1}{2}K_{11}(\nabla \cdot \hat{\mathbf{n}})^2 + \frac{1}{2}K_{22}(\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}} + q_0)^2 + \frac{1}{2}K_{33}(\hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}})^2, \quad (3.67)$$

where $q_0 = 2\pi/p$ and p is the cholesteric pitch (see Subsection 2.1.2). The sign of q_0 dictates the cholesteric handedness, i.e. if in a right-handed coordinate frame $q_0 > 0$ then the cholesteric is right-handed and on contrary when $q_0 < 0$ then it is left-handed. The ground state (undistorted) of Eq. (3.67) is represented by helicoidal structure. Taking $\lim_{q_0 \rightarrow 0} f_{\text{elastic}}^{\text{Ch}}(\hat{\mathbf{n}}, \nabla \hat{\mathbf{n}})$ we retrieve Eq. (3.63), provided that the system under consideration is perceived as “bulk” and defect-free.

The construction of the elastic free energy density based on the director approach is legitimate if the scalar order parameter S does not depend on position and biaxial distortions are disregarded. If this is not the case, then in order to properly characterize the distortion modes, the tensorial order parameter $Q_{\alpha\beta}$ is needed. As previously, the same assumption is made about the smallness of amplitudes of deformations and the elastic free energy is expanded into series over invariant terms up to quadratic order in $\partial_\alpha Q_{\alpha\beta}$.

Additionally, one has to properly account for quantities that are invariants under the same operations to as the free energy density. Bearing in mind the above aspects, the bulk distortion free energy density¹² takes the following form (note $\partial_\gamma Q_{\alpha\beta} \equiv \partial Q_{\alpha\beta} / \partial x_\gamma$):

$$f_{\text{elastic}}(\partial \mathbf{Q}) = \frac{1}{2} L_1^{(2)} \partial_\gamma Q_{\alpha\beta} \partial_\gamma Q_{\alpha\beta} + \frac{1}{2} L_2^{(2)} \partial_\beta Q_{\alpha\beta} \partial_\gamma Q_{\alpha\gamma}, \quad (3.68)$$

where L_1 and L_2 are elastic constants¹³ and summation is over repeated indices. Stability conditions reads [147]:

$$L_1^{(2)} > 0, \quad L_1^{(2)} + \frac{3}{2} L_2^{(2)} > 0. \quad (3.69)$$

Likewise to previous considerations, in order to describe a chiral nematic phase the Eq. (3.68) has to be supplemented with chiral term [147]:

$$L_4^{(2)} q_0 \varepsilon_{\alpha\beta\gamma} Q_{\alpha\rho} \partial_\gamma Q_{\beta\rho}, \quad (3.70)$$

where $L_4^{(2)}$ is the elastic constant, q_0 is the wavevector, and $\varepsilon_{\alpha\beta\gamma}$ denotes Levi-Civita tensor.

Tensorial form of Eq. (3.68) can be straightforwardly mapped onto vectorial form, Eq. (3.63), by assuming the uniaxial form of $\mathbf{Q}$ tensor (see Subsection 3.1.2). By inserting $Q_{\alpha\beta}$ defined by Eq. (3.23) into Eq. (3.68), along with the use of the identities $n_\alpha n_\alpha = 1$, $n_\alpha \partial_\gamma n_\alpha = 0$ and assumption that S is positionally independent, then $f_{\text{elastic}}(\partial \mathbf{Q})$ can be mapped onto $f_{\text{elastic}}(\hat{\mathbf{n}}, \nabla \hat{\mathbf{n}})$. Using the notation that $A_1 = (\nabla \cdot \mathbf{n})^2$, $A_2 = (\mathbf{n} \cdot \nabla \times \mathbf{n})^2$ and $A_3 = (\mathbf{n} \times \nabla \times \mathbf{n})^2$ we have following relations [148]:

$$\begin{aligned} \frac{\partial Q_{\alpha\beta}}{\partial x_\gamma} \frac{\partial Q_{\alpha\beta}}{\partial x_\gamma} &= 2S^2(A_1 + A_2 + A_3), \\ \frac{\partial Q_{\alpha\beta}}{\partial x_\beta} \frac{\partial Q_{\alpha\gamma}}{\partial x_\gamma} &= S^2(A_1 + A_3). \end{aligned} \quad (3.71)$$

Now it is possible to re-write Eq. (3.68) using Eq. (3.71) and collecting common terms in the A_i 's ($i = 1, 2, 3$):

$$\begin{aligned} f_{\text{elastic}}(S) &= L_1^{(2)} S^2 (A_1 + A_2 + A_3) + \frac{1}{2} L_2^{(2)} S^2 (A_1 + A_3) \\ &= \frac{1}{2} A_1 S^2 (2L_1^{(2)} + L_2^{(2)}) + \frac{1}{2} A_2 S^2 (2L_1^{(2)}) + \frac{1}{2} A_3 S^2 (2L_1^{(2)} + L_2^{(2)}). \end{aligned} \quad (3.72)$$

Comparing Eq. (3.72) to Eq. (3.63) one can find:

$$\begin{aligned} K_{11} &= K_{33} = S^2 (2L_1^{(2)} + L_2^{(2)}), \\ K_{22} &= S^2 (2L_1^{(2)}). \end{aligned} \quad (3.73)$$

Usual decomposition of the terms to second order in $\partial_\alpha Q_{\alpha\beta}$ leaves degeneracy in the splay and bend elastic constants, which contradicts many experimental results at least away from N - I phase transition.

¹² Similar to the OZF free energy density.

¹³ Superscript (2) indicates that those elastic constants are associated with terms quadratic in spatial derivatives of $\mathbf{Q}$ tensor.

However, this degeneracy can be lifted by taking higher order terms in the expansion, like $\mathbf{Q}(\partial\mathbf{Q})(\partial\mathbf{Q})$ or $\mathbf{Q}\mathbf{Q}(\partial\mathbf{Q})(\partial\mathbf{Q})$ [147].

An interesting conclusion can be additionally drawn, if one notices that when $L_2 = 0$ then the spatial gradients decouple from the tensorial indices for $Q_{\alpha\beta}$. In the literature it is referred to as “one-constant approximation”, which reads:

$$\tilde{f}_{\text{elastic}}(\nabla\mathbf{Q}) = \frac{1}{2}L_1\partial_\gamma Q_{\alpha\beta}\partial_\gamma Q_{\alpha\beta} \equiv \frac{1}{2}L_1|\nabla\mathbf{Q}|^2, \quad (3.74)$$

and equivalently ($K_{11} = K_{22} = K_{33} \equiv K$):

$$\tilde{f}_{\text{elastic}}(\nabla\hat{\mathbf{n}}) = \frac{K}{2}[(\nabla \cdot \hat{\mathbf{n}})^2 + (\nabla \times \hat{\mathbf{n}})^2]. \quad (3.75)$$

Elastic constants K_{11} , K_{22} and K_{33} can be measured by different experimental methods (see e.g. [143] and references therein). In the case of calamatic LCs elastic constants usually obey following relation $K_{33} > K_{11} > K_{22}$ [149], on contrary to the discotic LCs where we have $K_{22} > K_{11} > K_{33}$ [150]. Recently, in the spotlight are LC materials that obey different elastic relations: $K_{11} > K_{22} > K_{33}$ [44] and $K_{11} > K_{33} > K_{22}$ [151].

3.5 Helicity modes expansion

In 1983 Grebel *et al.* [152] proposed a convenient method, which in its foundations was constructed for calculating equilibrium order parameters of the BPs, appeared to also be useful in the description of the one dimensional modulated structures (ODMS) [153–156]. Twist-bend nematic belongs to the class of ODMS and accounting for its one-dimensional periodicity, one can expand order parameter $\mathbf{Q}$ into Fourier series

$$\mathbf{Q}(\mathbf{r}) = \sum_{\mathbf{k}} \mathbf{Q}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (3.76)$$

where $\mathbf{k}$ are the wave vectors from the cubic reciprocal space and Fourier components $\mathbf{Q}(\mathbf{k})$ are defined as

$$\mathbf{Q}(\mathbf{k}) = \frac{1}{V} \int \mathbf{Q}(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}. \quad (3.77)$$

Since $\mathbf{Q}(\mathbf{k})$ are symmetric and traceless tensors of second rank, they can be usefully represented in the basis of spherical tensors of momentum $L = 2$:

$$\mathbf{Q}(\mathbf{r}) = \sum_{\mathbf{k}} \left(\sum_{m=-2}^2 Q_m(\mathbf{k}) \mathbf{M}_m^{(2)}(\mathbf{k}) \right) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (3.78)$$

where $\mathbf{M}_m^{(2)}(\mathbf{k})$ is the tensor part, which gives the director symmetry of particular Fourier component and $Q_m(\mathbf{k})$ is a scalar, which represents the amplitude of that particular Fourier component with symmetry $\mathbf{M}_m^{(2)}(\mathbf{k})$. The tensors $\mathbf{M}_m^{(2)}(\mathbf{k})$, transforming under rotation like spherical harmonics $Y_m^{(2)}(\Omega)$ [157], can be

defined in a local right-handed coordinate system: $\{\hat{\xi}, \hat{\eta}, \hat{\mathbf{k}}\}$, with $\hat{\mathbf{k}} = \mathbf{k}/k$ as z -axis. From this tripod the spherical vectors are constructed

$$\begin{cases} \mathbf{u}(\hat{\mathbf{k}}) = (\hat{\xi} + i\hat{\eta}) / \sqrt{2}, \\ \mathbf{u}^*(\hat{\mathbf{k}}) = (\hat{\xi} - i\hat{\eta}) / \sqrt{2}, \\ \hat{\mathbf{k}} = \mathbf{k}/k. \end{cases} \quad (3.79)$$

In this basis the spherical tensors $\mathbf{M}_m^{(2)}(\hat{\mathbf{k}})$ read:

$$\begin{aligned} \mathbf{M}_0^{(2)}(\hat{\mathbf{k}}) &= \frac{1}{\sqrt{6}} (3\hat{\mathbf{k}} \otimes \hat{\mathbf{k}} - \mathbb{1}), \\ \mathbf{M}_1^{(2)}(\hat{\mathbf{k}}) &= \frac{1}{\sqrt{2}} (\mathbf{u} \otimes \hat{\mathbf{k}} + \hat{\mathbf{k}} \otimes \mathbf{u}), \\ \mathbf{M}_{-1}^{(2)}(\hat{\mathbf{k}}) &= \frac{1}{\sqrt{2}} (\mathbf{u}^* \otimes \hat{\mathbf{k}} + \hat{\mathbf{k}} \otimes \mathbf{u}^*) = \mathbf{M}_1^{*(2)}(\hat{\mathbf{k}}), \\ \mathbf{M}_2^{(2)}(\hat{\mathbf{k}}) &= \mathbf{u} \otimes \mathbf{u}, \\ \mathbf{M}_{-2}^{(2)}(\hat{\mathbf{k}}) &= \mathbf{u}^* \otimes \mathbf{u}^* = \mathbf{M}_2^{*(2)}(\hat{\mathbf{k}}), \end{aligned} \quad (3.80)$$

and according to this definition they fulfill the orthogonality relation

$$\mathbf{M}_m^{(2)}(\hat{\mathbf{k}}) \cdot \mathbf{M}_{m'}^{(2)}(\hat{\mathbf{k}}) \stackrel{\text{def}}{=} [\mathbf{M}_m^{(2)}(\hat{\mathbf{k}})]_{ij} [\mathbf{M}_{m'}^{(2)}(\hat{\mathbf{k}})]_{ij} = \delta_{m,m'}. \quad (3.81)$$

Additionally, reality of $\mathbf{Q}(\mathbf{r})$ impose:

$$\begin{aligned} \mathbf{u}(-\hat{\mathbf{k}}) &= \mathbf{u}^*(\hat{\mathbf{k}}), \\ \mathbf{M}_m^{(2)}(-\hat{\mathbf{k}}) &= (-1)^m (\mathbf{M}_m^{(2)}(\hat{\mathbf{k}}))^*, \\ \mathbf{M}_m^{(2)}(\hat{\mathbf{k}}) \cdot \mathbf{M}_{m'}^{(2)}(-\hat{\mathbf{k}}) &= (-1)^m \delta_{m,m'}. \end{aligned} \quad (3.82)$$

It is worth to point out that the change of sign from $\mathbf{k}$ to $-\mathbf{k}$ leads to the transition from $\{\hat{\xi}, \hat{\eta}, \hat{\mathbf{k}}\}$ frame to $\{\hat{\xi}, -\hat{\eta}, -\hat{\mathbf{k}}\}$. This is because of necessity to preserve the handedness of the coordinate system.

The spherical tensors $\mathbf{M}_m^{(2)}(\hat{\mathbf{k}})$ together with the phase factor $e^{i\mathbf{k} \cdot \mathbf{r}}$ form the so-called *helicity modes*, i.e., tensor waves whose structures can be visualized considering a rotation operator $\mathbf{S}(\hat{\mathbf{k}}, \varphi)$. Since the action of this operator on a spherical vector $\mathbf{u}(\hat{\mathbf{k}})$ is

$$\mathbf{S}(\hat{\mathbf{k}}, \varphi) \mathbf{u}(\hat{\mathbf{k}}) = \mathbf{u}(\hat{\mathbf{k}}) e^{-i\varphi}, \quad (3.83)$$

then, on a tensor mode $\mathbf{M}_m^{(2)}(\hat{\mathbf{k}})$ it is

$$\mathbf{S}(\hat{\mathbf{k}}, \varphi) \mathbf{M}_m^{(2)}(\hat{\mathbf{k}}) = \mathbf{M}_m^{(2)}(\hat{\mathbf{k}}) e^{-im\varphi}. \quad (3.84)$$

The aforementioned relation helps to describe the Fig. 3.9 where the helicity modes are represented in “brick-like” manner. The mode with helicity $m = 0$ corresponds to “longitudinal wave”, while the remaining helicities represent “transversal waves”. For instance, the nematic phase can be described by the $m = 0$ mode with the wave vector $k = 0$, whereas cholesteric phase is a combination of the helicity $m = 0$ and $m = 2$ (or $m = -2$) with the wave vector $k = 2\pi/p$, where p denotes the cholesteric pitch (Fig. 3.10). On the other hand, twist-bend nematic can be illustrated by the set of modes: $m = 0$, along with $m = 1$ and $m = 2$ or $m = -1$ and $m = -2$. Although, it would be an incomplete picture. As we know from Subsection 2.1.3, the symmetry N_{TB} implies that the structure must be locally polar with the polarization vector $\mathbf{P}$ being perpendicular both to the director and the wave vector. Thus, we have to supplement our collection with the polarization field $\mathbf{P}$ expanded into spin tensor modes of $L = 1$ and plane waves [36]. As an outcome, N_{TB} can be represented by modes shown in Fig. 3.11.

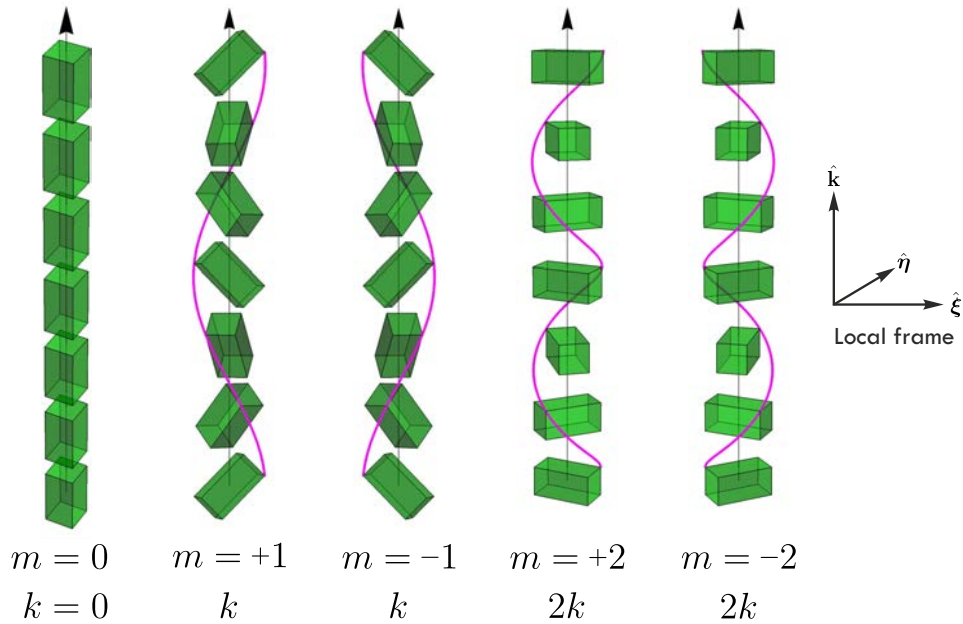


FIGURE 3.9: Visualization of helicity modes: $m = 0$, $m = \pm 1$ and $m = \pm 2$ (change of m into $-m$ corresponds to replacement of k by $-k$). Bricks represent the tensor $\mathbf{Q}(\mathbf{r})$ where the eigenvectors of $\mathbf{Q}(\mathbf{r})$ are parallel to brick’s arms, while the absolute values of eigenvalues are brick’s lengths.

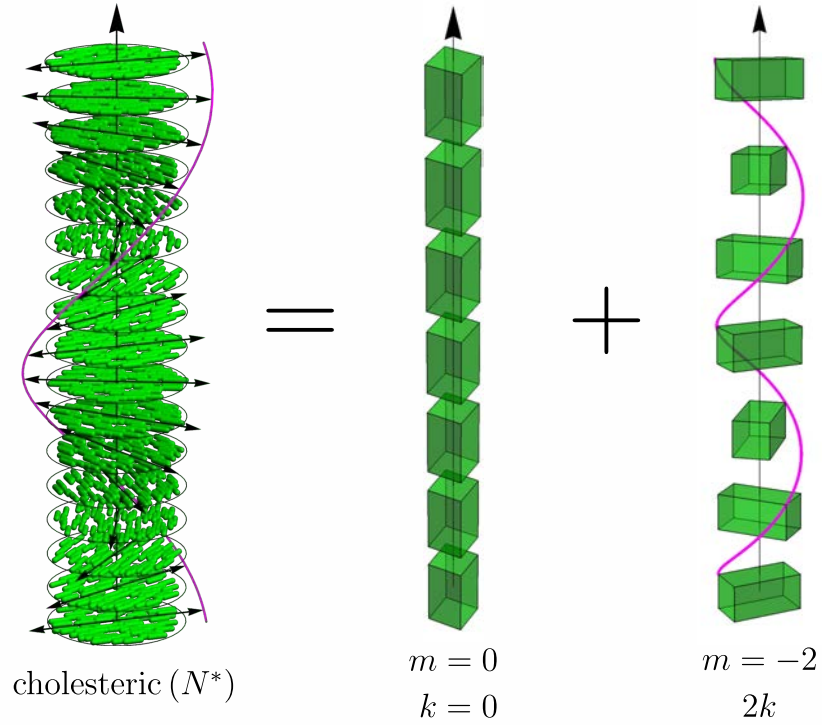


FIGURE 3.10: Illustration of cholesteric phase in the framework of helicity modes expansion, being represented by the superposition of modes $m = 0$ and $m = -2$.

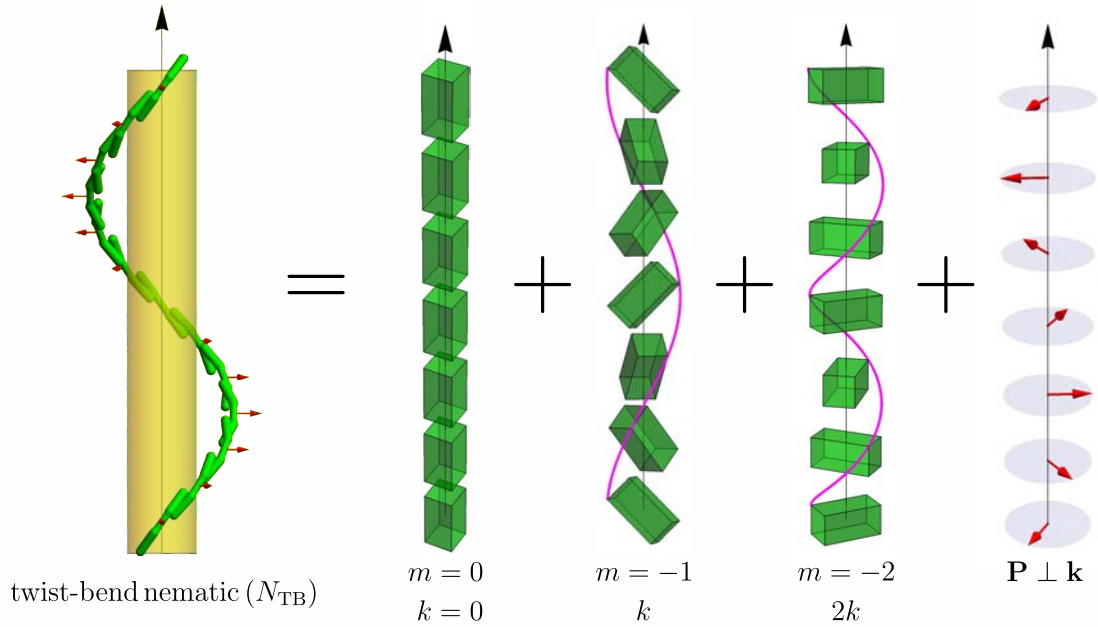


FIGURE 3.11: Illustration of twist-bend nematic phase in the framework of helicity modes expansion, being represented by the superposition of modes $m = 0$, $m = -1$, $m = -2$ and polarization.

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Results

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4.1 Synopsis

Issues raised in [Article 1](#) and [Article 2](#) are focused on implications arising from the interplay between molecule's degree of bent and molecule's arms biaxiality, along with its incidence on the formation of twist-bend nematic phase. It should be pointed out, that in general, bent-shaped molecules are biaxial due to their C_{2v} symmetry, and this is a (bent-)shape-originating biaxiality. In our model, we let the molecular arms's biaxiality to be a part of total molecular biaxiality. This extension allows the arms-related biaxiality to be treated as an extra parameter characterizing bent-shaped molecules, in addition to the bend angle.

We undertake a microscopic approach, which is the generalization of the Maier-Saupe theory for conventional nematics. We formulate it for a bent-core molecule possessing two symmetrical arms. Mutual position of those arms is quantified by the bend angle χ , whereas their biaxiality is governed by a 3×3 , second-rank, traceless symmetric tensor $\mathbf{Q}$. Within the assumptions of the model, biaxial and polar order and the character of phase transitions were examined. We showed that in addition to uniaxial phases: N_U and N_{TB} , two extra (biaxial) phases emerge: homogeneous N_B and periodic $N_{TB,B}$, which is the analog of N_{TB} with a local biaxial order of the molecular arms. What is more, N_B appears in a natural way as a limiting case of $N_{TB,B}$. We were able to identify a direct phase transition sequence between all phases anticipated by our model, i.e. $I \leftrightarrow N_U \leftrightarrow N_B \leftrightarrow N_{TB} \leftrightarrow N_{TB,B}$. In great detail, we have also investigated how the biaxiality reshapes the “landscape” of respective phase diagrams in the $\{\chi, t^*\}$ plane, for $\chi \in [90^\circ, 180^\circ]$, as all reported up-to-date N_{TB} -forming molecules posses bend angle, which falls within that range.

In [Article 3](#), we present investigations that are molecular model independent and are based on the minimal coupling Landau-de Gennes (LdG) theory of chiral nematics, supplemented by terms representing molecular steric polarization. What is more, our model represents the first attempt to look into the interplay between chirality of N_{TB} and chirality introduced at the molecular level. With the helicity modes expansion for the alignment tensor $Q_{\alpha\beta}(\mathbf{r})$ and the polarization $P_\alpha(\mathbf{r})$ fields we study systems without and with the presence of molecular chirality to answer some of the questions concerning number and relative stability of homogeneous nematic states that can be linked with the nematic/cholesteric phase. Within the model, we have identified twelve structures, which were envisaged as candidates for equilibrium homogeneous phases. It turned out, that many new polar phases, in addition to N , N_{TB} and their chiral counterparts, could be found on a single phase diagram. Interestingly, through a competition between various terms of LdeG expansion we found a class of phenomena involving large biaxialities in some regions of stability of N_{TB} and N_{TB}^* , and the reentrant phase transitions.

Fundamental description of orientational properties of nematics based on minimal coupling Landau-de Gennes theory of flexopolarization suggests that softening of K_{33} does not need to be a universal mechanism. Even when both K_{11} and K_{33} are simultaneously reduced due to splay-bend degeneracy (inherent to the minimal coupling LdeG expansion) the N_{TB} phase can still become absolutely stable among all possible one dimensional periodic structures. Since this case has not been observed experimentally to date, an important question that arises is whether the flexopolarization mechanism is indeed sufficient to explain the experimental observations at the level of the “first principles” Landau-de Gennes theory of orientational order. To address this issue a quantitative theory of N_{TB} would then require the presence of higher order elastic invariants of the form $\mathbf{Q}(\partial\mathbf{Q})(\partial\mathbf{Q})$ and the stabilizing terms $\mathbf{Q}\mathbf{Q}(\partial\mathbf{Q})(\partial\mathbf{Q})$.

In [Article 4](#) we extend the minimal coupling LdG free energy expansion in terms of the symmetric and traceless tensor order parameter $Q_{\alpha\beta}(\mathbf{r})$ and its first-order derivatives $Q_{\alpha\beta,\gamma}(\mathbf{r})$ supplemented by the couplings with the polar field $P_\alpha(\mathbf{r})$. The main purpose of these studies was to test whether flexopolarization scenario, claimed to be responsible for observed chiral symmetry breaking, is capable of accounting quantitatively for experimental data known to date. Majority of constitutive parameters (e.g. elastic constants, flexopolarization coefficient, polar coupling etc.) of the model are estimated from experimental data acquired for CB7CB flexible dimers in the nematic phase (N). Then we seek for relative stability and properties of the so-called homogeneously deformed structures (among which is the N_{TB} phase) with reference to the isotropic and nematic phases. Finally, we evaluate various properties of N_{TB} like temperature variation of the structure’s wave vector, conical angle, polarization and remaining order parameters. As it turns out, the extended theory accounts not only for qualitative but also quantitative features of nematic and N_{TB} supporting that flexopolarization induced instability is a viable mechanism for N - N_{TB} phase transition. We also give the first consistent explanation of a puzzling lack of half-pitch band in the resonant soft X-ray scattering and insight into the biaxiality of N_{TB} .

Article 1

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Twist-bend nematic phases of bent-shaped biaxial molecules

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How can a change in molecular structure affect the relative stability and structural properties of the twist-bend nematic phase (N_{TB})? Here we extend the mean-field model¹ (C. Greco, G. R. Luckhurst and A. Ferrarini, *Soft Matter*, 2014, 10, 9318) for bent-shaped achiral molecules, to study the influence of arm molecular biaxiality and the value of the molecule's bend angle on the relative stability of N_{TB} . In particular we show that by controlling the biaxiality of the molecule's arms, up to four ordered phases can become stable. They involve local uniaxial and biaxial variants of N_{TB} , together with uniaxial and biaxial nematic phases. However, a V-shaped molecule shows a stronger ability to form stable N_{TB} than a biaxial nematic phase, where the latter phase appears in the phase diagram only for bend angles greater than 140° and for large biaxiality of the two arms.

1 Introduction

One of the most surprising recent discoveries in the field of soft matter physics is the identification of a new nematic phase, known as the nematic twist-bend phase (N_{TB}).^{2–4} This phase is stabilized as a result of spontaneous chiral symmetry breaking in liquid crystalline systems composed of achiral bent-core,⁵ dimeric⁶ and trimeric⁷ mesogens. The director in N_{TB} forms a conical helix with nanoscale periodicity, while molecular achirality implies that coexisting domains of opposite chirality are formed. Up to now, only some characteristic features of this elusive phase are known, for *e.g.*, the tilt angle and pitch length or the values of the elastic constants in the vicinity of the uniaxial nematic (N_U)– N_{TB} phase transition.^{8–13} Experiments show that the N_{TB} phase usually occurs within the stability regime of N_U ,¹⁴ but for some compounds a direct transition between N_{TB} and the isotropic phase (Iso) has also been found.¹⁵ Although a mechanism leading to a long-range chiral order of N_{TB} is to a large

extent unknown, the issue of stable, modulated nematic phases has been addressed theoretically in a series of papers.^{16–27}

Meyer^{25,26} and subsequently Dozov²⁷ have shown that flexo-polarization can be the driving force leading to twist-bend and splay-bend distortions of the director field. Lorman and Mettout^{28,29} suggested that the formation of the N_{TB} , and other unconventional periodic structures can be facilitated by the shape of bent-core molecules, which seems to be in line with experimental results^{14,30} and computer simulations.^{3,22,31,32}

Out of the alternative theoretical approaches undertaken to tackle the nature of N_{TB} we will focus on the generic, mean-field model introduced by Greco, Luckhurst and Ferrarini (GLF).¹ In the GLF model N_{TB} is treated as an inhomogeneous and locally uniaxial heliconical periodic distortion of the nematic phase, characterized at each point by a single local director $\hat{n}(\mathbf{r}) \equiv \hat{n}(z)$ ^{1,27} (see Fig. 1):

$$\hat{n}(z) = [-\sin(\theta)\sin(\phi), \sin(\theta)\cos(\phi), \cos(\theta)], \quad (1)$$

where θ is the conical angle and $\phi = kz = 2\pi z/p$ with wave vector $\mathbf{k} = k\hat{z}$ ($k = \pm 2\pi/p$) and with period p of the phase. The wave vector, being parallel to the average direction of the main director over one period p : $\mathbf{k} \parallel \langle \hat{n} \rangle_p$, can be identified with an effective optical axis.^{16,17,19}

Heliconical precession is assumed arbitrarily to take place around the $\hat{z}$ -axis of the laboratory system of frame. The helix of N_{TB} can be right-handed or left-handed, depending on the sign of k , and both of these mono-domains have the same free energy. Moreover, a rigid, biaxial bent-core molecule is represented by two mesogenic arms of cylindrical symmetry, each assumed to align preferentially to $\hat{n}(z)$. The latter is taken at the position of the midpoint of the arm. Only N_{TB} , N_U and isotropic liquid can be stabilized by the GLF model.

The effective mean-field potential acting on the molecular arms is defined by the well-known Maier-Saupe P_2 potential, with P_2 being the second Legendre polynomial. Despite its simplicity the GLF model correctly predicts N_U to N_{TB} and Iso to N_{TB} phase transitions, the weak temperature dependence of the pitch and consistent descriptions of the elastic properties of

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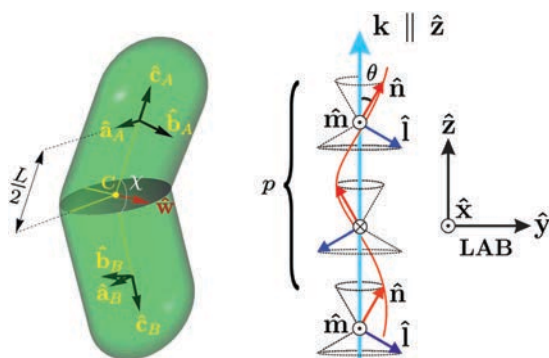


Fig. 1 On the left side is a schematic representation of the extended biaxial model for a bent-shaped molecule with both arms of equal length L . The molecular basis for arm A is given by an orthonormal tripod of vectors $\Omega_A = \{\hat{\mathbf{a}}_A, \hat{\mathbf{b}}_A, \hat{\mathbf{c}}_A\}$, and for arm B by $\Omega_B = \{\hat{\mathbf{a}}_B, \hat{\mathbf{b}}_B, \hat{\mathbf{c}}_B\}$. The C_2 axis of the molecule is along the unit vector $\hat{\mathbf{w}}$, attached at point C. The bend angle is denoted as χ . The sketch on the right-hand side of the figure shows a visualization of the local directors used in the mean-field ansatz for the N_{TB} structure, where the local director basis $\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}\}$ on each arm precesses on a cone of pitch p and tilt angle θ between the primary director $\hat{\mathbf{n}}$ and wave vector $\mathbf{k}$.

the N_{TB} . Tailoring molecules with particular shapes and interactions, it seems interesting to study extensions of the GLF model to molecules of a more complex structure.

While there are many paths that can be followed, one obvious observation is that bent-shaped molecules, including the famous N_{TB} -forming compound CB7CB, can acquire biaxiality not only due to their average “V” shape, but also as a result of the biaxiality of the molecule’s arms and conformational degrees of freedom.^{33,34} Importantly, they can form a stable biaxial nematic phase,^{35–37} and, hence, this structure should be included in theoretical analysis as a possible competitor of N_{TB} .

Biaxiality is also regarded as a key factor to achieve spontaneous chiral symmetry breaking from first principles.³⁸ These symmetry arguments are supported by recent phenomenological analysis of modulated nematic structures using the generalized Landau-de Gennes–Ginzburg theory, where the key ingredients were couplings between the alignment tensor field and steric polarization.²⁴ In this theory the N_{TB} phase, described by the locally uniaxial distortion of the director field, appears less stable than its locally biaxial counterpart, *i.e.* where the full spectrum of distortions of the alignment tensor are taken into account. Following this direction we extend the GLF model to study the effect of molecular biaxiality of bent-core molecules on the stability of N_{TB} and of the competing nematic phases, including the biaxial one. For this purpose we replace the local twist-bend spatial modulation of the director field (1) by its biaxial counterpart, given by the local alignment tensor. We also let the molecular biaxiality of banana-shaped molecules enter not only through their “V” shape but also through the biaxiality of the molecular arms. This extension allows for the treatment of arm molecular biaxiality as an extra parameter characterizing bent-shaped molecules, in addition to the bend angle.

This paper is organized as follows. In the second section we define extension of the GLF model and underline its important features. We interpret the acquired results in the third section. The last section is devoted to a short discussion.

2 The model

2.1 Molecular geometry and director profiles

Here we keep parametrization¹ for the molecular reference frames, where two mesogenic arms A and B, each of length L , are joined at the bend angle χ (Fig. 1). At the midpoint of each arm a molecular basis is placed. The unit vector $\hat{\mathbf{w}}$ at the center (C) of the particle describes the molecular C_2 axis. In line with the present model of the N_{TB} phase^{1,27} we generalize the local uniaxial ansatz, represented by the main director (1), by its local biaxial counterpart (kept from the start in the variational ansatz for the local environment of the molecule). That is, we assume two other directors to follow the precession of $\hat{\mathbf{n}}$ (Fig. 1):

$$\hat{\mathbf{m}}(z) = [\cos(\phi), \sin(\phi), 0], \quad (2)$$

$$\hat{\mathbf{l}}(z) \equiv \hat{\mathbf{n}}(z) \times \hat{\mathbf{m}}(z) = [-\cos(\theta)\sin(\phi), \cos(\theta)\cos(\phi), -\sin(\theta)]. \quad (3)$$

As for GLF the parametrization (1)–(3) permits the N_{TB} phase for $0^\circ < \theta < 90^\circ$ and a finite pitch p , with the wave vector $\mathbf{k}$ being parallel to the $\hat{\mathbf{z}}$ axis.

2.2 Formulation of the mean-field potential

In the first step we extend the GLF model by introducing molecular biaxiality on both arms of the molecule, which is achieved *via* a second-rank, 3×3 , symmetric and traceless tensor $\mathbf{Q}$. The basis of the $\mathbf{Q}$ tensors, defined with respect to the orthonormal right-handed tripod, say $\{\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}\}$, comprises both uniaxial $\mathbf{Q}_U$ and biaxial $\mathbf{Q}_B$ parts, given in the general form as:³⁹

$$\mathbf{Q}_U(\hat{\mathbf{z}}) \stackrel{\text{def}}{=} \frac{1}{\sqrt{6}}(3\hat{\mathbf{z}} \otimes \hat{\mathbf{z}} - \mathbb{1}), \quad (4)$$

$$\mathbf{Q}_B(\hat{\mathbf{x}}, \hat{\mathbf{y}}) \stackrel{\text{def}}{=} \frac{1}{\sqrt{2}}(\hat{\mathbf{x}} \otimes \hat{\mathbf{x}} - \hat{\mathbf{y}} \otimes \hat{\mathbf{y}}), \quad (5)$$

where $\otimes$ denotes the tensor product and $\mathbb{1}$ is the identity matrix. Taking the linear combination of $\mathbf{Q}_U$ and $\mathbf{Q}_B$ the molecular tensors for each arm are now defined as:

$$\mathbf{Q}(\Omega_i) \stackrel{\text{def}}{=} \mathbf{Q}_U(\hat{\mathbf{c}}_i) + \lambda\sqrt{2}\mathbf{Q}_B(\hat{\mathbf{a}}_i, \hat{\mathbf{b}}_i), \quad (6)$$

where the λ parameter is a measure of the arm’s biaxiality and where $\Omega_i = \{\hat{\mathbf{a}}_i, \hat{\mathbf{b}}_i, \hat{\mathbf{c}}_i\}$ is the molecular right-handed tripod attached to arm $i = A, B$ (Fig. 1). Please observe that the GLF model¹ corresponds to $\lambda = 0$. In addition we should mention that the $\mathbf{Q}(\Omega_i)$ tensor can be linked to the diagonal elements of the molecular polarizability tensor⁴⁰ for arm i .

The next step is the decomposition of the tensor $\langle \mathbf{Q}(\Omega_j) \rangle \stackrel{\text{def}}{=} \bar{\mathbf{Q}}(\hat{\mathbf{n}}(R_j), \hat{\mathbf{m}}(R_j), \hat{\mathbf{l}}(R_j)) \equiv \bar{\mathbf{Q}}(R_j)$, which is obtained

from eqn (6) by performing thermodynamic average. In basis (4) and (5) it reads:

$$\begin{aligned}\bar{\mathbf{Q}}(\mathbf{R}_j) &= \bar{\mathbf{Q}}_U(\mathbf{R}_j) + \bar{\mathbf{Q}}_B(\mathbf{R}_j) \\ &= q_0 \mathbf{Q}_U(\hat{\mathbf{n}}(\mathbf{R}_j)) + q_2 \mathbf{Q}_B(\hat{\mathbf{m}}(\mathbf{R}_j), \hat{\mathbf{l}}(\mathbf{R}_j)),\end{aligned}\quad (7)$$

where $\{\hat{\mathbf{n}}(\mathbf{R}_j), \hat{\mathbf{m}}(\mathbf{R}_j), \hat{\mathbf{l}}(\mathbf{R}_j)\}$ are the three local directors at the position $\mathbf{R}_j$ of the midpoint of the j -th arm ($j = A, B$), and where q_0 and q_2 are the uniaxial and biaxial order parameters of an arm, respectively. The local directors are identified with eigenvectors of the $\bar{\mathbf{Q}}$ tensor and the corresponding eigenvalues⁴¹ are given by $\mu_m = -q_0/\sqrt{6} + q_2/\sqrt{2}$, $\mu_l = -q_0/\sqrt{6} - q_2/\sqrt{2}$ and $\mu_n = -\mu_m - \mu_l = \sqrt{2/3}q_0$. From this perspective the locally isotropic phase is met when all three eigenvalues of $\bar{\mathbf{Q}}$ are equal, which means $\bar{\mathbf{Q}} \equiv \mathbf{0}$. For the local $D_{\infty h}$ -symmetric uniaxial states two out of three eigenvalues of $\bar{\mathbf{Q}}$ are equal, i.e., $q_0 \neq 0$, $q_2 = 0$ or $q_0 \neq 0$, $q_2 = \sqrt{3}q_0$ or $q_0 \neq 0$, $q_2 = -\sqrt{3}q_0$. In the general case, $\bar{\mathbf{Q}}$ has three different real eigenvalues that correspond to the local D_{2h} -symmetric biaxial state.

Finally, we can write down a full mean-field potential as a natural extension of that proposed by GLF.¹ It reads

$$H_{\text{MF}}(\Omega) = -\varepsilon \text{Tr}[\mathbf{Q}(\Omega_A) \cdot \bar{\mathbf{Q}}(\mathbf{R}_A) + \mathbf{Q}(\Omega_B) \cdot \bar{\mathbf{Q}}(\mathbf{R}_B)], \quad (8)$$

where ε is the coupling constant, ‘ $\cdot$ ’ denotes matrix multiplication and Ω stands for the molecular orientation expressed in terms of Euler angles that define this orientation in a local $\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}\}$ frame. The corresponding mean-field equilibrium free energy per particle resulting from the orientational degrees of freedom is given by:

$$f = q_0^2 + q_2^2 - t^* \ln Z, \quad (9)$$

where Z is the orientational one-particle partition function:

$$Z = \int e^{-H_{\text{MF}}(\Omega)/t^*} d\Omega, \quad (10)$$

and where $t^* \stackrel{\text{def}}{=} k_B T / \varepsilon$ is the (dimensionless) reduced temperature. Orientational averages of any one-particle quantity $X(\Omega)$ are calculated in a standard way as:

$$\langle X(\Omega) \rangle = \frac{1}{Z} \int X(\Omega) e^{-H_{\text{MF}}(\Omega)/t^*} d\Omega. \quad (11)$$

Taking the parametric form (1)–(3) and (7) of the alignment tensor $\bar{\mathbf{Q}}$, the equilibrium structure can be obtained by the minimization of the free energy, eqn (9), with respect to the order parameters q_0 and q_2 and the ‘‘local environment’’ parameters θ and p . The former ones are given self-consistently by:

$$q_n = \frac{1}{2} (q_n(\{\mathbf{R}_A\}, \Omega_A) + q_n(\{\mathbf{R}_B\}, \Omega_B)), \quad n = 0, 2, \quad (12)$$

where the orientational averaging applies to the symmetry adapted functions which are given in a typical form:^{39,41}

$$\begin{aligned}q_0(\{\mathbf{R}_k\}, \Omega_k) &= -\frac{1}{2} + \frac{3}{2} (\hat{\mathbf{n}}(\mathbf{R}_k) \cdot \hat{\mathbf{c}}_k)^2 \\ &+ \lambda \sqrt{\frac{3}{2}} [(\hat{\mathbf{n}}(\mathbf{R}_k) \cdot \hat{\mathbf{a}}_k)^2 - (\hat{\mathbf{n}}(\mathbf{R}_k) \cdot \hat{\mathbf{b}}_k)^2],\end{aligned}\quad (13)$$

$$\begin{aligned}q_2(\{\mathbf{R}_k\}, \Omega_k) &= \frac{\sqrt{3}}{2} [(\hat{\mathbf{l}}(\mathbf{R}_k) \cdot \hat{\mathbf{c}}_k)^2 - (\hat{\mathbf{m}}(\mathbf{R}_k) \cdot \hat{\mathbf{c}}_k)^2] \\ &+ \lambda \sqrt{2} [(\hat{\mathbf{l}}(\mathbf{R}_k) \cdot \hat{\mathbf{a}}_k)^2 + (\hat{\mathbf{m}}(\mathbf{R}_k) \cdot \hat{\mathbf{b}}_k)^2 \\ &- \frac{1}{2} (\hat{\mathbf{n}}(\mathbf{R}_k) \cdot \hat{\mathbf{c}}_k)^2 - \frac{1}{2}],\end{aligned}\quad (14)$$

and where the symbol $\{\mathbf{R}_k\} \stackrel{\text{def}}{=} \{\hat{\mathbf{n}}(\mathbf{R}_k), \hat{\mathbf{m}}(\mathbf{R}_k), \hat{\mathbf{l}}(\mathbf{R}_k)\}$ stands for the right-handed tripod of the directors ($k = A, B$).

Before going further it seems appropriate to discuss similarities and differences between the present model (8) and that of GLF. To this end we rewrite the GLF Hamiltonian in our notation:

$$H_{\text{MF}}^{\text{GLF}} = -\varepsilon \text{Tr}[\mathbf{Q}_U(\hat{\mathbf{c}}_A) \cdot \bar{\mathbf{Q}}_U(\mathbf{R}_A) + \mathbf{Q}_U(\hat{\mathbf{c}}_B) \cdot \bar{\mathbf{Q}}_U(\mathbf{R}_B)]. \quad (15)$$

The form of the $\bar{\mathbf{Q}}_U$ and $\bar{\mathbf{Q}}$ tensors accounts in both models for the global D_{∞} symmetry point group of the N_{TB} phase with the (optical) C_{∞} axis parallel to the helix axis.^{11,42} N_{TB} is also invariant for the twofold rotation around a local vector $\hat{\mathbf{m}}$, where $\hat{\mathbf{m}}$ is perpendicular to the plane containing the helix axis $\hat{\mathbf{z}}$ and the local director. This local C_2 symmetry causes N_{TB} to be locally polar. As $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$ and $\hat{\mathbf{k}}$ are linearly independent the structure is also locally biaxial.

The difference between the two models lies in the primary order parameters entering the heliconical variational ansatz (7) on the N_{TB} structure. While in the GLF model the conical twist-bend helix $\bar{\mathbf{Q}}_U$ is approximated by a locally uniaxial distortion of the director field weighted by q_0 , our $\bar{\mathbf{Q}}$ tensor comprises a full set of the directors (1)–(3) which, along with the variational parameters q_0 and q_2 , permits the helix to be locally biaxial. Both order parameters, q_0 and q_2 , can be determined experimentally along the effective optical axis $\mathbf{k} \parallel \langle \hat{\mathbf{n}} \rangle_p$,^{16,17,19} which is an eigenvector of $\langle \bar{\mathbf{Q}} \rangle_p$, where $\langle \dots \rangle_p$ denotes the average over one period p along $\mathbf{k}$. Indeed, the averaged alignment tensor $\langle \bar{\mathbf{Q}} \rangle_p$ is diagonal, uniaxial and of zero trace, and the eigenvector $\langle \hat{\mathbf{n}} \rangle_p$ corresponds to the non-degenerate eigenvalue Λ_k , given by a linear combination of q_0 and q_2 :

$$\Lambda_k = \frac{q_0(3\cos(2\theta) + 1)}{2\sqrt{6}} + \frac{q_2\sin^2(\theta)}{\sqrt{2}}. \quad (16)$$

Our extension is also important as it obeys two nematic phases, uniaxial and biaxial, both recovered for pitch $p \rightarrow \infty$, while in the GLF model only a uniaxial nematic phase is present. A further difference between the models concerns the treatment of molecular biaxiality, which we discuss below.

2.3 Effective molecular shape in the nematic limit

V-shaped molecules of both models are biaxial due to their C_{2v} symmetry. In the GLF model they are represented by two uniaxial arms with a bend angle χ , while our model permits molecular arms to be biaxial, with the arm's biaxiality controlled by λ . Clearly, in both cases the total molecule is biaxial, but the model (8) allows for full control of a composite molecular biaxiality. In order to illustrate this, we study the effective molecular shape of the two models as seen in the nematic

limit ($\phi = 0$ in eqn (1)–(3)). Since in this limit directors become positionally independent, it implies that $\bar{\mathbf{Q}}(\mathbf{R}_A) = \bar{\mathbf{Q}}(\mathbf{R}_B) \stackrel{\text{def}}{=} \bar{\mathbf{Q}}$ and

$$H_{\text{MF,N}}(\Omega) = -\varepsilon \text{Tr}[(\mathbf{Q}(\Omega_A) + \mathbf{Q}(\Omega_B)) \cdot \bar{\mathbf{Q}}]. \quad (17)$$

That is, with the nematic ansatz the segmental mean-field model (8) can be mapped into a single site, mean-field version of the dispersion model,³⁹ where the bent-shaped molecule is represented by an effective molecular quadrupolar tensor

$$\mathbf{Q}_{\text{mol}} \stackrel{\text{def}}{=} \mathbf{Q}(\Omega_A) + \mathbf{Q}(\Omega_B). \quad (18)$$

The $\mathbf{Q}_{\text{mol}}$ tensor is biaxial, also for the GLF model of $\lambda = 0$. The biaxiality of $\mathbf{Q}_{\text{mol}}$ can be quantified by calculating the invariant, normalized biaxiality parameter $w = \sqrt{6} \text{Tr}[\mathbf{Q}_{\text{mol}}^3] / \text{Tr}[\mathbf{Q}_{\text{mol}}^2]^{3/2}$ ($w^2 \leq 1$).^{39,41} It reads

$$w = \frac{3\sqrt{6}(2\lambda^2 + 1)\lambda \sin^2(\chi) + (9 - 30\lambda^2)\cos^2(\chi) - 18\lambda^2 - 1}{(\lambda^2 \cos(2\chi) + 7\lambda^2 - 2\sqrt{6}\lambda \sin^2(\chi) + 3\cos^2(\chi) + 1)^{3/2}}. \quad (19)$$

For the uniaxial states $w^2 = 1$, whereas nonzero biaxiality is monitored by $w^2 < 1$ approaching the maximal value for $w = 0$. The case $w > 0$ ($w < 0$) corresponds to prolate (oblate) states of $\mathbf{Q}_{\text{mol}}$. The variation of w with the angle between the two arms calculated from eqn (19) for a selection of the values of the λ parameter is given in Fig. 2.

For the GLF model ($\lambda = 0$) the V-shaped molecule exhibits an effectively disc-like uniaxial shape at $\chi = 90^\circ$, which evolves to a rod-like uniaxial one at $\chi = 180^\circ$. The curve in the (w, χ) plane passes through zero, the point of maximal molecular biaxiality, when the bend angle is equal to the tetrahedral value ($\chi = \arccos(-1/3) \cong 109.47^\circ$). In spite of this molecular biaxiality the GLF ansatz (15) permits only uniaxial structures, which excludes *e.g.* the biaxial nematic phase.

For $\lambda > 0$ the effective molecular biaxiality can be made less dependent on χ and already for $\lambda \gtrsim 0.15$ the arm-induced biaxiality starts prevailing over steric biaxiality. In the limit of the maximal biaxial arms ($\lambda = 1/\sqrt{6}$), the effective molecule

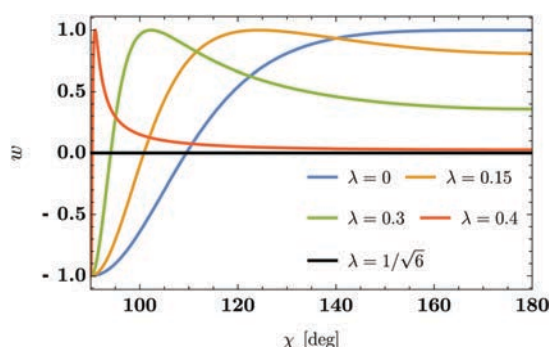


Fig. 2 Molecular biaxiality parameter (19) in the nematic phase as a function of the bend angle for λ equal to: 0 (blue), 0.15 (orange), 0.3 (green), 0.4 (red) and $1/\sqrt{6}$ (black).

becomes maximally biaxial irrespective of the angle between the arms. Hence, the simple mean-field model (8) with only two molecular parameters, λ and χ , allows us to control almost independently molecular anisotropy and the angle between the arms. They both seem primary to the liquid crystal behavior of bent-core, dimeric and trimeric mesogens, especially in the view that compounds composed of these molecules are also candidates to exhibit the elusive biaxial nematic phase.

3 Results

Throughout the remaining discussion, we use the following notation for the phases: N_U for the uniaxial nematic phase, N_B for the biaxial nematic phase, N_{TB} for the twist-bend nematic phase with a heliconical uniaxial ansatz ($\bar{\mathbf{Q}}_U$), $N_{TB,B}$ for the twist-bend nematic phase with a heliconical biaxial ansatz ($\bar{\mathbf{Q}}$) and Iso for the isotropic phase.

Phase diagrams for the banana-shaped biaxial molecules for three typical values: 130° , 135° and 140° of the bend angle χ are presented in Fig. 3. For $\chi = 130^\circ$ three phases: N_{TB} , $N_{TB,B}$, and Iso become stable for λ ranging from 0 to the so-called self-dual point,³⁹ where $\lambda = 1/\sqrt{6}$. In Fig. 3a the $N_{TB,B}$ phase becomes stable below the uniaxial N_{TB} with the phase sequence: Iso $\rightarrow$ N_{TB} $\rightarrow$ $N_{TB,B}$, or directly below Iso through the sequence: Iso $\rightarrow$ $N_{TB,B}$. Widening the bend angle (see Fig. 3b and c) leads to stable regions of the N_U and even N_B phases, although N_B is visible only in a very narrow region of λ (in the closest vicinity of the self-dual point) for $\chi = 140^\circ$. Apart from the phase transitions that are present for $\chi = 130^\circ$ we can identify the following sequences: Iso $\rightarrow$ $N_U \rightarrow N_{TB} \rightarrow N_{TB,B}$, Iso $\rightarrow$ $N_U \rightarrow N_B \rightarrow N_{TB,B}$ and Iso $\rightarrow$ $N_B \rightarrow N_{TB,B}$. The broadening of the regions of the nematic phases, both uniaxial and biaxial, starts with a further widening of the bend angle ($\chi > 140^\circ$), where the more ordered twist-bend nematics are moved to lower temperatures, similar to the tetrahedral nematic phases.^{43–45} Interestingly, for $\chi \lesssim 140^\circ$ the twist-bend nematic phase is always more stable than N_B .

In order to better understand the identified phases, we have analyzed temperature variations of the uniaxial (q_0) and biaxial (q_2) order parameters, tilt angle (θ) and pitch (p) for the selected cases. Additionally, we have calculated the order parameter $\langle \hat{\mathbf{w}} \cdot \hat{\mathbf{n}}(z = R_C) \rangle$, which gives a signature of polar order in the system, and hence allows us to identify the nematic twist-bend phases. Fig. 4 shows exemplary results for the Iso $\rightarrow$ $N_{TB,B}$ phase sequence, where discontinuity in all parameters indicates the first order phase transition between these phases. The tilt angle in N_{TB} tends to $\theta = 25^\circ$ and the pitch is almost constant, smaller than the length of a stretched molecule.

These results are very close to the exact value for θ that can be obtained for the ground state ($t^* = 0$):

$$\theta(t^* = 0) = \frac{1}{2}(180^\circ - \chi). \quad (20)$$

Indeed, the substitution of $\chi = 130^\circ$ gives 25° for θ in this limit. The relation (20), being valid for the arbitrary bend angle χ , is also regained for θ in the bottom panel of Fig. 5. Concerning the pitch of the twist-bend phase, it should never exceed

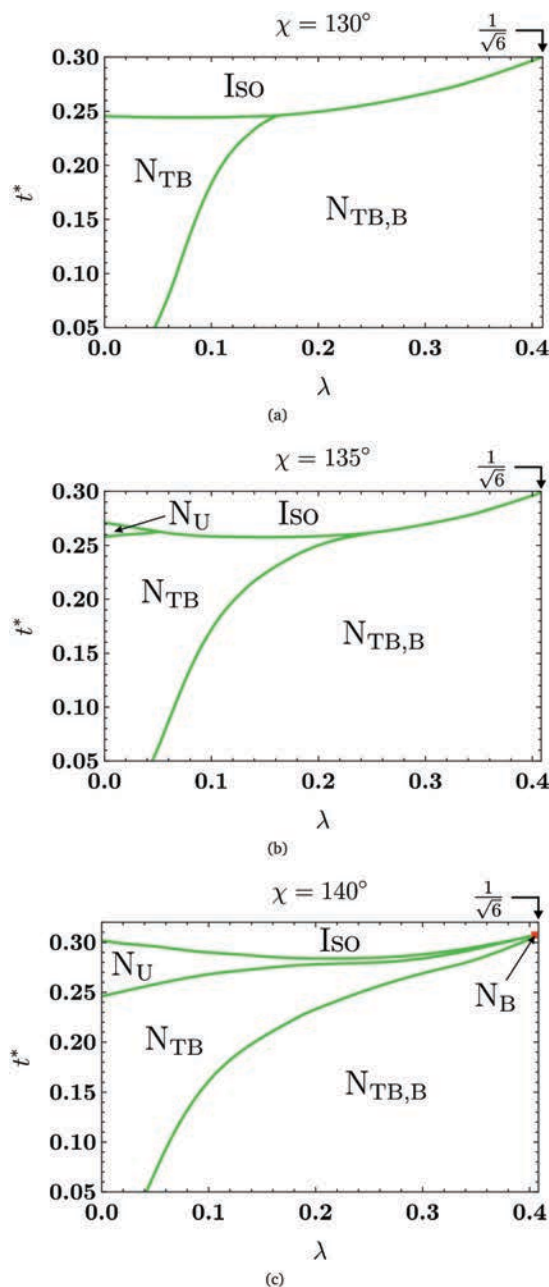


Fig. 3 Phase diagrams on the (λ, t^*) plane for bend angles equal to (a) 130° , (b) 135° and (c) 140° . The red square in panel (c) represents the tiny region where the stable N_B phase occurs; its area enhances with a further increase of the bending angle χ .

4L in the ground state, but can be larger than this value for high temperatures. This is illustrated in Fig. 5, where the pitch becomes divergent in the vicinity of the $N_{TB} \leftrightarrow N_U$ phase transition.

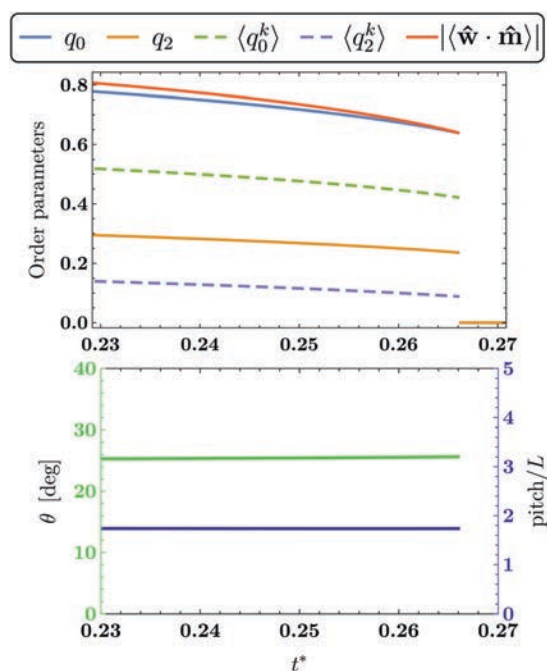


Fig. 4 Behavior of order parameters, tilt angle and pitch for phase transition $Iso \rightarrow N_{TB,B}$ when $\lambda = 0.3$ and $\chi = 130^\circ$. q_0 and q_2 are obtained by the direct minimization of the free energy (9). $\langle q_0^k \rangle$ and $\langle q_2^k \rangle$ are uniaxial and biaxial order parameters calculated with respect to the wave vector $\mathbf{k}$, and $|\langle \hat{\mathbf{w}} \cdot \hat{\mathbf{m}} \rangle| \stackrel{\text{def}}{=} |\langle \hat{\mathbf{w}} \cdot \hat{\mathbf{m}}(z = R_C) \rangle|$ is the modulus of the polar order parameter.

The phase diagram (Fig. 3c) is especially rich in sequence of phase transitions. More specifically, we can identify first order phase transitions between the $N_{TB,B}$ and N_{TB} phases and between the N_U and Iso phases with discontinuity in the order parameters (Fig. 5), and the second order phase transition between N_{TB} and N_U . The second-order nature of the $N_{TB} \leftrightarrow N_U$ transition can be recognized from the temperature variations of the conical angle and pitch, where the first goes continuously to zero while the latter diverges at the transition point. We also calculate the mean values of the uniaxial ($\langle q_0^k \rangle$) and biaxial ($\langle q_2^k \rangle$) order parameters with respect to the optical axis ($\hat{\mathbf{k}} = \mathbf{k}/k$) reference frame: $\{\mathbf{R}_{\hat{\mathbf{k}}}\} \stackrel{\text{def}}{=} \{\hat{\mathbf{k}}, \hat{\mathbf{m}}(z = R_C), \hat{\mathbf{k}} \times \hat{\mathbf{m}}(z = R_C)\}$. The following averages need to be determined:

$$\langle q_n^k \rangle = \frac{1}{2} \langle q_n(\{\mathbf{R}_{\hat{\mathbf{k}}}\}, \Omega_A) + q_n(\{\mathbf{R}_{\hat{\mathbf{k}}}\}, \Omega_B) \rangle, \quad n = 0, 2. \quad (21)$$

In the homogeneous N_U phase we expect $\langle q_0^k \rangle = q_0$, which should hold for any non-tilted phase.^{46–48} The same relation is fulfilled by the mean value of the biaxial order parameters q_2 and $\langle q_2^k \rangle$ in the N_B phase. Note, however, the discrepancies between the order parameters of the twist-bend phases calculated in various reference frames. Locally in the arm reference frames q_2 is zero in the N_{TB} phase, while in the $\hat{\mathbf{k}}$ -frame both $\langle q_0^k \rangle$ and $\langle q_2^k \rangle$ are nonzero for any twist-bend phase.

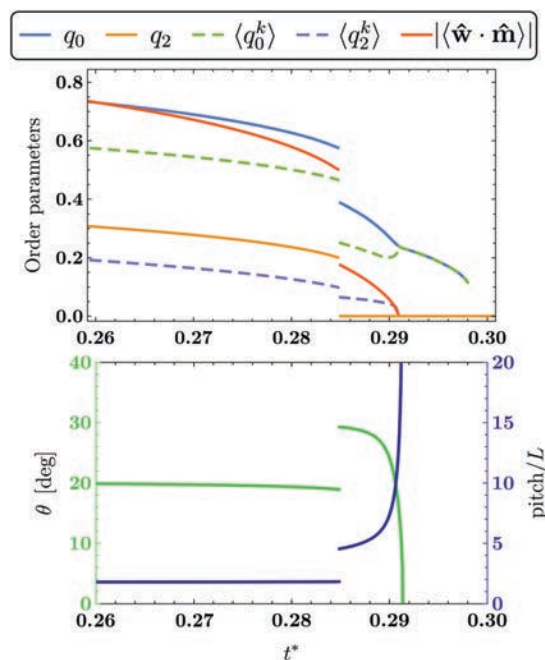


Fig. 5 Behavior of the order parameters, tilt angle and pitch for Iso $\rightarrow$ $N_U \rightarrow N_{TB} \rightarrow N_{TB,B}$ phase transitions when $\lambda = 0.36$ and $\chi = 140^\circ$. For further details see caption to Fig. 4.

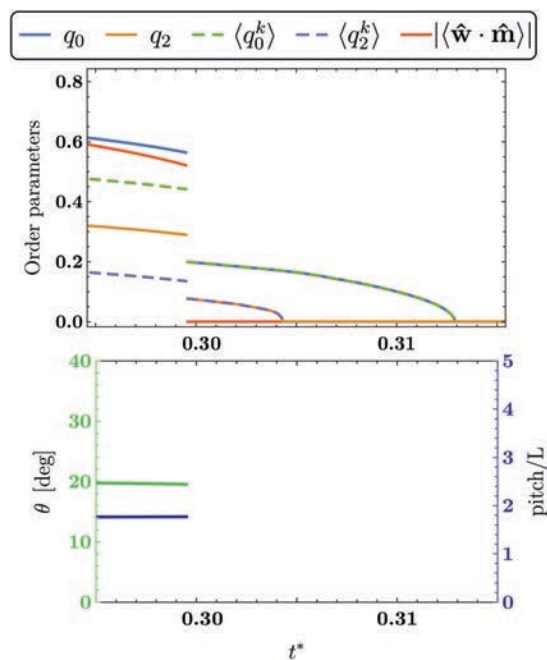


Fig. 7 Behavior of the order parameters, tilt angle and pitch for the sequence of phase transitions Iso $\rightarrow N_U \rightarrow N_B \rightarrow N_{TB,B}$ when $\lambda = 0.408$ and $\chi = 140^\circ$. For further details see the caption to Fig. 4.

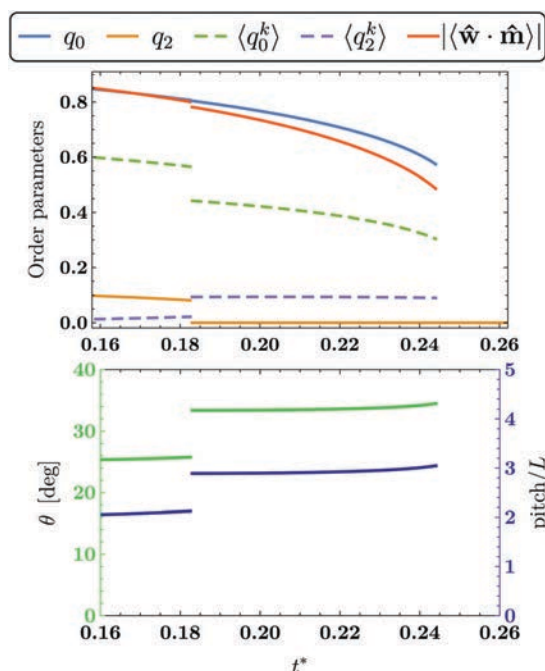


Fig. 6 Behavior of the order parameters, tilt angle and pitch for the phase transitions Iso $\rightarrow N_{TB} \rightarrow N_{TB,B}$ when $\lambda = 0.1$ and $\chi = 130^\circ$. For further details see the caption to Fig. 4.

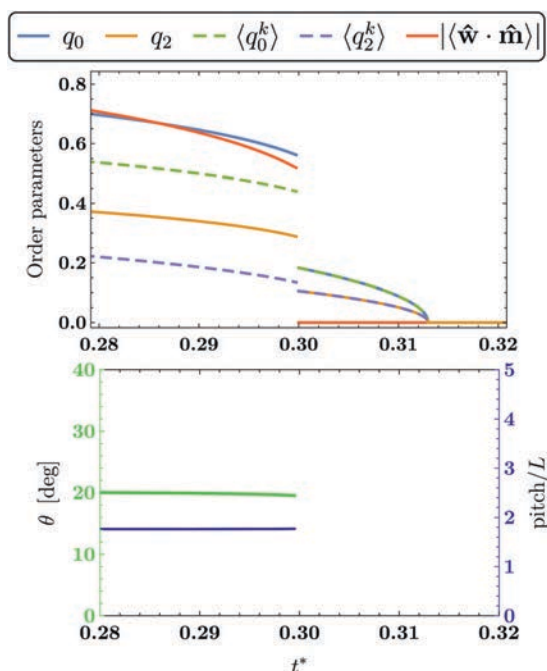


Fig. 8 Behavior of the order parameters, tilt angle and pitch for the successive phase transitions: Iso $\rightarrow N_B \rightarrow N_{TB,B}$ when $\lambda = 1/\sqrt{6}$ and $\chi = 140^\circ$. For further details see the caption to Fig. 4.

Further examples of phase sequences are presented in Fig. 6–8, where the $N_B \leftrightarrow N_{TB,B}$ phase transition is of first order, while $N_U \leftrightarrow N_B$ and $Iso \leftrightarrow N_B$ are of second order.^{39–41,43–46,49,50} Interestingly, the conical angle and the pitch in N_{TB} are *ca.* 1.3 to 1.5 and 0.8 to 2.5 times larger, respectively, than those in $N_{TB,B}$ (see Fig. 5 and 6). Both twist-bend nematic phases are strongly polar, however the $N_{TB,B}$ phase is favorably more polar. Additionally, it is also noticeable that depending on the value of the bending angle χ and biaxiality parameter λ the transition between $N_{TB,B} \leftrightarrow N_{TB}$ may be characterized by a significant (Fig. 5) or slight (Fig. 6) decrease in the values of the polar order parameter.

Fig. 7 shows a magnification of the phase sequence for $\chi = 140^\circ$ in the proximity of the self-dual point (red square in Fig. 3c). A noticeable feature of this region is the high biaxiality of the molecular arms. Though the biaxial phases play a dominant role here, in a small temperature interval, in addition to the N_B and $N_{TB,B}$ phases, it is possible to stabilize the N_U phase, as well. The last plot (Fig. 8) depicts a phase transition between N_B and $N_{TB,B}$ at the self-dual point ($\lambda = 1/\sqrt{6}$) for the arms at $\chi = 140^\circ$. Here the bent-core molecular arms are maximally biaxial (*i.e.* they are neither prolate nor oblate). The $N_B \leftrightarrow N_{TB,B}$ phase transition is first order as can be deduced from a discontinuity in all of the order parameters (see Fig. 7 and 8).

4 Summary

In conclusion, we analyzed an extension of the generic GLF mean-field model¹ to study the role that biaxiality of the V-shaped molecules can play in the stabilization of N_{TB} relative to the nematic and isotropic phases. We assumed that each of the two arms of a bent-shaped molecule is intrinsically biaxial and took the local biaxial ansatz for the alignment tensor. In the limit of the uniaxial particles ($\chi = 0^\circ, 180^\circ$ and $\lambda = 0$) we recover the mean-field results of Maier and Saupe. For ordinary biaxial molecules ($\chi = 0^\circ, 180^\circ$ and $\lambda \neq 0$) the model becomes reduced to the mean-field version of the well known Lebwohl–Lasher dispersion model.^{39,50} As all bent-core molecules are biaxial⁵¹ our generalization seems important because it allows us to control intrinsic molecular biaxiality (by two molecular features: bend angle and arm anisotropy).

We showed that in our extended model, in addition to N_U and N_{TB} , two extra phases: homogeneous N_B and periodic $N_{TB,B}$ – the analog of N_{TB} with a local biaxial order of the molecular arms – can be studied, where N_B appears in a natural way as a limiting case of $N_{TB,B}$. For small bend angles the phase diagram becomes dominated by the $N_{TB,B}$ phase with no homogeneous nematics present, even for a relatively small molecular biaxiality ($\lambda \lesssim 0.18$). Here, both of the twist-bend structures are reachable directly from the isotropic phase, similar to recently reported experiments.^{15,52} Widening the bend angle opens the path for the stabilization of standard nematics, where they start to dominate over less conventional phases as in ref. 43–45. However, the stable N_B phase is not found for $\chi \lesssim 140^\circ$.

One can see from Fig. 4–8 that the asymptotic relation for the tilt angle (20) is actually the limit for θ in the $N_{TB,B}$ phase,

as this structure is a ground state for $0 < \lambda \leq 1/\sqrt{6}$. At the transition between the two twist-bend nematics both the pitch and the cone angle in $N_{TB,B}$ are smaller than in the N_{TB} phase.

Finally, the model introduced in this paper can be extended further to include competition between such molecular/external factors as (steric/electric) dipolar forces and external field(s).^{46,53,54} Then, further nematic structures with one-dimensional modulation are also expected.^{24–29,55,56}

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Article 2

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Role of molecular bend angle and biaxiality in the stabilization of the twist-bend nematic phase†

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What are the prerequisites for acquiring a stable twist-bend nematic phase (N_{TB})? Addressing this question has led to the synthesis of a vast number of new compounds, concluding each time that the molecule's shape is one of the predominant factors. Inspired by the expanding knowledge of different achiral bent-shaped molecules forming a twist-bend nematic phase, we reinvestigate the interplay between a molecule's bend angle and a molecule's arms molecular biaxiality. Employing our previously developed generalized mean-field model, we explore more obtuse bend angles. We observe direct phase transition sequences between locally biaxial and uniaxial variants of N_{TB} , along with biaxial and uniaxial nematic phases. Additionally, we present a comprehensive overview of how phase diagrams evolve according to alterations in the value of the bend angle and the magnitude of biaxiality.

Twist-bend nematic (N_{TB}) is a one dimensional modulated phase, which forms through spontaneous chiral symmetry breaking in the isotropic and nematic phases of liquid crystalline systems. As it contradicted common knowledge, the discovery of N_{TB} engulfed the interest of the worldwide liquid crystal community.¹ In N_{TB} , the nematic director $\hat{n}$ is spontaneously distorted:

$$\hat{n}(z) = [-\sin(\theta)\sin(\phi), \sin(\theta)\cos(\phi), \cos(\theta)], \quad (1)$$

where θ is the conical angle, and $\phi = kz = 2\pi z/p$ is the azimuthal angle associated with the wavevector $\mathbf{k} = k\hat{z}$ ($k = \pm 2\pi/p$) and period p . This distortion leads to the formation of a conical helix (like in the smectic C^* , but without long-range positional order of molecules) with a nanoscale period. The $\pm$ sign indicates the degeneracy in the handedness of chiral domains (either left- or right-handed), called ambidextrous chirality.

Conclusions drawn from the theoretical foundations provided by Meyer² and Dozov³ regarding the influence of flexopolarization and conditions imposed on elastic constants indicated that the emergence of N_{TB} can be facilitated by the structure of a properly

“bent” molecule. Thus, the first compound that exhibited long sought-after N_{TB} was a dimer, 4',4'-(heptane-1,7-diyl)bis([1',1'-biphenyl]-4"-carbonitrile) (abbreviated as CB7CB^{4–6}), where two 4-cyanobiphenyls (CB) are linked by an alkylene spacer (C_7H_{14}). CB7CB is a member of the 1,ω-bis(4-cyanobiphenyl-4'-yl) alkane homologous series, which is denoted by the acronym CB n CB, where n refers to the number of methylene units in the flexible spacer. Within this series, only molecules with an odd number of methylene units in the spacer are able to form N_{TB} .⁷

Further, structure-focused,^{8–13} research solidified the molecular curvature as one of the profound driving forces in the stabilization of N_{TB} . Even a small change in molecular structure, like taking CB7CB and substituting each of the methylene units linked with the 4-cyanobiphenyls by oxygen or sulfur,¹⁴ can result in a substantial modification of the molecule's average bend. Since the discovery of N_{TB} , the “family of compounds” capable of forming this phase has been expanded, *i.e.* by hybrid bent-core LC trimers,¹⁵ hydrogen-bonded oligomers,¹⁶ a duplexed hexamer,¹⁷ trimers, oligomers and polymers.^{18–20} Moreover, due to the tremendous interest in resolving the ambiguities linked to the structural features of N_{TB} , new phases have been discovered: twist-bend smectic C (SmC_{TB})²¹ and twist-grain-boundary-twist-bend (TGB_{TB}).²²

Inspired by continuing advances in the synthesis of new N_{TB} -forming compounds with different degrees of molecule's core bent,^{14,23–26} we reinvestigate our generalized mean-field model²⁷ for V-shaped molecules.

We start our considerations by recalling the assumptions of the model. Molecular reference frames are constructed out of two mesogenic arms, A and B , each of length L , arranged reciprocally at an angle χ (Fig. 1). It is assumed that the precession of $\hat{n}(z)$ is followed by two other directors:

$$\hat{m}(z) = [\cos(\phi), \sin(\phi), 0], \quad (2)$$

$$\hat{l}(z) \equiv \hat{n}(z) \times \hat{m}(z) = [-\cos(\theta)\sin(\phi), \cos(\theta)\cos(\phi), -\sin(\theta)]. \quad (3)$$

This parametrization (eqn (1)–(3)) permits the N_{TB} phase for $0^\circ < \theta < 90^\circ$ and finite pitch p , with wave vector $\mathbf{k}$ being parallel to the $\hat{z}$ axis.

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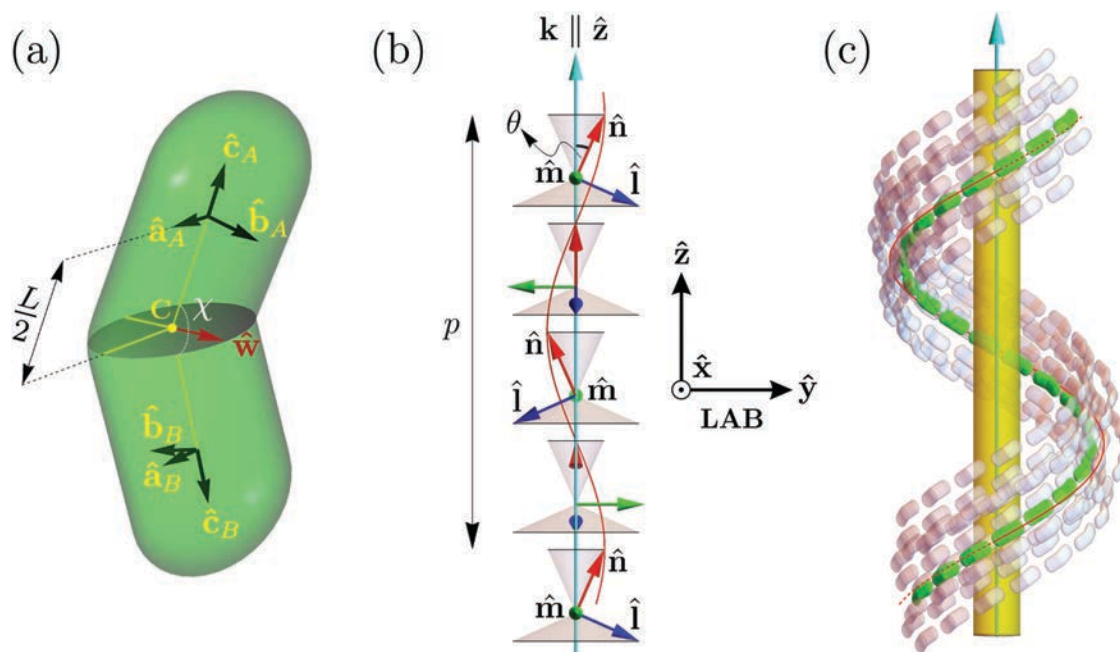


Fig. 1 (a) Features of the bent-shaped molecule adopted within our generalized mean-field model. The lengths of the arms L are taken to be equal. The mutual positioning of the arms is implied by the bend angle χ . The molecular basis for arm A is given by an orthonormal tripod of vectors $\Omega_A = \{\hat{\mathbf{a}}_A, \hat{\mathbf{b}}_A, \hat{\mathbf{c}}_A\}$, and by $\Omega_B = \{\hat{\mathbf{a}}_B, \hat{\mathbf{b}}_B, \hat{\mathbf{c}}_B\}$ for arm B. The molecule's C_2 (molecular) symmetry axis coincides with the unit vector $\hat{\mathbf{w}}$ attached at point C. Figure reproduced from ref. 27 with permission from the Royal Society of Chemistry. (b) Visualization of the local directors used in the mean-field ansatz for the N_{TB} structure, where the local director basis $\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}\}$ on each arm undergoes a helical precession around an axis $\hat{\mathbf{z}}$ ($\phi = kz = (2\pi/p)z$). This structure is characterized by the finite period p , which can also be expressed via wavevector $\mathbf{k}$ ($\mathbf{k} = k\hat{\mathbf{z}} = \pm(2\pi/p)\hat{\mathbf{z}}$) and helical tilt angle θ between the primary director $\hat{\mathbf{n}}$ and the $\mathbf{k}$ axis. (c) Due to the ambidextrous chirality, the N_{TB} helix can be either left- or right-handed. This figure is a schematic depiction of the molecular arrangement in the right-handed N_{TB} phase.

Going forward, the molecular basis is placed at the midpoint of each arm, which will be reflecting the arm's molecular biaxiality. The arms are expressed in terms of a molecular (symmetric and traceless) quadrupolar tensor $\mathbf{Q}$, which is composed of uniaxial ($\mathbf{Q}_U$) and biaxial ($\mathbf{Q}_B$) parts of $D_{\infty h}$ and D_{2h} symmetry, respectively. The expression reads:

$$\mathbf{Q}(\Omega_i) \stackrel{\text{def}}{=} \mathbf{Q}_U(\hat{\mathbf{c}}_i) + \lambda\sqrt{2}\mathbf{Q}_B(\hat{\mathbf{a}}_i, \hat{\mathbf{b}}_i), \quad (4)$$

where

$$\mathbf{Q}_U(\hat{\mathbf{c}}_i) \stackrel{\text{def}}{=} \frac{1}{\sqrt{6}}(3\hat{\mathbf{c}}_i \otimes \hat{\mathbf{c}}_i - \mathbb{1}), \quad (5)$$

$$\mathbf{Q}_B(\hat{\mathbf{a}}_i, \hat{\mathbf{b}}_i) \stackrel{\text{def}}{=} \frac{1}{\sqrt{2}}(\hat{\mathbf{a}}_i \otimes \hat{\mathbf{a}}_i - \hat{\mathbf{b}}_i \otimes \hat{\mathbf{b}}_i), \quad (6)$$

are built out of the right-handed orthonormal tripod $\Omega_i = \{\hat{\mathbf{a}}_i, \hat{\mathbf{b}}_i, \hat{\mathbf{c}}_i\}$ of vectors defining the orientational degrees of freedom of the arm $i = A, B$ (Fig. 1). Parameter λ is a measure of the arm's biaxiality, $\otimes$ denotes the tensor product and $\mathbb{1}$ is the identity matrix.

V-shaped molecules are biaxial due to their C_{2v} symmetry, and this is a shape-originating biaxiality (called λ_{shape}). Thus, for a V-shaped molecule with uniaxial arms, λ_{shape} can be

intertwined with molecule's bend angle χ through the formula:^{28–30}

$$\lambda_{\text{shape}} = \frac{\sqrt{6}(\cos(\chi) + 1)}{2 - 6\cos(\chi)}. \quad (7)$$

In our model, we let the molecular biaxiality of banana-shaped molecules enter not only through their “V” shape, but also through the biaxiality of molecular arms. This extension allows the arms' molecular biaxiality to be treated as an extra parameter characterizing bent-shaped molecules, in addition to the bend angle.

The last element of the molecule's structure is the unit vector $\hat{\mathbf{w}}$ at the center (C) of the molecule (associated with the molecular C_2 axis, see Fig. 1a), which, combined with $\hat{\mathbf{m}}$ through calculating $\langle \hat{\mathbf{w}} \cdot \hat{\mathbf{m}}(z = R_C) \rangle$, gives an indication of the polar order in the system.

In the next step the director basis is constructed:

$$\bar{\mathbf{Q}}(R_i) = \bar{\mathbf{Q}}_U(R_i) + \bar{\mathbf{Q}}_B(R_i) = q_0\mathbf{Q}_U(\hat{\mathbf{n}}(R_i)) + q_2\mathbf{Q}_B(\hat{\mathbf{m}}(R_i), \hat{\mathbf{l}}(R_i)), \quad (8)$$

wherein $\{\hat{\mathbf{n}}(R_i), \hat{\mathbf{m}}(R_i), \hat{\mathbf{l}}(R_i)\}$ are three local directors at the position R_i of the midpoint of the i -th arm ($i = A, B$), and q_0 and q_2 are the uniaxial and biaxial order parameters of an arm, respectively. The local directors are identified with eigenvectors

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of the $\bar{\mathbf{Q}}$ tensor and the corresponding eigenvalues³¹ are given by $\mu_m = -q_0/\sqrt{6} + q_2/\sqrt{2}$, $\mu_l = -q_0/\sqrt{6} - q_2/\sqrt{2}$ and $\mu_n = -\mu_m - \mu_l = \sqrt{2/3}q_0$. In this framework the locally isotropic phase is realized when all three eigenvalues of $\bar{\mathbf{Q}}$ are equal ($\bar{\mathbf{Q}} \equiv \mathbf{0}$). On the other hand, when two out of the three eigenvalues of $\bar{\mathbf{Q}}$ are identical, i.e. $q_0 \neq 0, q_2 = 0$ or $q_0 \neq 0, q_2 = \sqrt{3}q_0$ or $q_0 \neq 0, q_2 = -\sqrt{3}q_0$, then this is referred to as a locally $D_{\infty h}$ -symmetric uniaxial state. Yet the most generic case is described by $\bar{\mathbf{Q}}$ possessing three different real eigenvalues, reflecting the local D_{2h} -symmetric biaxial state. Generally, these properties can be expressed using the inequality:^{31,32}

$$\text{Tr}(\bar{\mathbf{Q}}^2)^3 - 6\text{Tr}(\bar{\mathbf{Q}}^3)^2 \geq 0, \quad (9)$$

which can be denoted with one condition, $w^2 \leq 1$, where:

$$-1 \leq w = \sqrt{6} \frac{\text{Tr}(\bar{\mathbf{Q}}^3)}{\text{Tr}(\bar{\mathbf{Q}}^2)^{3/2}} \leq 1. \quad (10)$$

Thus, w is now a scalar measure of how strongly uniaxial/biaxial the local order is. The edges of eqn (10) are represented by oblate ($w = -1$) and prolate ($w = 1$) uniaxial states, whereas the biaxial state is bounded in between ($w^2 < 1$). In addition, if $w = 0$, this is attributed to a state with so-called “maximal biaxiality”.³³

The complete mean-field Hamiltonian and equilibrium free energy per particle are given by:

$$H_{\text{MF}}(\Omega) = -\varepsilon \text{Tr}[\mathbf{Q}(\Omega_A) \cdot \bar{\mathbf{Q}}(\mathbf{R}_A) + \mathbf{Q}(\Omega_B) \cdot \bar{\mathbf{Q}}(\mathbf{R}_B)] = -\varepsilon A_{\text{MF}}(\Omega), \quad (11)$$

$$f = q_0^2 + q_2^2 - t^* \ln Z, \quad (12)$$

where ε is the coupling constant, ‘.’ denotes matrix multiplication, and Ω stands for the molecular orientation expressed in terms of Euler angles that define this orientation in a local $\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}\}$ frame.

The orientational one-particle partition function Z is given by:

$$Z = \int \exp[-H_{\text{MF}}(\Omega)/(k_B T)] d\Omega = \int \exp[A_{\text{MF}}(\Omega)/t^*] d\Omega, \quad (13)$$

where $t^* \stackrel{\text{def}}{=} k_B T/\varepsilon$ is the (dimensionless) reduced temperature. Orientational averages of any one-particle quantity $X(\Omega)$ are calculated in the usual manner as:

$$\langle X(\Omega) \rangle = \frac{1}{Z} \int X(\Omega) e^{A_{\text{MF}}(\Omega)/t^*} d\Omega. \quad (14)$$

The equilibrium structure can be obtained by taking the parametric form of the alignment tensor $\bar{\mathbf{Q}}$ (eqn (1)–(3) and (8)) and minimizing the free energy, eqn (12), with respect to the

order parameters q_0 and q_2 along with the “local environment” parameters θ and k (see ESI†). The order parameters are given consistently by:

$$q_n = \frac{1}{2} \langle q_n(\{\mathbf{R}_A\}, \Omega_A) + q_n(\{\mathbf{R}_B\}, \Omega_B) \rangle, \quad n = 0, 2, \quad (15)$$

where orientational averaging applies to the symmetry adapted functions given in a basic form:^{31,32}

$$q_0(\{\mathbf{R}_i\}, \Omega_i) = -\frac{1}{2} + \frac{3}{2} (\hat{\mathbf{n}}(\mathbf{R}_i) \cdot \hat{\mathbf{c}}_i)^2 + \lambda \sqrt{\frac{3}{2}} [(\hat{\mathbf{n}}(\mathbf{R}_i) \cdot \hat{\mathbf{a}}_i)^2 - (\hat{\mathbf{n}}(\mathbf{R}_i) \cdot \hat{\mathbf{b}}_i)^2], \quad (16)$$

$$q_2(\{\mathbf{R}_i\}, \Omega_i) = \frac{\sqrt{3}}{2} [(\hat{\mathbf{l}}(\mathbf{R}_i) \cdot \hat{\mathbf{c}}_i)^2 - (\hat{\mathbf{m}}(\mathbf{R}_i) \cdot \hat{\mathbf{c}}_i)^2] + \lambda \sqrt{2} \left[(\hat{\mathbf{l}}(\mathbf{R}_i) \cdot \hat{\mathbf{a}}_i)^2 + (\hat{\mathbf{m}}(\mathbf{R}_i) \cdot \hat{\mathbf{b}}_i)^2 - \frac{1}{2} (\hat{\mathbf{n}}(\mathbf{R}_i) \cdot \hat{\mathbf{c}}_i)^2 - \frac{1}{2} \right], \quad (17)$$

and where the symbol $\{\mathbf{R}_i\} \stackrel{\text{def}}{=} \{\hat{\mathbf{n}}(\mathbf{R}_i), \hat{\mathbf{m}}(\mathbf{R}_i), \hat{\mathbf{l}}(\mathbf{R}_i)\}$ stands for the right-handed tripod of directors ($i = A, B$).

For additional quantitative information about phases, we also calculate the mean values of the uniaxial ($\langle q_0^k \rangle$) and biaxial ($\langle q_2^k \rangle$) order parameters with respect to the modulation axis $\mathbf{k} \parallel \hat{\mathbf{z}}$ ($\hat{\mathbf{k}} = \mathbf{k}/k$) of reference frame $\{\mathbf{R}_{\hat{\mathbf{k}}}\} \stackrel{\text{def}}{=} \{\hat{\mathbf{k}}, \hat{\mathbf{m}}(z = R_C), \hat{\mathbf{k}} \times \hat{\mathbf{m}}(z = R_C)\}$:

$$\langle q_n^k \rangle = \frac{1}{2} \langle q_n(\{\mathbf{R}_{\hat{\mathbf{k}}}\}, \Omega_A) + q_n(\{\mathbf{R}_{\hat{\mathbf{k}}}\}, \Omega_B) \rangle, \quad n = 0, 2. \quad (18)$$

For non-tilted phases ($\theta = 0$) the following relation holds:^{34–36}

$$\langle q_n^k \rangle = q_n \quad n = 0, 2, \quad (19)$$

whereas for tilted phases ($\theta \neq 0$) there will be discrepancies between the order parameters calculated in various reference frames. It means that locally, in the arm reference frames q_2 is zero in the N_{TB} phase, while in the $\hat{\mathbf{k}}$ -frame $\langle q_2^k \rangle$ is non-zero.

The notation for the phases used within the framework of this communication is presented in Table 1.

Fig. 2a shows the phase diagram in the $\{\lambda, t^*\}$ plane for the case where $\chi = 150^\circ$. In this scenario, nematic phases excel over twist-bend nematics through the whole range of λ . Fig. 2b is a magnification of a particularly narrow region of Fig. 2a (bounded by red rectangle), where straight phase transitions occur between all the nematic phases anticipated by the model: $N_U \leftrightarrow N_B \leftrightarrow N_{\text{TB}} \leftrightarrow N_{\text{TB,B}}$. Details of the nature of the sequence are shown in Fig. 3. The subsequent transitions $N_B \leftrightarrow N_{\text{TB}} \leftrightarrow N_{\text{TB,B}}$ are first order with visible discontinuity

Table 1 Five phases described within the generalized mean-field model

Symbol	Description
N_{TB}	Twist-bend nematic phase with a heliconical uniaxial ansatz ($\bar{\mathbf{Q}}_U$)
$N_{\text{TB,B}}$	Twist-bend nematic phase with a heliconical biaxial ansatz ($\bar{\mathbf{Q}}_B$)
N_U	Uniaxial nematic
N_B	Biaxial nematic
I	Isotropic phase

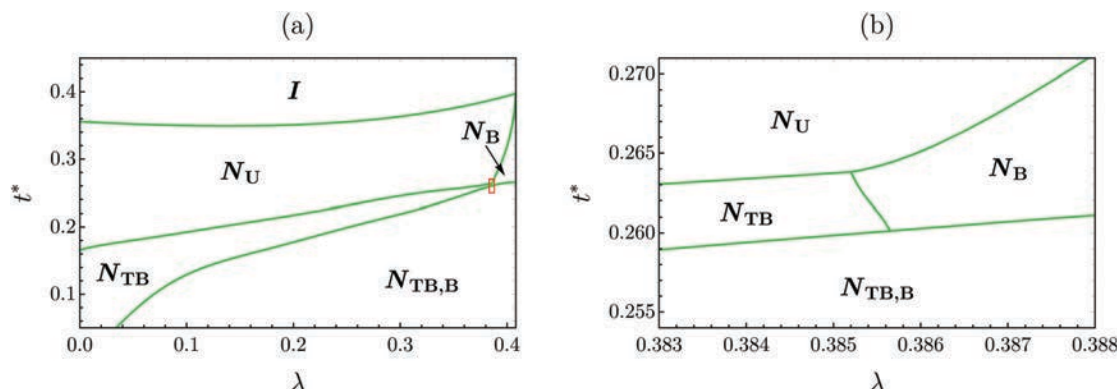


Fig. 2 (a) Phase diagram in the (λ, t^*) plane for bend angle χ equal to 150° . (b) Magnification of area bounded by red rectangle on panel (a) where $N_U \leftrightarrow N_B \leftrightarrow N_{TB} \leftrightarrow N_{TB,B}$ phase transitions occur.

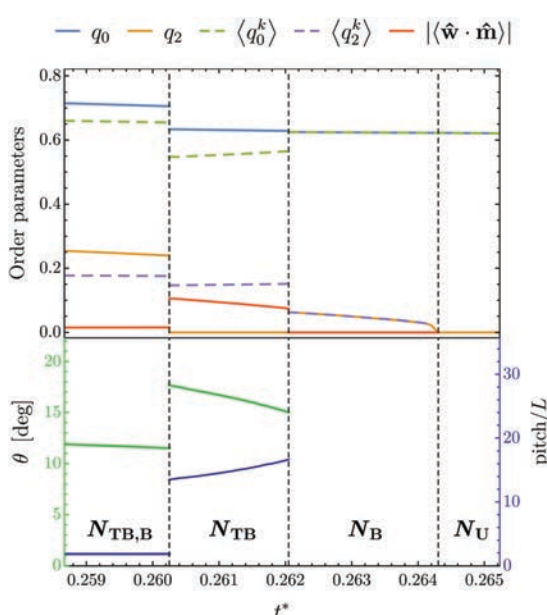


Fig. 3 Behavior of order parameters, tilt angle and pitch for the sequence of phase transitions: $N_U \leftrightarrow N_B \leftrightarrow N_{TB} \leftrightarrow N_{TB,B}$, when $\lambda = 0.3854$ and $\chi = 150^\circ$. Parameters q_0 , q_2 , θ and k are obtained by the direct minimization of the free energy (eqn (12)); $\langle q_0^k \rangle$ and $\langle q_2^k \rangle$ are uniaxial and biaxial order parameters calculated with respect to the wave vector $\mathbf{k}$, and $|\langle \hat{\mathbf{w}} \cdot \hat{\mathbf{m}} \rangle| \stackrel{\text{def}}{=} |\langle \hat{\mathbf{w}} \cdot \hat{\mathbf{m}}(z = R_C) \rangle|$ is the modulus of the polar order parameter.

in the order parameters, whereas $N_U \leftrightarrow N_B$ is a second order phase transition. The attributes of the $N_B \leftrightarrow N_{TB} \leftrightarrow N_{TB,B}$ transitions are similar to those shown in Fig. 5 of ref. 27 for $\lambda = 0.36$ and $\chi = 140^\circ$. Both the tilt angle θ and the pitch are weakly temperature-dependent in $N_{TB,B}$, as opposed to N_{TB} , where the aforementioned parameters strongly depend on the temperature up to the transition to the nematic phase. Additionally, there is a large jump in θ and pitch at the verge of the $N_{TB} \leftrightarrow N_{TB,B}$

phase transition. In the limit $t^* \rightarrow 0$ it has been shown²⁷ that θ obeys the relation:

$$\theta(t^* = 0) = \frac{1}{2}(180^\circ - \chi), \quad (20)$$

which for $\chi = 150^\circ$ yields $\theta = 15^\circ$.

Incrementally increasing the bend angle up to 160° paves the way for the even more dominant presence of nematic phases (Fig. 4a). Shrinkage of the N_{TB} stability range exposes the $N_{TB,B}$ region, which can be reached directly from N_U (Fig. 4b). Hence the phase sequence: $I \leftrightarrow N_U \leftrightarrow N_{TB,B}$, which is a first order phase transition with visible discontinuity in the order parameters (Fig. 5), exhausts the pool of all possible phase transitions within this model.²⁷ One can see that there is a lesser discrepancy between the local set q_0 and that measured with respect to the modulation axis ($\langle q_0^k \rangle$), and the polar order is feeble compared to the scenario with $\chi = 150^\circ$. According to eqn (20), the limiting value of θ for $\chi = 160^\circ$ is 10° (Fig. 5).

For a comprehensive overview, we also investigated how the λ parameter reshapes the “landscape” of respective phase diagrams in the $\{\chi, t^*\}$ plane. We have intentionally focused on χ from 90° to 180° , as all N_{TB} -forming molecules reported to date possess a bend angle which falls within that range. Furthermore, we have chosen a reference set of points lying on the line $\{\chi, t^* = 0.22\}$ (purple points in Fig. 6a–e) in order to analyze the impact of λ on the behavior of tilt angle, pitch and $w(\bar{\mathbf{Q}}(R_A)) \equiv w(\bar{\mathbf{Q}}_A)$ and compare between the phase diagrams.

The data presented in Fig. 6a significantly broadens the results of Greco *et al.*³⁷ and T. T. To *et al.*³⁸ (both are depicted in Fig. 2 herein³⁸), which were carried out with a uniaxial approach ($\lambda = 0$). Here, all occurring nematic phases are locally uniaxial (N_U^+ , prolate) and N_{TB} is visibly predominant over the range of N_U^- (oblate) and N_B . Direct $I \leftrightarrow N_{TB}$ occurs for $\chi \in [90^\circ, 132^\circ]$ and $I \leftrightarrow N_U$ for $\chi = 180^\circ$, whereas for $\chi \in (132^\circ, 180^\circ)$ the following phase sequence occurs: $I \leftrightarrow N_U \leftrightarrow N_{TB}$. The tilt angle decreases approximately linearly with the increasing bend angle, in contrast to the pitch, which increases with the augmentation of the bend angle up to the phase transition to N_U .

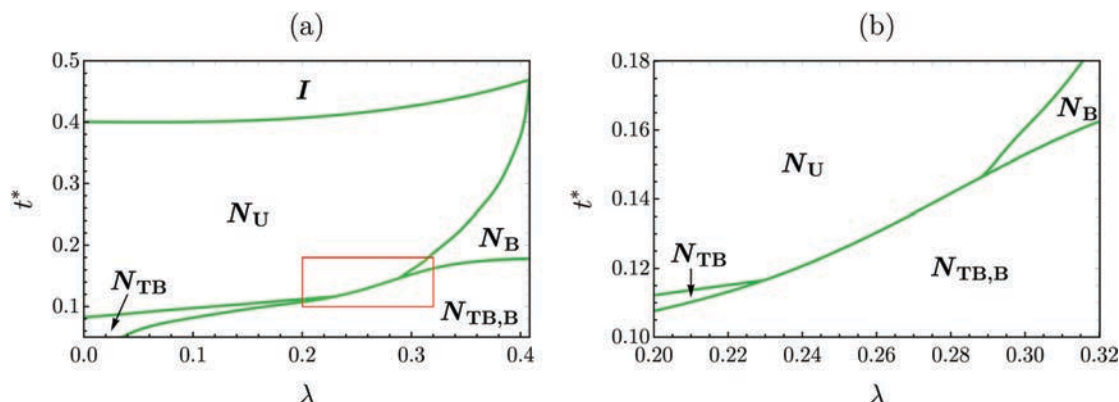


Fig. 4 (a) Phase diagram in the $\{\lambda, t^*\}$ plane for bend angle χ equal to 160° . (b) Magnification of area bounded by red rectangle on panel (a) where $N_U \leftrightarrow N_{TB,B}$ phase transition occurs.

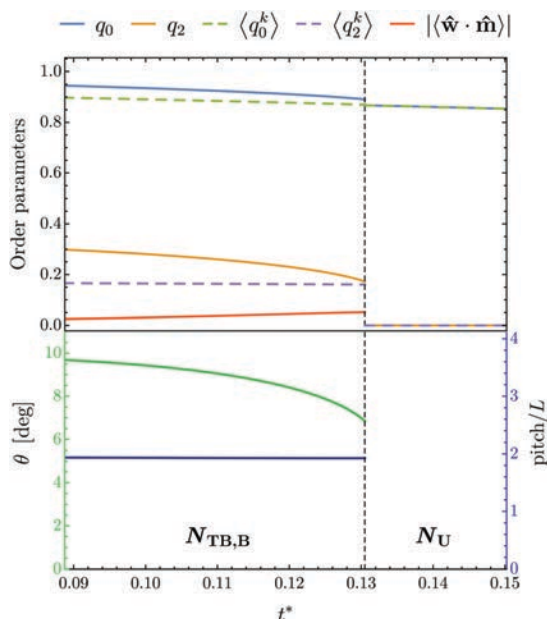


Fig. 5 Behavior of order parameters, tilt angle and pitch for the phase transition: $N_U \leftrightarrow N_{TB,B}$, when $\lambda = 0.26$ and $\chi = 160^\circ$. For further details see the caption for Fig. 3.

Both $I \leftrightarrow N_U$ and $I \leftrightarrow N_U \leftrightarrow N_{TB}$ are frequently observed,^{1,39} while straightforward phase transition from isotropic to N_{TB} has been found for only a few compounds^{40,41} and mixtures.⁴² Fig. 6a supports the conclusions drawn in ref. 38 that N_{TB} might be blocking the formation of N_B for $\lambda = 0$. On the other hand, the inclusion of $\lambda \neq 0$ rearranges the positions in competition between N_B and N_{TB} .

Fig. 6b–e illustrate how the magnitude of biaxiality reshapes the phase diagrams in the domain of $\{\chi, t^*\}$. A common feature of all the presented phase diagrams (Fig. 6a–e) is direct accessibility of a twist-bend nematic (either N_{TB} or $N_{TB,B}$) from

the isotropic phase within the spectrum of χ in the interval between 90° and 132° ($\lambda = 0$), and from 90° to 139° ($\lambda = 1/\sqrt{6}$). The boundary case, *i.e.* $\chi = 180^\circ$, reflects the results of the previously studied Maier–Saupe model for biaxial rod-like molecules.^{43,44} Increasing λ (Fig. 6b) by small increments of 0.1 wholly reorganizes the previous phase arrangement. Lower temperature N_{TB} is substituted by $N_{TB,B}$ and shifted towards higher temperatures. In an analogous scheme applied to N_U , N_B emerged at lower temperatures, modifying the regime of stability for N_U . For χ from 90° to 118° only a $I \leftrightarrow N_{TB,B}$ phase transition is present. For $\chi \in (118^\circ, 136^\circ]$, the aforementioned sequence is separated by N_{TB} , leading to $I \leftrightarrow N_{TB} \leftrightarrow N_{TB,B}$. Changing χ within the range of 136° to 169° introduces an additional phase, namely N_U , between I and N_{TB} . Within a narrow span of $\chi \in (169^\circ, 172^\circ]$, the area of N_{TB} vanishes in favor of the $I \leftrightarrow N_U \leftrightarrow N_{TB,B}$ sequence. However, for $\chi \in (172^\circ, 180^\circ)$, $N_{TB,B}$ and N_U are separated by N_B . The boundary scenario, *i.e.* $\chi = 180^\circ$, is solely represented by a phase sequence involving the isotropic phase and non-modulated nematics: $I \leftrightarrow N_U \leftrightarrow N_B$.

Increasing λ incrementally (Fig. 6b–e) leads to shrinkage of the stability regions for N_U and N_{TB} at the price of expanding the areas of N_B and $N_{TB,B}$. A climax is reached at the so-called “self-dual point” ($\lambda = 1/\sqrt{6}$) where exclusively N_B and $N_{TB,B}$ are present. Similarly to the phase diagram in Fig. 6a, three sets of phase sequences are achievable: $I \leftrightarrow N_{TB,B}$ ($\chi \in [90^\circ, 138^\circ]$), $I \leftrightarrow N_B \leftrightarrow N_{TB,B}$ ($\chi \in (138^\circ, 180^\circ)$), and $I \leftrightarrow N_B$ ($\chi = 180^\circ$), with the difference that uniaxial phases are replaced by their biaxial counterparts. The evolution of θ , p and $w(\hat{Q}(R_A))$ as a function of χ alongside the increase in magnitude of λ is also prominent (Fig. 6b–e). In particular, it applies to the behavior of $w(\hat{Q}(R_A))$, which indicates that the biaxial nature of $N_{TB,B}$ intensifies in parallel with increasing λ , and at the self-dual point in the range of χ from 90° to 120° it switches sign and attains 0 (maximal biaxiality) at $\chi = 90^\circ$ (see inset of Fig. 6e).

Our results are in line with experimental data,⁸ which means that the postulate about the stability of the twist-bend nematic phase being governed by the molecule’s bend angle is legitimate and crucial. Mandle *et al.*⁸ examined a family of

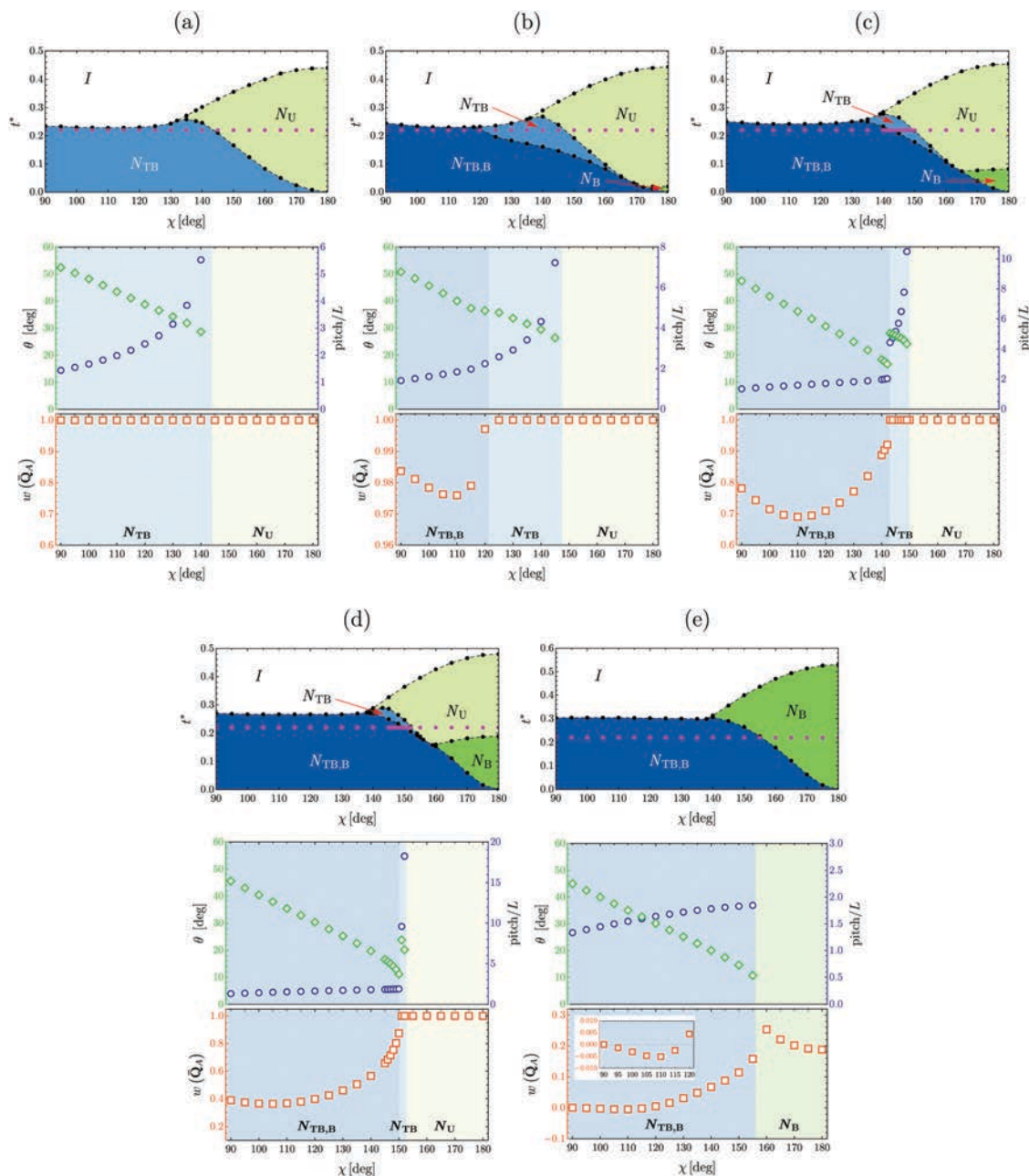


Fig. 6 Panel illustrating five phase diagrams in the domain of (χ, t^*) for a representative set of λ : 0 (a), 0.1 (b), 0.2 (c), 0.3 (d) and $1/\sqrt{6}$ (e). Below each phase diagram are two plots depicting the behavior of pitch, tilt angle (θ) and $w(\mathbf{Q}_A) \equiv w(\mathbf{Q}_A)$ (eqn (8) and (10)) as a function of the bend angle χ for the respective points on the main phase diagram (purple points at $t^* = 0.22$). Inset in the bottom plot of (e) delineates the magnification of this plot in the range $\chi \in [90^\circ, 120^\circ]$ and $w(\mathbf{Q}_A) \in [-0.01, 0.01]$.

cyanobiphenyl dimers with varying linking groups and stated that the twist-bend nematic is thermally stable when χ is between 110° and 130° . Further increasing χ leads to the destabilization of N_{TB} .

Within the mean-field approach, we have investigated in detail two additional phase diagrams, with respect to our previous work,²⁷ for bent-core molecules with bend angles equal to 150° and 160° . It was possible to qualitatively identify

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new phase transitions, namely: $I \leftrightarrow N_U \leftrightarrow N_{TB,B}$, and a straightforward transition between all phases anticipated by the mean-field model, *i.e.* $I \leftrightarrow N_U \leftrightarrow N_B \leftrightarrow N_{TB} \leftrightarrow N_{TB,B}$. Moreover, within the broad spectrum of bend angles we have shown how the interplay between χ and λ affects both the structural features and the mutual stability of nematic phases.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Supplemental Material for
**“Role of molecular bend angle and biaxiality
 in the stabilization of the twist-bend nematic phase”**

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Free energy f (eqn (12) in main manuscript) is minimized with respect to four parameters: q_0 , q_2 , θ and k , whereas adjustable are χ and λ . Here, we present selected exemplary results concerning the confirmation that the acquired states are equilibrium states. As initial parameters we take those that were obtained through direct minimization of eqn (12) (in main manuscript) for $t^* = 0.22$. Onward, we plot the evolution of free energy in (q_0, q_2) and (k, θ) domain for representative temperatures t^* .

Fig.S.1 ($\chi = 130^\circ$) and Fig.S.2 ($\chi = 140^\circ$) illustrate results for $\lambda = 0$. Columns (A) and (B) present contour plots of free energy in (q_0, q_2) and (k, θ) domain for twist-bend nematic (N_{TB}) state, while column (C) presents contour plots of free energy in (q_0, q_2) domain for nematic (N) state ($k = \theta = 0$). The parameters from direct minimization for $t^* = 0.22$ are:

$\chi = 130^\circ$ ($\lambda = 0$)

- $q_0 = 0.68$, $q_2 = 0$, $k = 1$ and $\theta = 34^\circ$,

$\chi = 140^\circ$ ($\lambda = 0$)

- $q_0 = 0.68$, $q_2 = 0$, $k = 0.56$ and $\theta = 29^\circ$,

and they remain as fixed. Therefore, we have:

for Fig.S.1

- in column (A): fixed $\chi = 130^\circ$, $\lambda = 0$, $k = 1$, $\theta = 34^\circ$ and t^* , plots are in (q_0, q_2) domain;
- in column (B): fixed $\chi = 130^\circ$, $\lambda = 0$, $q_0 = 0.68$, $q_2 = 0$ and t^* , plots are in (k, θ) domain;
- in column (C): fixed $\chi = 130^\circ$, $\lambda = 0$, $k = 0$, $\theta = 0$ and t^* , plots are in (q_0, q_2) domain;

for Fig.S.2

- in column (A): fixed $\chi = 140^\circ$, $\lambda = 0$, $k = 0.56$, $\theta = 29^\circ$ and t^* , plots are in (q_0, q_2) domain;
- in column (B): fixed $\chi = 140^\circ$, $\lambda = 0$, $q_0 = 0.68$, $q_2 = 0$ and t^* , plots are in (k, θ) domain;
- in column (C): fixed $\chi = 140^\circ$, $\lambda = 0$, $k = 0$, $\theta = 0$ and t^* , plots are in (q_0, q_2) domain;

Fig.S.3 ($\chi = 130^\circ$) and Fig.S.4 ($\chi = 145^\circ$) depict results for $\lambda = 0.3$. Idea behind columns (A), (B) and (C) is the same as in Fig.S.1 and Fig.S.2. The parameters from direct minimization for $t^* = 0.22$ are:

$\chi = 130^\circ$ ($\lambda = 0.3$)

- $q_0 = 0.8$, $q_2 = 0.3$, $k = 1.81$ and $\theta = 25^\circ$,

$\chi = 145^\circ$ ($\lambda = 0.3$)

- $q_0 = 0.8$, $q_2 = 0.24$, $k = 1.7$ and $\theta = 17^\circ$,

and they remain as fixed. Therefore, we have:

for Fig.S.3

- in column (A): fixed $\chi = 130^\circ$, $\lambda = 0.3$, $k = 1.81$, $\theta = 25^\circ$ and t^* , plots are in (q_0, q_2) domain;
- in column (B): fixed $\chi = 130^\circ$, $\lambda = 0.3$, $q_0 = 0.8$, $q_2 = 0.3$ and t^* , plots are in (k, θ) domain;
- in column (C): fixed $\chi = 130^\circ$, $\lambda = 0.3$, $k = 0$, $\theta = 0$ and t^* , plots are in (q_0, q_2) domain;

for Fig.S.4

- in column (A): fixed $\chi = 145^\circ$, $\lambda = 0.3$, $k = 1.7$, $\theta = 17^\circ$ and t^* , plots are in (q_0, q_2) domain;
- in column (B): fixed $\chi = 145^\circ$, $\lambda = 0.3$, $q_0 = 0.8$, $q_2 = 0.24$ and t^* , plots are in (k, θ) domain;
- in column (C): fixed $\chi = 145^\circ$, $\lambda = 0.3$, $k = 0$, $\theta = 0$ and t^* , plots are in (q_0, q_2) domain;

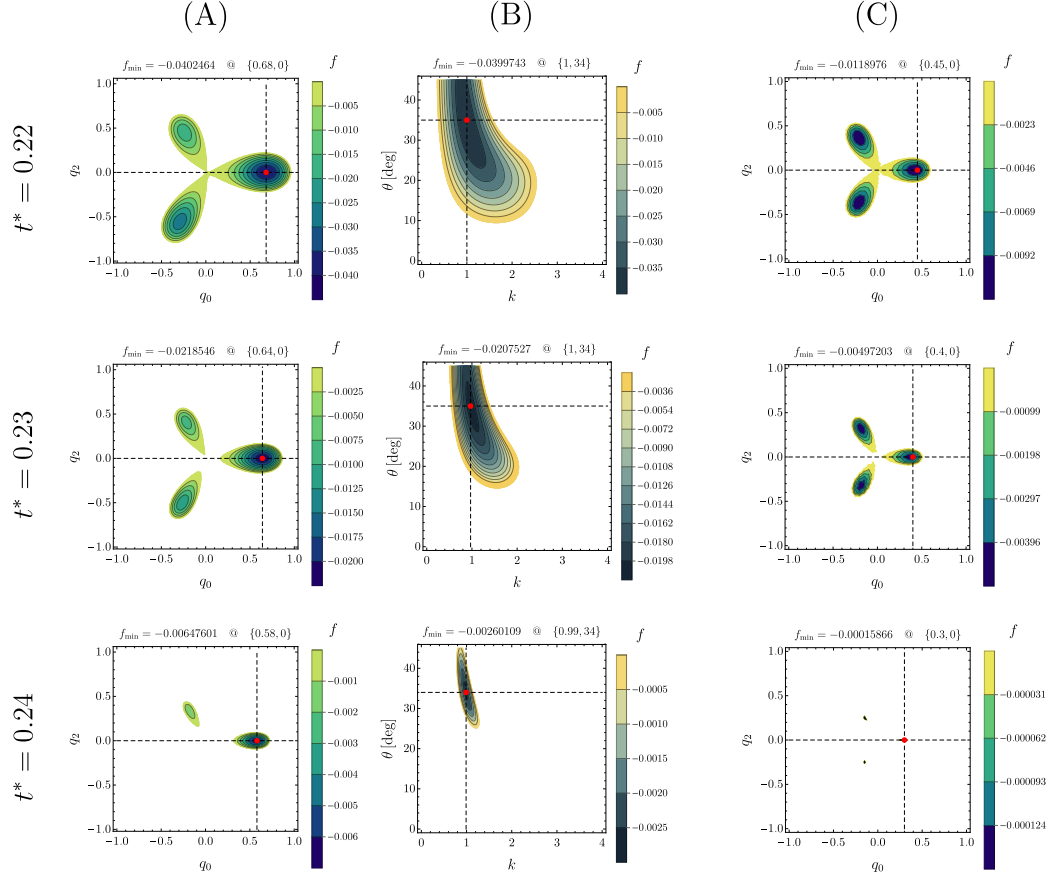
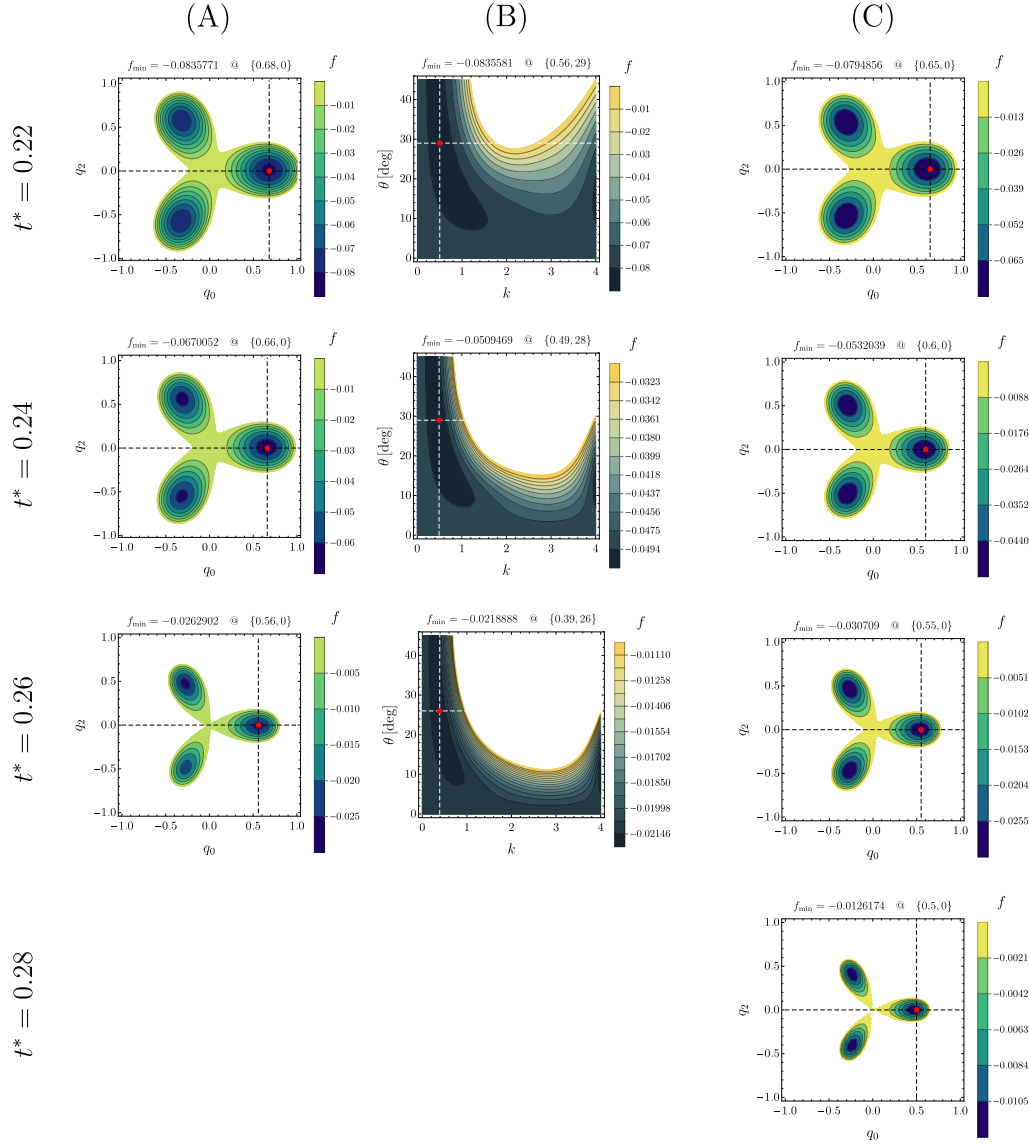


Figure S.1: Contour plots of free energy in (q_0, q_2) and (k, θ) domain for $\chi = 130^\circ$ and $\lambda = 0$ (see the text of this Supplemental Material). Above each contour plot is printed a set of numbers, which designate for what pair (q_0, q_2) or (k, θ) the lowest value of free energy is attained (red dot). White space in plots is associated with the area where $f \geq 0$. The resolution in (q_0, q_2) plots is 0.05 and in (k, θ) plots is 0.05 (for k) and 1° (for θ). According to the values of f in this scenario N_{TB} prevail over N_U .



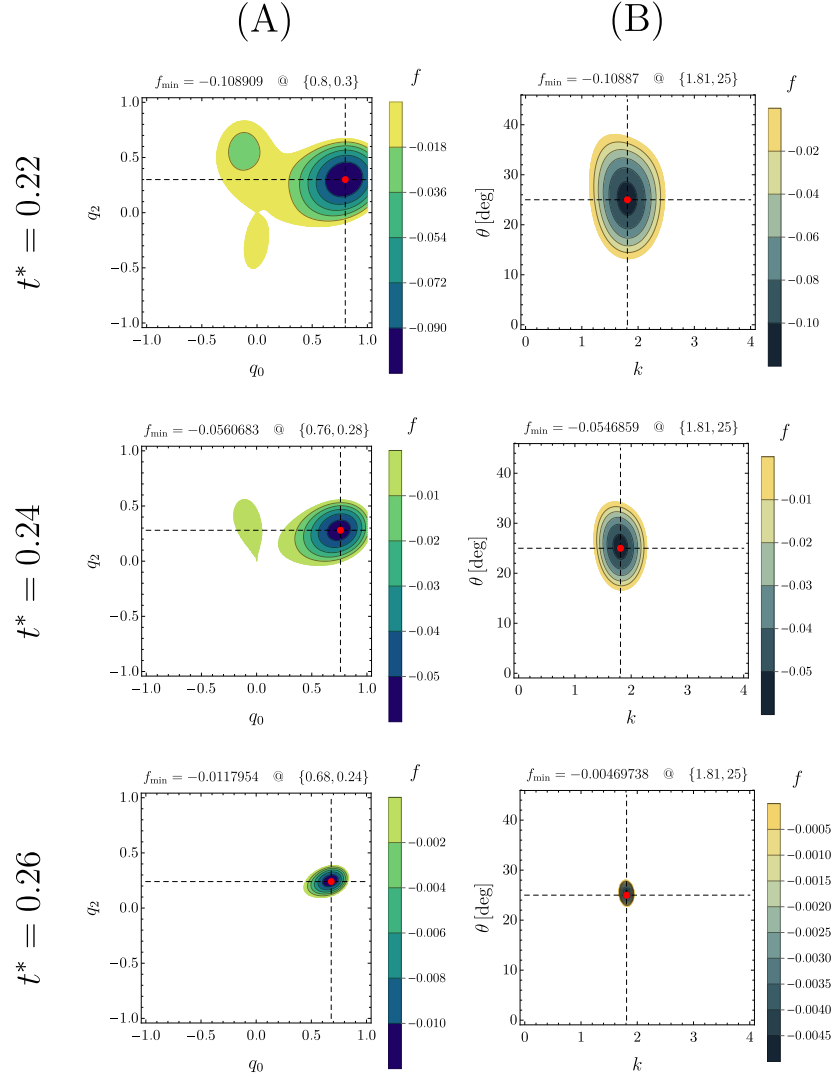


Figure S.3: Contour plots of free energy in (q_0, q_2) and (k, θ) domain for $\chi = 130^\circ$ and $\lambda = 0.3$ (see the text of this Supplemental Material). Above each contour plot is printed a set of numbers, which designate for what pair (q_0, q_2) or (k, θ) the lowest value of free energy is attained (red dot). White space in plots is associated with the area where $f \geq 0$. Lack of column (C) indicate that for whole set of (q_0, q_2) $f \geq 0$ ($N_{TB,B}$ phase dominates). The resolution in (q_0, q_2) plots is 0.05 and in (k, θ) plots is 0.05 (for k) and 1° (for θ). According to the values of f in this scenario $N_{TB,B}$ prevail over N_U .

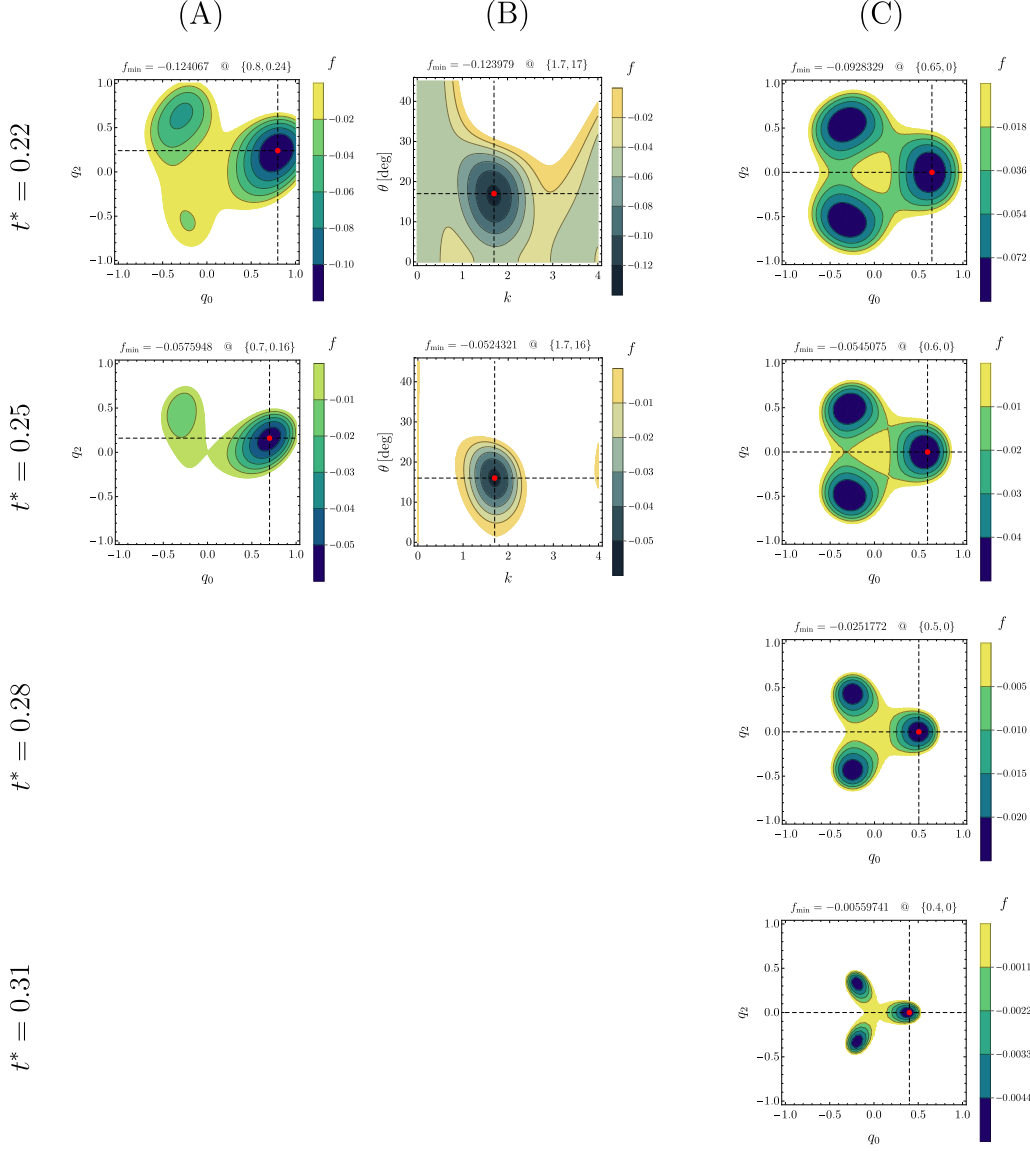


Figure S.4: Contour plots of free energy in (q_0, q_2) and (k, θ) domain for $\chi = 145^\circ$ and $\lambda = 0.3$ (see the text of this Supplemental Material). Above each contour plot is printed a set of numbers, which designate for what pair (q_0, q_2) or (k, θ) the lowest value of free energy is attained (red dot). White space in plots is associated with the area where $f \geq 0$. Lack of plots in column (A) and (B) for $t^* = 0.28$ and $t^* = 0.31$ indicate that for whole set of either (q_0, q_2) or (k, θ) $f \geq 0$ (N_U phase dominates). The resolution in (q_0, q_2) plots is 0.05 and in (k, θ) plots is 0.05 (for k) and 1° (for θ). According to the values of f in this scenario a phase transition between $N_{TB,B}$ and N_U occurs.

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Article 3

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Among TOP 5 (out of 240) articles nominated¹ for the Luckhurst-Samulski Prize 2018

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Twist-bend nematic phase in the presence of molecular chirality

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ABSTRACT

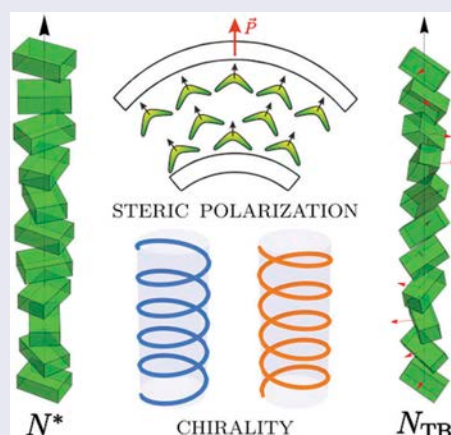
One of the interesting questions related to bent-shaped materials is how structural chirality of the twist-bend nematic (N_{TB}) phase can respond to the presence of molecular chirality, with later being introduced through chiral centers incorporated in the molecules or chiral dopants. We study this problem using minimal coupling Landau-de Gennes theory of N_{TB} , supplemented by a term representing intrinsic molecular chirality. Relative stability and properties of cholesteric (N^*), chiral twist-bend nematic with heliconical structure (N_{TB}^*), and other homogeneous phases are studied. Besides nematic, chiral twist-bend nematic and cholesteric phases of vanishing global polarization, we find their polar analogues. In particular, a coupling between molecular chirality, alignment tensor and polarization fields can promote a globally polar and chiral twist-bend nematic (N_{TBp}^*) with period comparable to that of N^* .

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1. Introduction

In 1973 Mayer predicted that bend deformations, favored by nonchiral bent-shaped molecules, might lead to flexopolarization-induced spontaneous chiral symmetry breaking [1]. As a result, the twist-bend nematic (N_{TB}) phase can emerge where the director $\hat{n}(z)$ simultaneously twists and bends in space by precessing on the side of a right circular cone

$$\hat{n}(z) = [\cos(\phi_{\hat{n}})\sin(\theta_{\hat{n}}), \sin(\phi_{\hat{n}})\sin(\theta_{\hat{n}}), \cos(\theta_{\hat{n}})], \quad (1)$$

with conical angle $\theta_{\hat{n}}$ being the angle between $\hat{n}$ and the wave vector $\mathbf{k}$. Assuming the wave vector to stay parallel to the $\hat{z}$ -axis of the laboratory frame of reference ($\mathbf{k} = k\hat{z}$) one should also have $\phi_{\hat{n}} = \pm kz = \pm 2\pi z/p$ for the azimuthal angle, where p is the pitch.

The $\pm$ sign indicates that both left-handed and right-handed chiral domains should form with the same probability, which is a prerequisite for chiral symmetry to be spontaneously broken in the bulk. In addition, the structure should be locally polar with the polarization vector $\mathbf{P}$ (irrespective of its origin) being perpendicular both to the director and the wave vector

$$\mathbf{P}(z) = p_0 [\sin(\phi_{\hat{n}}), -\cos(\phi_{\hat{n}}), 0]. \quad (2)$$

The issue of stable N_{TB} has further been addressed by Dozov [2] who correlated the heliconical order of the structure with the sign change of the bend Frank elastic constant. Subsequently, N_{TB} was also found in simulations by Memmer [3]. Aided by these theoretical predictions, the N_{TB} structure has been looked for experimentally and the intensive quest has been crowned with success many years

later [4–9]. Currently, about 100 of mesogens are known to exhibit N_{TB} either below the uniaxial nematic phase (N) or directly below the isotropic phase (I) [10,11]. The structure emerges as a result of first order $N - N_{TB}$ or $I - N_{TB}$ phase transition on the temperature scale. As regards the theoretical analysis the equivalence of Mayer's idea of flexopolarization-induced N_{TB} with that of Dozov's was demonstrated by Shamid *et al.* [12]. They correlated flexoelectricity, negative bend elastic constant, and stability of N_{TB} and predicted a second-order phase transition from N to N_{TB} . At the transition, the bend elastic constants indeed changes sign and, consequently, the corresponding structure develops modulated polar order, averaging to zero globally.

The N_{TB} phase has also been found for chemically chiral asymmetric dimers [13,14], where it was called N_{TB}^* indicating that molecular chirality selects one handedness of N_{TB} out of the two possibilities. Interestingly, up to seven chiral nematic phases were observed in one system [13], which involved N^* , a blue phase and variants of N_{TB}^* . Given that the N^* phase ($\theta_n = \pi/2$ and $p_0 = 0$ in Equations (1) and (2)) is structurally linked with N_{TB} ($0 < \theta_n < \pi/2$) and assuming the flexopolarization mechanism is responsible for the periodicity of N_{TB} for nonchiral materials this rises a question about how chiralities of different origin (structural chirality of N_{TB} vs molecular chirality that leads to ordinary N^*) can influence the stability of phases. The question is intriguing since we know that the molecular chirality introduced through chiral carbons, or chiral dopants, leads to a typical characteristic length scale (pitch of N^*) being about two orders of magnitude larger than the 10 nm scale related to periodicity of N_{TB} . Should we then expect anything else than just a lifting of the free energy degeneracy of ambidextrous chiral domains characterizing the N_{TB} structure (which transforms N_{TB} into N_{TB}^*)? Vice-versa, should flexopolarization of bent-core mesogens have no or minor effect on the overall molecular chirality of N^* ? We will seek an answer to these questions within the frame of minimal coupling Landau-de Gennes (LdeG) theory with flexopolarization and molecular chirality. These studies should also help identifying relevant interactions that stabilize N_{TB} . The present analysis extends our earlier work [15].

2. Mesoscopic model of spatially homogeneous modulated structures

In general, the orientational properties of a liquid crystal are characterized by order parameters [16,17]. A unique order parameter set is then divided into primary order parameters and secondary ones where the primary set is

used to account for experimental observations through microscopic or phenomenological Landau theories. Lubensky and Radzihovsky [18] have argued that for a proper characterization of orientational order exhibited by bent-core liquid-crystal phases, a set of important order parameters should include three fields: the vector order parameter $\mathbf{P}$, the second-rank traceless symmetric alignment tensor $\mathbf{Q}$ and the third-rank traceless symmetric tensor $\mathbf{T}$ of octupolar symmetry. The $\mathbf{T}$ field is needed here to characterize spontaneously ordered chiral phases in spatially uniform liquid states. One case when $\mathbf{T}$ was shown explicitly to trigger chiral symmetry breaking were simulations of conformational chirality of the achiral flexible, bent-shape molecules [19–22]. There, an average bent-core shape was modeled by the biaxial quadrupolar tensor while the presence of conformational chirality added to that the non-zero coupling to octupolar tensor whose fluctuating sign represented mirror image chiral conformations fluctuating with equal probabilities (*for more details see discussion in [19]*). Very recent experiments of Srigengan *et al.* [23] suggest that we may be close to the discovery of a new N_{TB} -like phase stabilized by this mechanism.

More conventionally, however, the chiral order of N_{TB} is linked with a steric, polar ordering of the molecular bent shapes [24–26]. In this latter case, which we are going to explore here, the relevant couplings obey only $\mathbf{Q}$ and $\mathbf{P}$ fields and their derivatives, in line with the flexopolarization mechanism suggested by Meyer [1]. As we shall see the mesoscopic theory, where the director is replaced by $\mathbf{Q}$, allows to account for a fine structure of the modulated phases and avoids limitations of the directors description, like *e.g.* (incorrect) prediction that the $N - N_{TB}$ transition is of second order.

De Gennes was the first to formulate a non-equilibrium Landau-Ginzburg free energy density f_Q for ordinary nematics and cholesterics (*see e.g.* [27,28]). It is constructed as an $SO(3)$ -symmetric expansion about the isotropic phase in $\mathbf{Q}(\mathbf{r})$ and its derivatives $\partial_\gamma Q_{\alpha\beta}$. General $SO(3)$ -symmetric non-equilibrium Landau-de Gennes free energy functional F that involves an extension containing additionally lowest order couplings with the polarization field $\mathbf{P}(\mathbf{r})$ and $\partial_\alpha P_\beta$ has been developed in [29,30]. Its minimal coupling version reads

$$F \equiv F[\mathbf{Q}, \mathbf{P}] = \frac{1}{V} \int_V (f_Q + f_P + f_{QP}) d^3\mathbf{r}, \quad (3)$$

where the lower indices of the free energy densities f_i indicate that f_i is constructed out of the field ' i ' or their couplings. The successive contributions to F are

$$f_Q = \frac{1}{4} [t_Q \text{Tr}(\mathbf{Q}^2) + (\nabla \otimes \mathbf{Q}) \cdot (\nabla \otimes \mathbf{Q}) + \rho (\nabla \cdot \mathbf{Q}) \cdot (\nabla \cdot \mathbf{Q}) - 2\kappa \mathbf{Q} \cdot (\nabla \times \mathbf{Q}) - \sqrt{6} B \text{Tr}(\mathbf{Q}^3) + \text{Tr}(\mathbf{Q}^2)^2], \quad (4)$$

$$f_P = \frac{1}{4} [t_P \mathbf{P}^2 + (\nabla \otimes \mathbf{P}) \cdot (\nabla \otimes \mathbf{P}) + a_c (\nabla \cdot \mathbf{P})^2 + (\mathbf{P}^2)^2], \quad (5)$$

$$f_{QP} = -\frac{1}{4} e_P \mathbf{P} \cdot (\nabla \cdot \mathbf{Q}) - \lambda P_\alpha Q_{\alpha\beta} P_\beta, \quad (6)$$

where the number of the constitutive parameters has been reduced by taking suitable units and by assuming that deformations appear only in a quadratic part of the free energy. There are 8 phenomenological parameters left, namely, t_Q and t_P , which are the reduced temperatures associated with $\mathbf{Q}$ and $\mathbf{P}$ fields, respectively; ρ is the relative elastic constant; a_c is the strength of longitudinal contribution from the steric polarization; e_P is the strength of flexopolarization; λ is the strength of coupling between $\mathbf{Q}$ and $\mathbf{P}$ fields. Taking $t_P > 0$ eliminates spontaneous polar order ($\mathbf{P} \neq 0$) in the absence of $\mathbf{Q}$. For the sake of thermodynamic stability of F it is mandatory that $\rho > -3/2$ and $1 + a_c > 0$. The term proportional to κ in f_Q violates parity and hence only appears in the elastic free energies of cholesteric liquid crystals. Its presence in the expansion results from intrinsic molecular chirality (which is measured by $\kappa \neq 0$) and is responsible for the formation of phases with broken chiral symmetry. Furthermore, the theory given by f_Q is fundamental to our present understanding not only of the cholesteric phase but also of the Blue Phases [31,32]. We would like to mention, however, that the role of the chirality parameter κ is not quite clear (see discussion after Equation (19)). Note that $\kappa = 0$ in N and N_{TB} . Finally, under the assumption that $\mathbf{Q}$ is uniaxial

$$Q_{\alpha\beta}(\mathbf{r}) = S \left(n_\alpha(\mathbf{r}) n_\beta(\mathbf{r}) - \frac{\delta_{\alpha\beta}}{3} \right) \quad (7)$$

the free energy densities containing derivatives of $\mathbf{Q}$ become reduced to the Frank elastic free energy density of the director field:

$$f_{Frank} = \frac{1}{2} [K_{11} (\nabla \cdot \hat{\mathbf{n}})^2 + K_{22} (\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}})^2 + K_{33} (\hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}})^2 - 2q_0 K_{22} (\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}})].$$

More specifically, up to S^2 -terms the following identification can be given [29]

$$\begin{aligned} & \frac{1}{4} [(\nabla \otimes \mathbf{Q}) \cdot (\nabla \otimes \mathbf{Q}) + \rho (\nabla \cdot \mathbf{Q}) \cdot (\nabla \cdot \mathbf{Q}) - 2\kappa \mathbf{Q} \cdot (\nabla \times \mathbf{Q})] \\ & \simeq \frac{S^2}{2} \left\{ \frac{1}{2} (2 + \rho) [(\nabla \cdot \hat{\mathbf{n}})^2 + (\hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}})^2] \right. \\ & \quad \left. + (\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}})^2 - \kappa (\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}}) \right\} \\ & = \frac{S^2 f_{Frank}}{K_{22}} \approx \frac{S^2}{2} \left\{ \frac{(K_{11} + K_{33})}{2K_{22}} [(\nabla \cdot \hat{\mathbf{n}})^2 \right. \\ & \quad \left. + (\hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}})^2] + (\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}})^2 - 2q_0 (\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}}) + \dots \right\}, \end{aligned} \quad (8)$$

which yields $\rho \approx (K_{11} + K_{33} - 2K_{22})/K_{22}$ and $\kappa \approx 2q_0$. Likewise [29]

$$e_P \mathbf{P} \cdot (\nabla \cdot \mathbf{Q}) \simeq S e_P [\mathbf{P}_\parallel (\nabla \cdot \hat{\mathbf{n}}) - \mathbf{P}_\perp (\hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}})], \quad (9)$$

where $\mathbf{P}_\parallel$ ($\mathbf{P}_\perp$) denotes a polar vector parallel (perpendicular) to $\hat{\mathbf{n}}$. Since for bent-core liquid crystals $\mathbf{P}$ does not need to be the electrostatic polarization the coefficient e_P does not correlate, in general, with the splay and bend flexoelectric coefficients.

Now, our objective is to identify the equilibrium structures that minimize $F[\mathbf{Q}(\mathbf{r}), \mathbf{P}(\mathbf{r})]$ for arbitrary t_Q and $t_P > 0$, given fixed the remaining parameters. Since in the free-energy F , gradient and bulk invariants usually favor different structures (frustration) the identification of equilibrium phases appears extremely difficult. In seeking for stable (quasi-) periodic structures the standard procedure involves expansion of the fields $\mathbf{Q}$ and $\mathbf{P}$ into a spin tensor modes of $L = 2$ and $L = 1$, respectively, and into plane waves [30]

$$\mathbf{Q}(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{m=-2}^2 Q_m(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{e}_{m,\hat{\mathbf{k}}}^{[2]}, \quad (10)$$

$$\mathbf{P}(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{m=-1}^1 P_m(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{e}_{m,\hat{\mathbf{k}}}^{[1]}, \quad (11)$$

where $\mathbf{e}_{m,\hat{\mathbf{k}}}^{[L]}$, $m = 0, \pm 1, \pm L$ are the base tensors defined in an orthonormal, right handed local coordinate system $\{\hat{\xi}, \hat{\eta}, \hat{\mathbf{k}}\}$ with $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$ as quantization axis. They read [30]

$$\begin{aligned} \mathbf{e}_{\pm 1, \hat{\mathbf{k}}}^{[1]} &= \mp \frac{1}{\sqrt{2}} (\hat{\xi} \pm i\hat{\eta}), \\ \mathbf{e}_{0, \hat{\mathbf{k}}}^{[1]} &= \hat{\mathbf{k}}, \\ \mathbf{e}_{\pm 2, \hat{\mathbf{k}}}^{[2]} &= \frac{1}{2} (\hat{\xi} \pm i\hat{\eta}) \otimes (\hat{\xi} \pm i\hat{\eta}), \\ \mathbf{e}_{\pm 1, \hat{\mathbf{k}}}^{[2]} &= \mp \frac{1}{2} [(\hat{\xi} \pm i\hat{\eta}) \otimes \hat{\mathbf{k}} + \hat{\mathbf{k}} \otimes (\hat{\xi} \pm i\hat{\eta})], \\ \mathbf{e}_{0, \hat{\mathbf{k}}}^{[2]} &= \frac{1}{\sqrt{6}} (3\hat{\mathbf{k}} \otimes \hat{\mathbf{k}} - \mathbf{1}). \end{aligned} \quad (12)$$

The variables $\{Q_m(\mathbf{k}), P_m(\mathbf{k})\}$ are the complex Fourier amplitudes of the mode $(\mathbf{k}, m)$, which should be found from the minimization of F . The only limitation that has to be taken into account is the reality condition: $\{\mathbf{Q}(\mathbf{r}) = \mathbf{Q}(\mathbf{r})^*, \mathbf{P}(\mathbf{r}) = \mathbf{P}(\mathbf{r})^*\}$, which implies that $Q_m(-\mathbf{k}) = (-1)^m Q_m(\mathbf{k})^*$ and $P_m(-\mathbf{k}) = (-1)^{m+1} P_m(\mathbf{k})^*$. The corresponding formula for F is given in [33]. To simplify the minimization of F further we only explore the relative stability of homogeneous structures periodic at most in one spatial direction [34], which obey, in particular, N^* and N_{TB} .

An assumption that a structure is spatially homogeneous, say in the $\hat{z}$ -direction of laboratory frame of reference, means that the tensors $\mathbf{Q}(z), \mathbf{P}(z)$ for arbitrary z and $\mathbf{Q}(0), \mathbf{P}(0)$ for $z = 0$ can be brought into coincidence by a rotation $\mathcal{R}_z(\pm kz)$ through the angle $\pm kz$ about $\hat{z}$. More specifically

$$\mathcal{R}_z(\pm kz)\mathbf{Q}(0) = \mathbf{Q}_\pm(z) \quad (13)$$

$$\mathcal{R}_z(\pm kz)\mathbf{P}(0) = \mathbf{P}_\pm(z)$$

where $\pm$ labels left- (+) and right-handed (−) helical structure. Applying rotation Equation (13) to the expansions Equations (10) and (11) we obtain a simpler form for $\mathbf{Q}$ and $\mathbf{P}$ given by the terms of $|n| \leq 2$. They read [34]

$$\mathbf{Q}_\pm(z) = Q_0(0)\mathbf{e}_{0,\hat{z}}^{[2]} + \sum_{m=1}^2 \left[Q_{\pm m}(m)\mathbf{e}_{\pm m,\hat{z}}^{[2]} e^{\pm imkz} + \text{c.c.} \right], \quad (14)$$

$$\mathbf{P}_\pm(z) = P_0(0)\mathbf{e}_{0,\hat{z}}^{[1]} + \left[P_{\pm 1}(1)\mathbf{e}_{\pm 1,\hat{z}}^{[1]} e^{\pm ikz} + \text{c.c.} \right]. \quad (15)$$

The explicit formulas for $\mathbf{Q}_\pm$ and $\mathbf{P}_\pm$ can be cast in a simpler form [34]

$$\begin{aligned} \mathbf{Q}_\pm(z) = & \frac{x_0}{\sqrt{6}} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix} \\ & + r_{\pm 1} \begin{bmatrix} 0 & 0 & -c_{\pm 1} \\ 0 & 0 & s_{\pm 1} \\ -c_{\pm 1} & s_{\pm 1} & 0 \end{bmatrix} \\ & + r_{\pm 2} \begin{bmatrix} c_{\pm 2} & -s_{\pm 2} & 0 \\ -s_{\pm 2} & -c_{\pm 2} & 0 \\ 0 & 0 & 0 \end{bmatrix}, \end{aligned} \quad (16)$$

$$\mathbf{P}_\pm(z) = \sqrt{2}p_{\pm 1} \begin{bmatrix} -\cos(\pm kz + \phi_{\pm p}) \\ \sin(\pm kz + \phi_{\pm p}) \\ 0 \end{bmatrix} + v_0 \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \quad (17)$$

where $c_{\pm m} = \cos(\pm mkz + \phi_{\pm m})$ and $s_{\pm m} = \sin(\pm mkz + \phi_{\pm m})$. In addition $r_{\pm i} \cos(\phi_{\pm i}) = x_{\pm i,i}$, $r_{\pm i} \sin(\phi_{\pm i}) = y_{\pm i,i}$ ($r_j \geq 0$), $p_{\pm 1} \cos(\phi_{\pm p}) = v_{\pm 1,1}$, $p_{\pm 1} \sin(\phi_{\pm p}) = z_{\pm 1,1}$ ($p_j \geq 0$), where $v_{i,j} = \Re P_i(j)$, $z_{i,j} = \Im P_i(j)$, $x_{i,j} = \Re Q_i(j)$, $y_{i,j} = \Im Q_i(j)$, $x_{0,0} \equiv x_0$ and $v_{0,0} \equiv v_0$. The representation of the fields in Equations (16) and (17) is insensitive to choice of the origin of the laboratory frame of reference, which allows to eliminate one of the phases $\phi_{\pm i}$ ($i = 1, 2, p$), independently for each of the two states with ‘+’ and ‘−’ subscripts. In what follows we set $\phi_{\pm 1} = 0$.

Together, $\mathbf{Q}_\pm$ and $\mathbf{P}_\pm$ characterize a family of all homogeneous (polar) helical/heliconical nematic phases that are structurally linked with the uniaxial nematic. In the absence of molecular chirality ($\kappa = 0$) only ambidextrous chiral states can be stabilized, where $F(\mathbf{Q}_+, \mathbf{P}_+) = F(\mathbf{Q}_-, \mathbf{P}_-)$. For nonzero κ generally only one of the two states of definite chirality is the equilibrium one. Since in this case the free energies fulfill the condition $F(\mathbf{Q}_+, \mathbf{P}_+, \kappa) = F(\mathbf{Q}_-, \mathbf{P}_-, -\kappa)$ we shall limit ourselves from the start to $\kappa > 0$, which selects one of the two chiralities ‘ $\pm$ ’ for equilibrium state and allows to simplify notation by dropping subscript ‘ $\pm$ ’. The homogeneous nematic states constructed out of $\mathbf{Q}$ and $\mathbf{P}$ fields would then be characterized by eight parameters $\{k, x_0, r_1, r_2, p_1, v_0, \phi_2, \phi_p\}$. Combinations of these parameters yield 12 structures, given in Table 1, which can be envisaged as candidates for equilibrium homogeneous phases of the model.

Values of the parameters entering Equations (16) and (17) can be found from the minimization of the free energy. The respective formulas are given in the Appendix. In particular, the wave vector of the helical/heliconical structures is easily found from the condition $\partial F / \partial k = 0$. It reads

$$k = \frac{\sqrt{2}p_1 r_1 e_p \sin(\phi_p) + 2\kappa(r_1^2 + 4r_2^2)}{2(2p_1^2 + (\rho + 2)r_1^2 + 8r_2^2)}. \quad (18)$$

For the cholesteric phase, where r_1 and p_1 vanish (Table 1 (c)), $\theta_a = \pi/2$, and where the only plane wave present in Equation (16) is that of $m = \pm 2$, the wave vector is defined as $k_{N^*} = 2k$. Then, from Equation (18) it becomes

$$k_{N^*} \equiv 2k = \kappa. \quad (19)$$

That is, within minimal coupling LdeG model of cholesteric and blue phases [31,32], the wave vector k_{N^*} of the cholesteric phase is temperature independent. We would like to mention that the pitch, which is inversely proportional to k_{N^*} , is known to depend strongly on

Table 1. Twelve homogeneous nematic structures constructed out of $\mathbf{Q}$ and $\mathbf{P}$ fields.

Nonzero parameters	Name of the structure	Abbreviation
Nonpolar structures		
(a) x_0	uniaxial nematic	N_U
(b) $x_0, r_1, r_2, k \rightarrow 0$	biaxial nematic	N_B
(c) $x_0, r_2, k_{N^*} = 2k \neq 0$	cholesteric	N^*
Locally polar structures		
(d) as in (c), p_1	locally polar cholesteric	N^*_p
(e) $x_0, r_1, r_2, p_1, k \neq 0$ ($\kappa = 0$)	(ambidextrously chiral) nematic twist-bend	N_{TB}
(f) as in (e), ($\kappa \neq 0$)	(chiral) nematic twist-bend	N^*_{TB}
Globally polar structures		
(g) any of (a)–(f), v_0	polar (a)–(f)	add subscript 'p' to abbreviations (a)–(f)

temperature [27]. Hence, inclusion of higher-order (chiral) elastic terms [35], which introduce dependence of k_{N^*} on t_Q , is generally needed although a qualitative description of cholesterics in the vicinity of the isotropic phase is accounted for by f_Q . Here we use k_{N^*} as reference and rescale k -vectors of equilibrium periodic structures relative to k_{N^*} . Following motivation given by Grebel *et al.* [31] we take as physical the chiralities lower than $\kappa \approx 2$.

The homogeneity of the structures implies that any invariant constructed out of $\mathbf{Q}$ and $\mathbf{P}$ fields are independent of the z -coordinate. For example, the normalized parameter $w = \sqrt{6}\text{Tr}(\mathbf{Q}^3)/\text{Tr}(\mathbf{Q}^2)^{3/2}$ ($-1 \leq w \leq 1$), which is often used to measure biaxiality of a structure [36], is given by

$$w = \frac{-6r_2^2x_0 + x_0^3 + 3r_1^2(\sqrt{6}\cos(\phi_2)r_2 + x_0)}{(2(r_1^2 + r_2^2) + x_0^2)^{3/2}}. \quad (20)$$

For locally biaxial (oblate or prolate) configurations $|w| < 1$. The biaxiality of a configuration increases with decreasing w and approaches its maximal value for $w = 0$, where one of the three eigenvalues of $\mathbf{Q}$ vanishes. For $w = 1$ the structure is prolate uniaxial while for $w = -1$ it is oblate uniaxial.

In the next Section, we will discuss structural features of equilibrium homogeneous structures for exemplary model parameters.

3. Results

The minimization of the free energy, Equation (A1), was carried out numerically at fixed values of chirality, temperature and remaining model parameters.

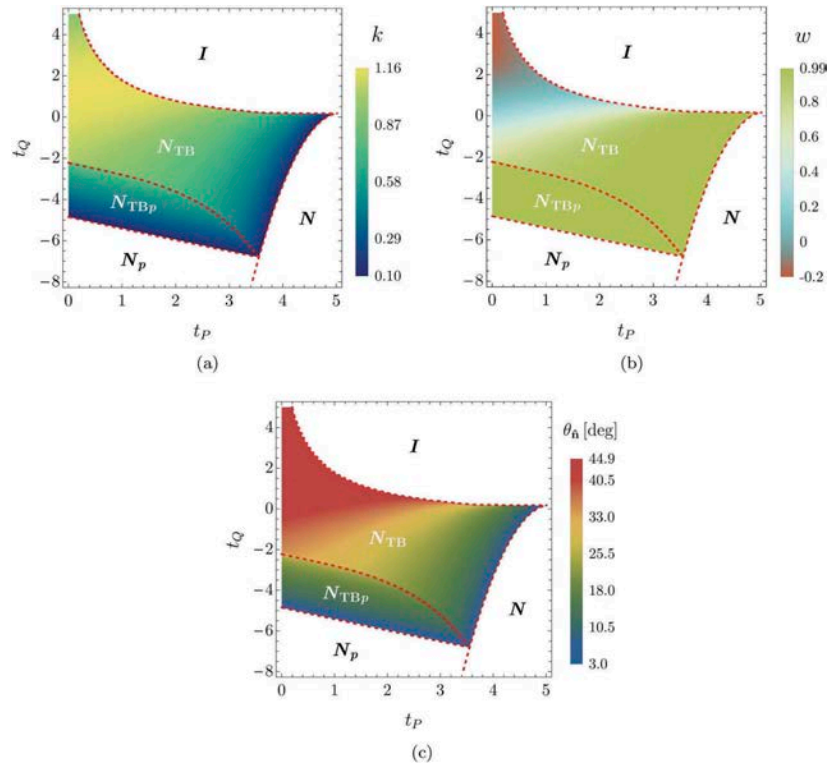


Figure 1. (Colour online) Phase diagram combined with density map of k (a), w (b) and θ_h (c) for $\kappa = 0$, $\lambda = 1$, $e_p = -8$, $a_c = \rho = 1$ and $B = 1/\sqrt{6}$.

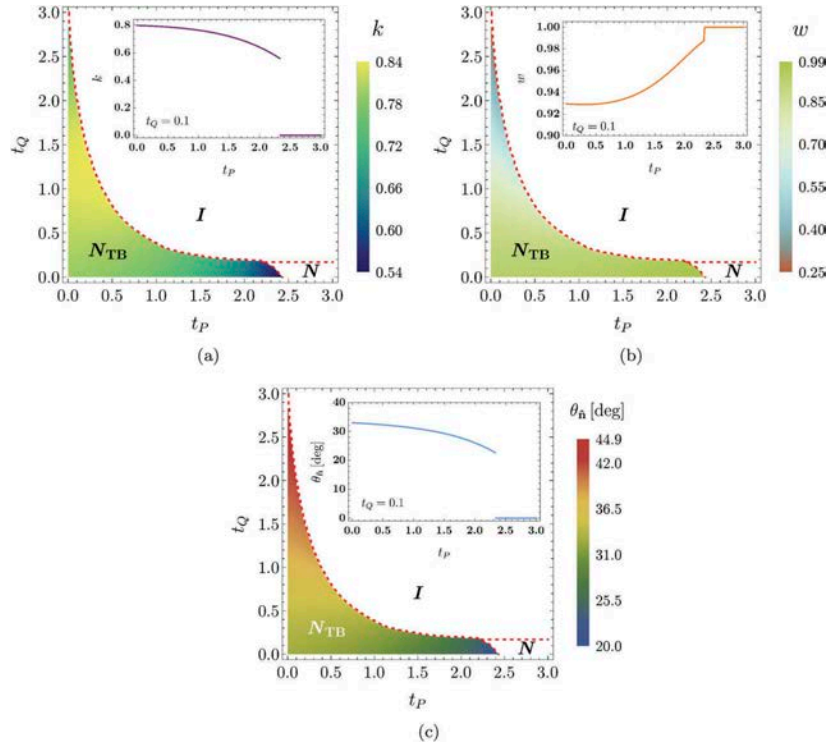


Figure 2. (Colour online) Phase diagram combined with density map of k (a), w (b) and θ_n (c) for $\kappa = 0$, $\lambda = -0.5$, $e_p = -6$, $a_c = \rho = 1$ and $B = 1/\sqrt{6}$. Insets depict plots of k (a), w (b) and θ_n (c) versus t_P for fixed t_Q .

The equilibrium structure was next identified by comparing the free energies of the trial homogeneous structures at the same values of the thermodynamic and material parameters. A possible phase behavior is shown in the $\{t_P, t_Q\}$ plane, where, as always in Landau theory, the temperatures $t_P = a_P(T - T_P)$ and $t_Q = a_Q(T - T^*)$ are connected with absolute temperature T of the system studied. Since $a_P > 0$, $a_Q > 0$, $T^* > T_P$ and $T > T_P$, any straight line in $\{t_P, t_Q\}$ plane with positive slope and negative t_Q -intercept represents a permissible physical system with no polar order for $\mathbf{Q} = 0$. Also note that the free energy F reflects prolate-oblate symmetry, which implies invariance of F with respect to a change of $\{B, e_p, \lambda, \mathbf{Q}\}$ into $\{-B, -e_p, -\lambda, -\mathbf{Q}\}$. Using this freedom we fix $B > 0$, which restricts further analysis to prolate liquid crystalline systems. We first consider a simpler case of $\kappa = 0$, which corresponds to the original LdeG theory of N_{TB} [15,30,34].

3.1. $\kappa = 0$

In this case there are maximally five stable structures in the $\{t_P, t_Q\}$ plane as depicted in Figure 1. They involve I , N ,

N_{TB} , N_{TBp} and N_p , where the globally polar order of N_{TBp} and N_p is a consequence of λ -coupling in Equation (6) with the polar structures appearing when $e_p \lambda < 0$. For $e_p \lambda > 0$, Figure 2, a more modest sequences are found with N and N_{TB} (cases a-b below), both observed experimentally [10,11]. It is also important to notice that the flexopolarization term alone ($e_p \neq 0$) is not sufficient to bring about stable N_{TB} structure. It needs to be accompanied, at least, by the non-vanishing λ -coupling ($\lambda \neq 0$) in F .

The ordered structures that minimize the free energy are predominantly the nematic twist-bend and the uniaxial nematic. Additionally, the globally polar nematic twist-bend and nematic phases are found in the admitted range of the t_P, t_Q parameters. Realization of phase sequences with decreasing temperature, along with the corresponding order of the phase transitions (which is given above the left-right arrows) presents as follows:

- a) $I \xleftrightarrow{I^{st}} N_{TB}$,
- b) $I \xleftrightarrow{I^{st}} N \xleftrightarrow{I^{st}} N_{TB}$,
- c) $I \xleftrightarrow{I^{st}} N_{TB} \xleftrightarrow{II^{nd}} N_{TBp}$,
- d) $I \xleftrightarrow{I^{st}} N_{TB} \xleftrightarrow{II^{nd}} N_{TBp} \xleftrightarrow{I^{st}} N_p$,
- e) $I \xleftrightarrow{I^{st}} N \xleftrightarrow{II^{nd}} N_p$,
- f) $I \xleftrightarrow{I^{st}} N \xleftrightarrow{I^{st}} N_{TB} \xleftrightarrow{II^{nd}} N_{TBp}$,

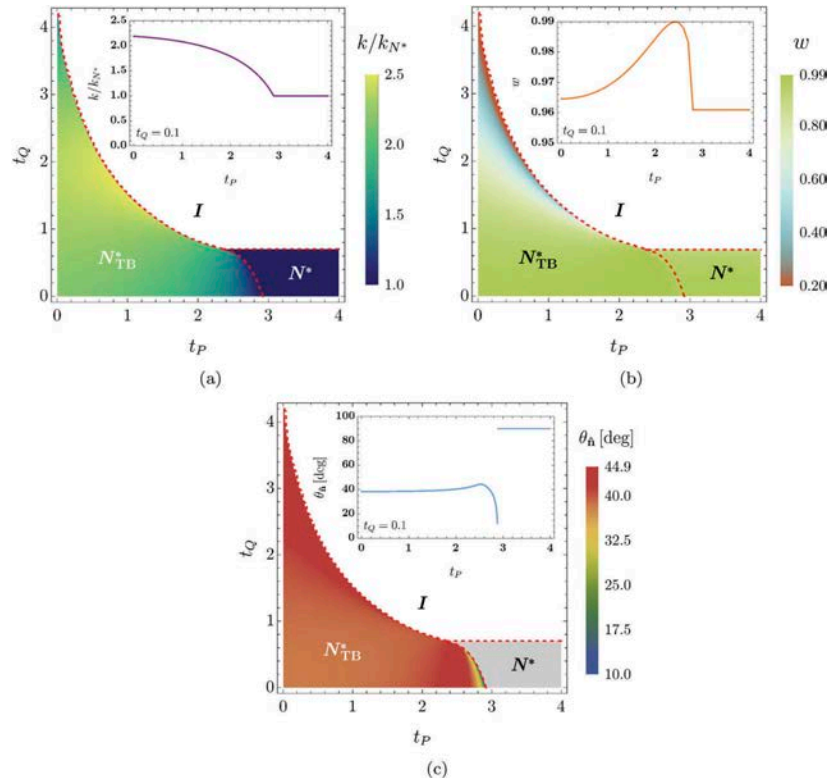


Figure 3. (Colour online) Phase diagram combined with density map of k (a), w (b) and θ_n (c) for $\kappa = 0.8$, $\lambda = -0.5$, $e_p = -6$, $a_c = \rho = 1$ and $B = 1/\sqrt{6}$. On Panel (c) area of N^* has been shown in gray as the conical angle in this phase is uniform and always equals to $\pi/2$.

$$g) I \xleftrightarrow{I^{st}} N \xleftrightarrow{I^{st}} N_{TB} \xleftrightarrow{II^{nd}} N_{TBp} \xleftrightarrow{I^{st}} N_p.$$

Given the bending of the $N - N_{TB}$ boundary in Figure 1 the reentrant nematic and/or reentrant nematic twist-bend structures are also found to be absolutely stable in a very limited slope ranges of the lines in the $\{t_P, t_Q\}$ plane. That is, the sequence (a–g) should be supplemented by

$$h) I \xleftrightarrow{I^{st}} N_{TB} \xleftrightarrow{I^{st}} N \xleftrightarrow{I^{st}} N_{TB} \xleftrightarrow{II^{nd}} N_{TBp} \xleftrightarrow{I^{st}} N_p.$$

Typical characteristics of N_{TB} , like the wave vector, the conical angle, and the biaxiality parameter are shown in Figures 1 and 2. As exemplary there are insets in Figure 2, which depict the first-order character of the phase transition between conventional N and N_{TB} phase, visible in discontinuity of the wave vector k and the conical angle θ_n . Highest values of k and θ_n are in the range of ascending t_Q alongside descending t_P .

Increasing the strength of flexopolarization enhances N_{TB} , displaces nematic range towards higher temperatures t_P and makes that value of

wave vector and conical angle rise. Finally, the biaxiality parameter of all periodic phases presented is within the range $-0.2 < w < 0.99$ indicating that the structures are biaxial.

3.2. $\kappa \neq 0$

As expected, for nonzero κ the N^* phase replaces N and chiral degeneracy of N_{TB} is removed giving N_{TB}^* . Reference phase diagrams from Figures 1 and 2 with addition of κ transform into ones in Figures 3 and 4 with all periodic structures being biaxial. All transition temperatures for N_{TB}^* and N^* are shifted towards higher values of t_Q and the period of N_{TB}^* has slightly increased (see Figure 2 (a)) as compared to the $\kappa = 0$ cases, but opposite behaviour for k is also possible. However, for respectively large κ , cholesteric overwhelms chiral twist-bend nematic. Addition of κ reduces heterogeneity of θ_n in N_{TB}^* , so in wide range on $\{t_P, t_Q\}$ plane differs only in range between $\approx 35^\circ$

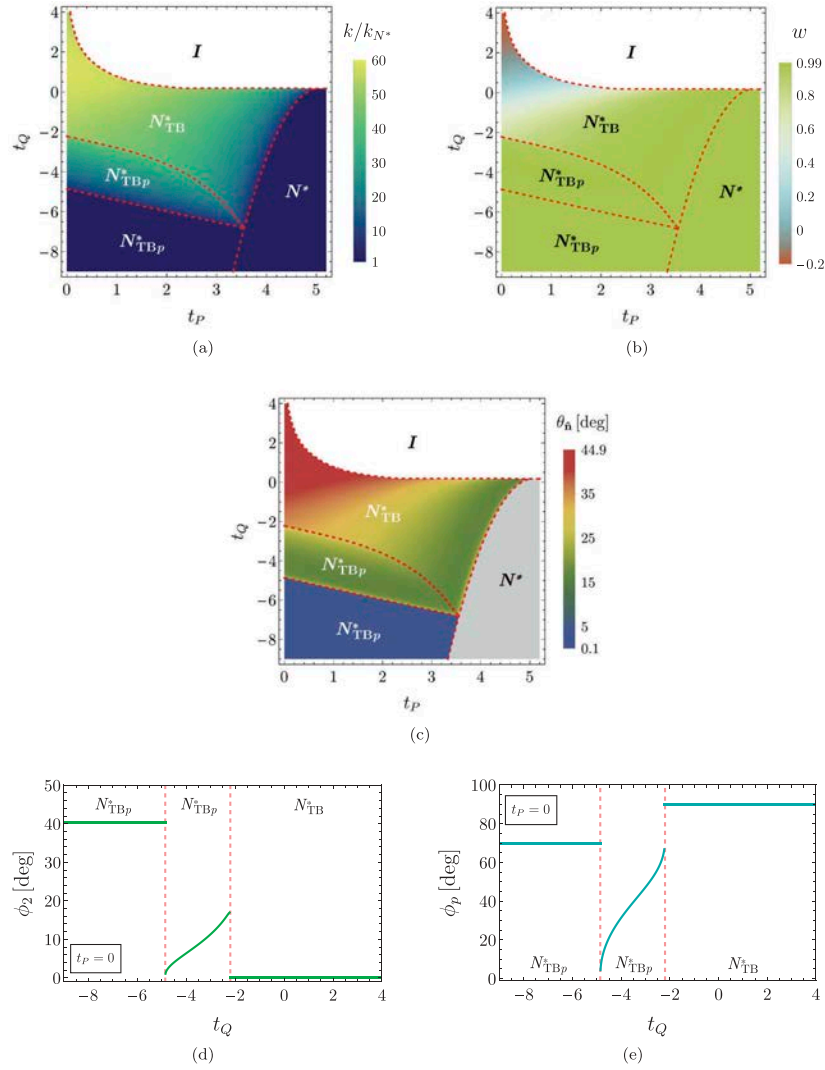


Figure 4. (Colour online) Phase diagram combined with density map of k (a), w (b) and θ_h (c) for $\kappa = 0.04$, $\lambda = 1$, $e_P = -8$, $a_c = \rho = 1$ and $B = 1/\sqrt{6}$. On Panel (c) area of N^* has been shown in gray as the conical angle in this phase is uniform and always equals to $\pi/2$. The dependence of ϕ_2 (d) and ϕ_p (e) on t_Q is given for fixed t_P .

and 45° . Notable changes occur only at the edge of phase transition (Figure 3 (c)). On the other hand, if we focus on pure cholesteric phase, the upsurge of κ , brings about only transition temperatures and wave vector changes [31]. For positive λ and $e_P \lambda < 0$ and for cases studied increase of λ wideness the landscape of new polar phases. Below N_{TB}^* emerges a globally polar, chiral twist-bend nematic (N_{TBp}^*) with k smaller than its nonpolar analogue.

As mentioned before, when molecular chirality is added, all phases of $\kappa = 0$ (Section 3.1 a–g) transform

into chiral equivalents, apart from N_p , which alters into N_{TBp}^* , with period comparable to N^* (Figure 4 (a)).

New phase sequence comprises:

- a) $I \xleftrightarrow{I^{st}} N_{TB}^* \xleftrightarrow{II^{nd}} N_{TBp}^*$
- b) $I \xleftrightarrow{I^{st}} N^* \xleftrightarrow{II^{nd}} N_{TB}^*$
- c) $I \xleftrightarrow{I^{st}} N_{TB}^* \xleftrightarrow{II^{nd}} N_{TBp}^*$
- d) $I \xleftrightarrow{I^{st}} N_{TB}^* \xleftrightarrow{II^{nd}} N_{TBp}^* \xleftrightarrow{II^{nd}} N_{TBp}^*$
- e) $I \xleftrightarrow{I^{st}} N^* \xleftrightarrow{II^{nd}} N_{TB}^* \xleftrightarrow{II^{nd}} N_{TBp}^*$
- f) $I \xleftrightarrow{I^{st}} N^* \xleftrightarrow{II^{nd}} N_{TB}^* \xleftrightarrow{II^{nd}} N_{TBp}^*$
- g) $I \xleftrightarrow{I^{st}} N^* \xleftrightarrow{II^{nd}} N_{TB}^* \xleftrightarrow{II^{nd}} N_{TBp}^* \xleftrightarrow{II^{nd}} N_{TBp}^*$

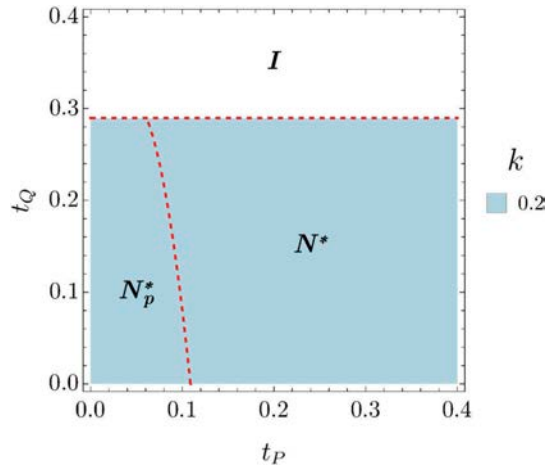


Figure 5. (Colour online) Density map of k combined with phase diagram for $\kappa = 0.4$, $\lambda = -0.2$, $e_p = 0$, $a_c = \rho = 1$ and $B = 1/\sqrt{6}$.

As in the case of $\kappa = 0$ the reentrant phase transitions are also predicted here, where the sequence (Section 3.1 h–i) is replaced by

- h) $I \xleftrightarrow{\text{I}^{\text{st}}} N_{\text{TB}}^* \xleftrightarrow{\text{I}^{\text{st}}} N^*$,
 i) $I \xleftrightarrow{\text{I}^{\text{st}}} N_{\text{TB}}^* \xleftrightarrow{\text{I}^{\text{st}}} N^* \xleftrightarrow{\text{I}^{\text{st}}} N_{\text{TBp}}^* \xleftrightarrow{\text{II}^{\text{nd}}} N_{\text{TBp}}^* \xleftrightarrow{\text{I}^{\text{st}}} N_p^*$.

Phases from Figure 4 (b) are weakly biaxial, apart from N_{TB}^* which is profoundly biaxial and can even transform from being prolate to oblate passing through a line of maximal biaxiality. Conical angle $\theta_{\hat{n}}$ varies from 45° to 15° for N_{TB}^* , where for the rest of phases is constant (N^* and N_{TBp}^* with cholesteric-like k), or almost constant (N_{TBp}^*) in the range of occurrence for particular phase on the phase diagram (Figure 4 (c)).

Figure 4 (d, e) present the behavior of phases ϕ_2 and ϕ_p (Equations (16) and (17)), respectively, for $t_p = 0$. Interestingly, the only structure where ϕ parameters vary with temperature is N_{TBp}^* , whereas for the remaining structures they are immutable.

Introduction of chirality into pure N_p state (see Section 3.1) makes that a globally polar cholesteric phase N_p^* (Table 1) can show up (Figure 5). Its wave vector is identical as that of conventional cholesteric, Equation (19), wherein difference lies in $\mathbf{P}$ parallel to k -vector.

4. Final remarks

We have studied the minimal coupling, Landau-de Gennes model of N_{TB} without and with the presence of molecular chirality to answer some of the

questions concerning number and relative stability of homogeneous nematic states that can be linked with the nematic/cholesteric phase. Detailed studies show that many new polar phases, in addition to N , N_{TB} and their chiral counterpart, could be found on a single diagram. In case of $k \neq 0$ the polarization can acquire the long-range, periodic component in the $\hat{x}$ – $\hat{y}$ plane ($p_1 \neq 0$), being perpendicular to $\hat{z}$ or global macroscopic polarization ($v_0 \neq 0$), parallel to $\hat{z}$. These scenarios can happen jointly or separately as discussed in the proceeding Section. Addition of κ makes that all phases undergo a transition to their chiral counterparts. In all structures increasing κ raises biaxiality. Interestingly, through a competition between various terms of LdeG expansion we found a class of phenomena: (a) large biaxialities in some regions of stability of N_{TB} and N_{TB}^* , and (b) the reentrant phase transitions.

In the LdeG theory the k -vector of the cholesteric phase is temperature independent and, consequently, flexopolarization has no or minor effect on the overall N^* . Due to this limitation, we cannot account for an interesting observation by Thisayukta *et al.* [37] who showed that the pitch of N^* can decrease when achiral bent-core molecules are added [37] (which is just opposite to what is observed when N^* is doped by ordinary rod-like liquid crystalline molecules). To account for such observations we need to go beyond the minimal-coupling LdeG model, where higher order elastic terms [29] are included in the expansion (3).

Somewhat different conclusions can be drawn for the k -vector of N_{TB}^* . Taking that ϕ_p in Equation (18) is equal to $\pi/2$ for both N_{TB} and N_{TB}^* and that p_1 , r_1 and r_2 are all positive the pitch of N_{TB}^* can be either larger or smaller than that measured for N_{TB} of achiral dimers, depending on the mutual sign between e_p and κ . So far only N_{TB}^* phases with the larger pitch were reported [14].

The presence of f_{QP} couplings causes that at sufficiently low temperatures all periodic structures should become globally polar (λ -term in Equation (6)) with polarization parallel to k -vector, as for N_p^* and N_{TBp}^* . In the N_p phase ($\lambda > 0$) the polarization vector would be parallel to $\hat{n}$. They are the only structures which have not been yet observed experimentally. One would expect that good candidates to form those globally polar structures should be (chiral) bent-core molecules with asymmetric arms, fine-tuned with electrostatic polar groups [38–40] to enhance λ -coupling in Equation (6).

Finally we should add that we did not include spatially inhomogeneous phases in our analysis, like blue phases. A full analysis of all consequences of the model

(Equation (3)) is, practically speaking, impossible. Already analysis including all one-dimensional periodic structures appears quite nontrivial [34].

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Appendix A.

Free energy of homogeneous structures and equations for stationary values of order parameters:

$$\begin{aligned}
 F = & \frac{1}{12} (3r_1^2 (2(-6B(\sqrt{6}r_2 \cos(\phi_2) + x_0) \\
 & + k^2 - k\kappa + t_Q + 8(2r_2^2 + x_0^2)) \\
 & + k^2 \rho) + 6r_2^2 (12Bx_0 + 4k(k - \kappa) + t_Q + 8x_0^2) \\
 & + 3x_0^2 (4x_0(x_0 - B) + t_Q) \\
 & + 3\sqrt{2}p_1 r_1 (-ke_p \sin(\phi_p) - 8\lambda v_0 \cos(\phi_p)) \\
 & + p_1^2 (6(k^2 + t_p + 8v_0^2) + 4\lambda(\sqrt{6}x_0 - 6r_2 \cos(\phi_2 - 2\phi_p))) \\
 & + 48p_1^4 + v_0^2 (3t_p - 4\sqrt{6}\lambda x_0) + 48r_1^4 + 48r_2^4 + 12v_0^4),
 \end{aligned} \tag{A1}$$

$$\begin{aligned}
 \frac{\partial F}{\partial x_0} = & \frac{1}{2} x_0 (-6Bx_0 + t_Q + 8x_0^2) + r_1^2 (8x_0 - 3B) \\
 & + r_2^2 (6B + 8x_0) + \sqrt{\frac{2}{3}} \lambda (p_1^2 - v_0^2) = 0,
 \end{aligned} \tag{A2}$$

$$\begin{aligned}
 \frac{\partial F}{\partial r_1} = & \frac{1}{4} (2r_1 (2(-6B(\sqrt{6}r_2 \cos(\phi_2) + x_0) \\
 & + k^2 - k\kappa + t_Q + 8(2r_2^2 + x_0^2)) + k^2 \rho) \\
 & - \sqrt{2}p_1 (ke_p \sin(\phi_p) + 8\lambda v_0 \cos(\phi_p)) + 64r_1^3) = 0,
 \end{aligned} \tag{A3}$$

$$\begin{aligned}
 \frac{\partial F}{\partial r_2} = & r_2 (12Bx_0 + 4k(k - \kappa) + t_Q + 16r_2^2 + 8x_0^2) \\
 & + r_1^2 (16r_2 - 3\sqrt{6}B \cos(\phi_2)) - 2\lambda p_1^2 \cos(\phi_2 - 2\phi_p) = 0,
 \end{aligned} \tag{A4}$$

$$\begin{aligned}
 \frac{\partial F}{\partial p_1} = & -\frac{r_1 (ke_p \sin(\phi_p) + 8\lambda v_0 \cos(\phi_p))}{2\sqrt{2}} \\
 & + p_1 \left(k^2 - 4\lambda r_2 \cos(\phi_2 - 2\phi_p) + t_p + 2\sqrt{\frac{2}{3}} \lambda x_0 + 8v_0^2 \right) \\
 & + 16p_1^3 = 0,
 \end{aligned} \tag{A5}$$

$$\begin{aligned}
 \frac{\partial F}{\partial v_0} = & \frac{1}{6} v_0 (48p_1^2 + 3t_p - 4\sqrt{6}\lambda x_0 + 24v_0^2) \\
 & - 2\sqrt{2}\lambda p_1 r_1 \cos(\phi_p) = 0,
 \end{aligned} \tag{A6}$$

$$\frac{\partial F}{\partial \phi_2} = r_2 (3\sqrt{6}B r_1^2 \sin(\phi_2) + 2\lambda p_1^2 \sin(\phi_2 - 2\phi_p)) = 0, \tag{A7}$$

$$\begin{aligned}
 \frac{\partial F}{\partial \phi_p} = & \frac{1}{4} p_1 (\sqrt{2}r_1 (8\lambda v_0 \sin(\phi_p) - ke_p \cos(\phi_p)) \\
 & - 16\lambda p_1 r_2 \sin(\phi_2 - 2\phi_p)) = 0.
 \end{aligned} \tag{A8}$$

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Article 4

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Twist-Bend Nematic Phase from Landau-de Gennes Perspective

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Abstract

A generalized Landau-de Gennes theory is proposed that comprehensively explains currently available experimental data for the heliconical twist-bend nematic (N_{TB}) phase observed in liquid crystalline systems of chemically *achiral* bent-core-like molecules. A bifurcation analysis gives insight into possible structures that the model can predict and guides in the numerical analysis of relative stability of the isotropic (I), uniaxial nematic (N_{U}) and twist-bend nematic phases. An estimate of constitutive parameters of the model from temperature variation of the nematic order parameter and the Frank elastic constants in the nematic phase enables to demonstrate quantitative agreement between the calculated and experimentally determined temperature dependence of the pitch and conical angle in N_{TB} . Properties of order parameters also explain a puzzling lack of half-pitch band in resonant soft X-ray scattering. Another key findings of the model are predictions of $I - N_{\text{TB}}$ and $N_{\text{U}} - N_{\text{TB}}$ tricritical points and insight into biaxiality of N_{TB} .

Introduction

Undoubtedly, the short-pitch heliconical structure formed by an ensemble of achiral bent-core-like mesogens and commonly referred to as the nematic twist-bend, is one of the most astonishing liquid crystalline phases. It is the first example in nature of a structure where mirror symmetry is spontaneously broken without any support from a long-range positional order. The structure itself is a part of an over 130-year-old tradition of liquid crystal science demonstrating that even a minor change in the molecular chemistry can lead to a new type of liquid crystalline order, which differs in the degree of orientational and translational self-organization, ranging from molecular to macro scales.¹⁻³

The most common of all known liquid crystalline phases is the uniaxial nematic phase (N_{U}), where anisotropic molecules or molecular aggregates orient, on the average, parallel to each other. Their local, mean orientation at the point $\tilde{\mathbf{r}}$ of coordinates $(\tilde{x}, \tilde{y}, \tilde{z})$ is described by

a single mesoscopic direction $\hat{\mathbf{n}}(\tilde{\mathbf{r}})$ ($|\hat{\mathbf{n}}(\tilde{\mathbf{r}})| = 1$), known as the director. Due to the statistical head-to-tail inversion symmetry of the local molecular arrangement the director states $\hat{\mathbf{n}}(\tilde{\mathbf{r}})$ and $-\hat{\mathbf{n}}(\tilde{\mathbf{r}})$ are equivalent. With an inversion symmetry and with a rotational symmetry of molecular orientational distribution about $\hat{\mathbf{n}}(\tilde{\mathbf{r}})$ the existence of the director is a basic property that distinguishes the uniaxial nematics from an ordinary isotropic liquid. That is, the N_U phase is a non-polar 3D liquid with long-range orientational order characterized by $\mathcal{D}_{\infty h}$ point group symmetry.

One important consequence of $\hat{\mathbf{n}}(\tilde{\mathbf{r}})$ being indistinguishable from $-\hat{\mathbf{n}}(\tilde{\mathbf{r}})$ is that the primary order parameter of the uniaxial nematics is the second-rank (3×3) traceless and symmetric alignment tensor (the quadrupole moment of the local angular distribution function of the molecules' long axes)

$$\tilde{\mathbf{Q}}_U(\tilde{\mathbf{r}}) = \tilde{S} \left(\hat{\mathbf{n}}(\tilde{\mathbf{r}}) \otimes \hat{\mathbf{n}}(\tilde{\mathbf{r}}) - \frac{1}{3} \mathbf{I} \right) \quad (1)$$

having components $\tilde{Q}_{U,\alpha\beta}$; $\tilde{S}$ is the scalar order parameter describing the degree of (local) molecular orientational ordering along $\hat{\mathbf{n}}(\tilde{\mathbf{r}})$ and $\mathbf{I}$ denotes the identity matrix.

Beyond conventional uniaxial nematics further nematic liquid phases, that (by definition) have only short-ranged positional ordering, were recognized. They involve $\mathcal{D}_{2h}$ symmetric biaxial nematics (N_B) for non-chiral materials and cholesteric (N^*) along with blue phases (BP) for chemically chiral mesogens, characterized locally by $\mathcal{D}_2$ point group symmetry. In order to account for their local orientational order we need a full, symmetric and traceless alignment tensor $\tilde{\mathbf{Q}}(\tilde{\mathbf{r}})$ with three different eigenvalues, as opposed to the uniaxial nematic (1), where only two eigenvalues of $\mathbf{Q} \equiv \mathbf{Q}_U$ are different.

This four-members nematic family is ubiquitous in nature and it has not been expanding for many years.¹ However, very recently the situation has changed with important discovery of two fundamentally new nematics: the twist-bend nematic phase (N_{TB})⁴⁻⁷ and the nematic splay phase (N_S),⁸ and it seems these discoveries only mark a beginning of new, fascinating

research direction in soft matter science.^{3,9-12}

Without any doubt the discovered N_{TB} phase is different than 3D liquids known to date, because it exhibits a macroscopic chirality, while formed from chemically achiral, bent-core-like molecules. A direct manifestation of chirality is an average orientational molecular order that forms a local helix with a pitch spanning from several to over a dozen of nanometers, in the absence of any long-range positional order of molecular centers of mass. N_{TB} is stabilized as a result of (weakly) first order phase transition from the uniaxial nematic phase, or directly from the isotropic phase^{13,14} and therefore (as already mentioned) its emergence is probably one of the most unusual manifestation of spontaneous mirror symmetry breaking (SMSB) in three-dimensional liquids.

At the theoretical level a possibility of SMSB in bent-shaped mesogens has been suggested by Meyer already in 1973. He pointed out that bend deformations, which should be favored by bent-shaped molecules, might lead to flexopolarization-induced chiral structures.¹⁵ About thirty years later Dozov¹⁶ considered the Oseen-Frank (OF) free energy $F_{\text{OF}} = \tilde{V}^{-1} \int_{\tilde{V}} f_{\text{OF}} d^3\tilde{\mathbf{r}}$ of the director field $\hat{\mathbf{n}}(\tilde{\mathbf{r}})$,^{17,18} where

$$f_{\text{OF}} = \frac{1}{2} [K_{11}(\tilde{\nabla} \cdot \hat{\mathbf{n}})^2 + K_{22}(\hat{\mathbf{n}} \cdot \tilde{\nabla} \times \hat{\mathbf{n}})^2 + K_{33}(\hat{\mathbf{n}} \times \tilde{\nabla} \times \hat{\mathbf{n}})^2], \quad (2)$$

and where K_{11} , K_{22} and K_{33} are splay, twist, and bend elastic constants, respectively. He correlated a possibility of SMSB in nematics with the sign change of the bend elastic constant, K_{33} . In this latter case, in order to guarantee the existence of a stable ground state, some higher order elastic terms had to be added to f_{OF} . Limiting to defect-free structures, Dozov predicted competition between a twist-bend nematic phase, where the director simultaneously twists and bends in space by precessing on the side of a right circular cone and a planar splay-bend phase with alternating domains of splay and bend, both shown in Figure 1. If we take into account temperature dependence of the Frank elastic constants then the uniaxial nematic phase becomes unstable to the formation of modulated structures

at $K_{33} = 0$, which is the critical point of the model. The behaviour of the system depends on the relationship between the splay and twist elastic constants. As it turns out the twist-bend ordering wins if $K_{11} > 2K_{22}$, while the splay-bend phase is more stable if $K_{11} < 2K_{22}$. Assuming that the wave vector $\tilde{\mathbf{k}}$ of N_{TB} stays parallel to the $\hat{\mathbf{z}}$ -axis of the laboratory reference frame ($\tilde{\mathbf{k}} = \tilde{k}\hat{\mathbf{z}}$), the symmetry-dictated, gross features of the heliconical N_{TB} structure are essentially accounted for by the uniform director modulation

$$\hat{\mathbf{n}}(\tilde{z}) = \mathcal{R}_{\hat{\mathbf{z}}}(\phi)\hat{\mathbf{n}}(0) = [\cos(\phi)\sin(\theta), \sin(\phi)\sin(\theta), \cos(\theta)], \quad (3)$$

where $\hat{\mathbf{n}}(0) = [\sin(\theta), 0, \cos(\theta)]$ and where $\mathcal{R}_{\hat{\mathbf{z}}}(\phi) = \mathcal{R}_{\hat{\mathbf{z}}}(\phi(\tilde{z}))$ is the homogeneous rotation about $\hat{\mathbf{z}}$ through the azimuthal angle $\phi(\tilde{z}) = \pm\tilde{k}\tilde{z} = \pm 2\pi\tilde{z}/p$ and where p is the pitch. The $\pm$ sign indicates that both left-handed and right-handed chiral domains should form with the same probability, which is manifestation of SMSB in the bulk. Note that the molecules in N_{TB} are inclined, on the average, from $\tilde{\mathbf{k}}$ by the conical angle θ – the angle between $\hat{\mathbf{n}}$ and the wave vector $\tilde{\mathbf{k}}$ (Figure 1). The symmetry of N_{TB} also implies that the structure must be locally polar with the polarization vector, $\tilde{\mathbf{P}}$, staying perpendicular both to the director and the wave vector

$$\tilde{\mathbf{P}}(\tilde{z}) = \mathcal{R}_{\hat{\mathbf{z}}}(\phi)\tilde{\mathbf{P}}(0) = \tilde{p}_0 [\sin(\phi), -\cos(\phi), 0]. \quad (4)$$

Hence, in the nematic twist-bend phase, both $\hat{\mathbf{n}}$ and $\tilde{\mathbf{P}}$ rotate along the helix direction $\tilde{\mathbf{k}}$ giving rise to a phase with constant bend and twist deformation of no mass density modulation (Figure 1).

In 2013 Shamid *et al.*¹⁹ developed a Landau theory for bend flexoelectricity and showed that the results of Dozov are in line with Meyer’s idea of flexopolarization-induced N_{TB} . Their theory predicts a continuous $N - N_{\text{TB}}$ transition, where the effective bend elastic constant, renormalized by the flexopolarization coupling, changes sign for sufficiently large coupling. The corresponding structure develops modulated polar order, averaging to zero globally as in Equation (4). The Dozov’s model is also supported by measurements of

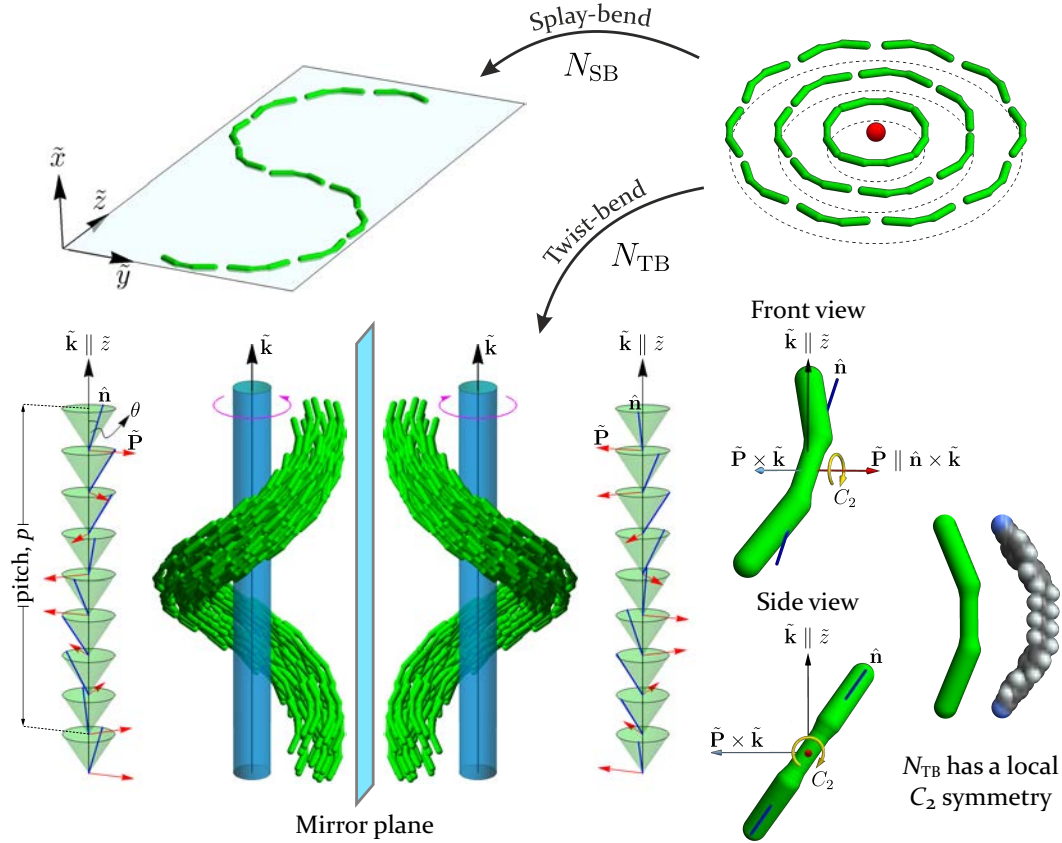


Figure 1: Schematic depiction of modulated nematic phases formed by achiral bent-shaped molecules. Pure bend distortion in 2D leads to the emergence of defects (red sphere). Their appearance can be circumvented by alternating the bend direction periodically or allowing nonzero twist by lifting bend into the third dimension. These possibilities, respectively, give rise to the two alternative nematic ground states: splay-bend (N_{SB}) and twist-bend (N_{TB}). Twist-bend nematic has been firstly observed in the phase sequence of liquid crystal dimer, 1'',7''-bis(4-cyanobiphenyl-4'-yl)heptane (CB7CB), where two identical cyanobiphenyl mesogenic groups are linked by a heptane spacer (CB7CB molecule can be viewed as having three parts: two identical rigid end groups connected by a flexible spacer). Schematic representation of molecular organization in the N_{TB} with right and left handedness (ambidextrous chirality) has been depicted at the bottom of the image. Right/left circular cone of conical angle θ shows the tilt between the director $\hat{n}$ and the helical symmetry axis, parallel to the wave vector $\tilde{k}$. Red arrow represents polarization $\tilde{P}$, where $\tilde{P} \parallel \hat{n} \times \tilde{k}$. Note that N_{TB} has a local C_2 symmetry with a two-fold symmetry axis around $\tilde{P}$.

anomalously small bend elastic constant (compared to the splay and twist elastic constants) in the nematic phase of materials exhibiting N_{TB} (*see e.g.* measurements for CB7CB dimer of Babakhanova *et al.*^{20–22}).

The second most widely used continuum model to characterize orientational properties of nematics is the minimal coupling, $SO(3)$ -symmetric Landau-de Gennes (LdeG) expansion in terms of the local alignment tensor. It allows not only to account for a fine structure of inhomogeneous nematic phases, but also shows important generalizations of the director's description in dealing with orientational degrees of freedom (*see e.g.*²³). In a series of papers,^{11,12,24} co-authored by one of us, we developed an extension of the LdeG theory to include flexopolarization couplings. The extended theory predicted that the flexopolarization mechanism can make the N_{TB} phase absolutely stable within the whole family of one-dimensional modulated structures.¹¹ A qualitatively correct account of experimental observations in N_{TB} (*see e.g.*³) was obtained, like trends in temperature variation of the helical pitch and conical angle, and behaviour in the external electric field.²⁵ The theory also predicted weakly first order phase transitions from the isotropic and nematic to the nematic twist-bend phase, again in agreement with experiments.^{14,26} Despite this qualitative success of the LdeG modelling one important theoretical issue still left unsolved is that associated with the elastic behaviour of the uniaxial nematic phase for materials with stable N_{TB} . A few existing measurements of all three elastic constants in the N_{U} phase show that $K_{11} \gtrsim 2K_{22}$ ($K_{22} \approx 3\text{--}4\text{ pN}$), while $K_{33} \approx 0.4\text{ pN}$ near the transition into N_{TB} .²⁰ That is, the splay elastic constant is about 20 times larger than the bend elastic constant. On the theoretical side, the LdeG expansion with only two distinct bulk elastic terms cannot explain this anomalously large disparity in the values of K_{11} and K_{33} . Actually, it predicts that they both are equal in the Oseen-Frank limit,^{27,28} where the alignment tensor is given by Equation (1). Therefore, there are anomalously small bend and splay Frank elastic constants on approaching N_{TB} in the LdeG model with flexopolarization.¹² Though this prediction might suggest a dominance of the structures with splay-bend deformations over the twist-bend ones, the N_{TB} phase, as

already discussed before, can still be found to be more stable than any of one-dimensional periodic structures, including the nematic splay-bend phase.¹¹ Most probably this is due to the remarkable (and unique) feature of N_{TB} of being uniform everywhere in space that makes the $SO(3)$ -symmetric elastic free energy density independent of space variables.¹¹

Central to quantitative understanding of N_{TB} and related phase transitions is then a construction of a generalized LdeG theory that releases the $K_{11} = K_{33}$ restriction of the minimal coupling model and accounts for the experimental behaviour of the Frank elastic constants in the vicinity of $N_{\text{U}} - N_{\text{TB}}$ phase transition. We expect that such a theory will allow for a systematic study of mesoscopic mechanisms that can be responsible for chiral symmetry breaking in nematics. It will also give a new insight into conditions that can potentially lead experimentalists to a discovery of new nematic phases. Although the choice of strategy has already been worked out in the literature^{24,29,30} the main problem lies in a huge number of elastic invariants in the alignment tensor, contributing to the generalized elastic free energy density of nematics. Here we show how the problem can be solved in a systematic way if we start from a theory which holds without limitations for arbitrary one-dimensional periodic distortions of the alignment tensor. These distortions form the most interesting class of structures for it obeys the recently discovered new nematic phases. An additional requirement for the generalized LdeG theory is that its ground state in the absence of flexopolarization should be that corresponding to a constant tensor field $\tilde{\mathbf{Q}}$. The theory so constructed will then be applied to characterize properties of N_{TB} formed in the class of CB7CB-like dimers and its constitutive parameters will be estimated from experimental data known for the CB7CB dimers in the N_{U} phase.

Theoretical Methods

Alignment tensor representation for homogeneously deformed nematic phases

In the N_{TB} phase the director $\hat{\mathbf{n}}$ and the polarization vector $\tilde{\mathbf{P}}$ are given by Equation (3) and (4), while the equivalent alignment tensor order parameter, $\tilde{\mathbf{Q}}_{U,TB}$, is obtained by substituting (3) into (1). Though these models seem to account for gross features of orientational order observed in N_{TB} they do not exhaust possible nematic structures that can fill space with twist, bend and splay. A full spectrum of possibilities is obtained by studying an expansion of the biaxial alignment tensor $\tilde{\mathbf{Q}}$ and the polarization field $\tilde{\mathbf{P}}$ in spin tensor modes of $L = 2$ and $L = 1$, respectively, and in plane waves (Figure S1).¹² Within this huge family of states an important class of nematic states is represented by uniformly deformed structures (UDS) where the elastic, $SO(3)$ -symmetric invariants contributing to the elastic free energy density of nematics^{24,30} are constant in space. For such structures the same tensor and polarization landscape is seen everywhere in space. They are periodic in, at most, one spatial direction, say $\tilde{z}$, and fill uniformly space without defects. In analogy to the conditions (3) and (4) for $\hat{\mathbf{n}}$ and $\mathbf{P}$, they are generated from the tensors $\tilde{\mathbf{Q}}(0)$ and $\tilde{\mathbf{P}}(0)$ for $\tilde{z} = 0$ by the previously defined homogeneous rotation $\mathcal{R}_{\tilde{\mathbf{z}}}(\pm\tilde{k}\tilde{z}) \equiv \mathcal{R}_{\tilde{\mathbf{z}}}(\phi)$.^{11,31} More specifically

$$\begin{aligned}\mathcal{R}_{\tilde{\mathbf{z}}}(\pm\tilde{k}\tilde{z})\tilde{\mathbf{Q}}(0) &= \tilde{\mathbf{Q}}(\tilde{z}), \\ \mathcal{R}_{\tilde{\mathbf{z}}}(\pm\tilde{k}\tilde{z})\tilde{\mathbf{P}}(0) &= \tilde{\mathbf{P}}(\tilde{z}),\end{aligned}\tag{5}$$

where $\pm$ labels left- (+) and right-handed (−) heliconical structures. Hence, the most general representations for UDS that generalizes Equation (3) and (4), can be cast in the

form:^{11,31}

$$\tilde{\mathbf{Q}}(\tilde{z}) = \frac{\tilde{x}_0}{\sqrt{6}} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix} + \frac{\tilde{r}_{\pm 1}}{\sqrt{2}} \begin{bmatrix} 0 & 0 & -c_{\pm 1} \\ 0 & 0 & s_{\pm 1} \\ -c_{\pm 1} & s_{\pm 1} & 0 \end{bmatrix} + \frac{\tilde{r}_{\pm 2}}{\sqrt{2}} \begin{bmatrix} c_{\pm 2} & -s_{\pm 2} & 0 \\ -s_{\pm 2} & -c_{\pm 2} & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad (6)$$

$$\tilde{\mathbf{P}}(\tilde{z}) = \tilde{p}_{\pm 1} \begin{bmatrix} -\cos(\pm \tilde{k}\tilde{z} + \phi_{\pm p}) \\ \sin(\pm \tilde{k}\tilde{z} + \phi_{\pm p}) \\ 0 \end{bmatrix} + \tilde{v}_0 \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \quad (7)$$

where $c_{\pm m} = \cos(\pm m\tilde{k}\tilde{z} + \phi_{\pm m})$ and $s_{\pm m} = \sin(\pm m\tilde{k}\tilde{z} + \phi_{\pm m})$ and where nine real parameters $\tilde{x}_0$, $\pm\tilde{k}$, $\tilde{r}_{\pm i} \geq 0$, $\tilde{p}_{\pm 1} \geq 0$, $\tilde{v}_0$, $\phi_{\pm m}$ and $\phi_{\pm p}$ for each of the $\pm$ labels characterize the fine structure of the phases, especially its biaxiality. Indeed, an arbitrary symmetric and traceless tensor field $\tilde{\mathbf{Q}}$ fulfills the inequalities (*see discussion in*³²):

$$-1 \leq w = \frac{\sqrt{6} \text{Tr}(\tilde{\mathbf{Q}}^3)}{\text{Tr}(\tilde{\mathbf{Q}}^2)^{\frac{3}{2}}} \leq 1, \quad (8)$$

which are satisfied as equalities for locally prolate ($w = 1$) and oblate ($w = -1$) uniaxial phases. States of nonzero biaxiality are realized for $-1 < w < 1$, with maximal biaxiality corresponding to $w = 0$. In particular, the parameter $w(\tilde{\mathbf{Q}}(\tilde{z}))$ for $\tilde{\mathbf{Q}}(\tilde{z})$ given by Equation (6) reads

$$w(\tilde{\mathbf{Q}}(\tilde{z})) = \frac{\frac{3}{2}\tilde{r}_{\pm 1}^2 (\sqrt{3}\tilde{r}_{\pm 2} \cos(2\phi_{\pm 1} - \phi_{\pm 2}) + \tilde{x}_0) - 3\tilde{r}_{\pm 2}^2 \tilde{x}_0 + \tilde{x}_0^3}{(\tilde{r}_{\pm 1}^2 + \tilde{r}_{\pm 2}^2 + \tilde{x}_0^2)^{3/2}}. \quad (9)$$

Note that in agreement with definition (5), the parameter $w(\tilde{\mathbf{Q}}(\tilde{z}))$ is position-independent and can take arbitrary value within the allowed $[-1, 1]$ interval, Equation (8). In contrast, for the uniaxial tensor $\tilde{\mathbf{Q}}_{U,TB}$, corresponding to $\tilde{x}_0 = \frac{\sqrt{6}S}{12}(1 + 3\cos(2\theta))$, $\tilde{r}_{\pm 1} = \frac{\sqrt{2}S}{2}\sin(2\theta)$ and $\tilde{r}_{\pm 2} = \frac{\sqrt{2}S}{2}\sin(\theta)^2$ the parameter $w(\tilde{\mathbf{Q}}_{U,TB}) = \text{Sign}(S) = \pm 1$ (θ is the conical angle).

We should mention that the fields in Equation (6) and (7) are insensitive to choice of

the origin of the laboratory system of frame, which allows to eliminate one of the phases $\phi_{\pm i}$ ($i = 1, 2, p$), independently for each of the two states with “+” and “−” subscripts. The coefficients in Equation (6) and (7) are chosen such that the norms squared of the order parameters are sums of squares of the coefficients: $\text{Tr}(\tilde{\mathbf{Q}}^2) = \tilde{x}_0^2 + \tilde{r}_{\pm 1}^2 + \tilde{r}_{\pm 2}^2$ and $\text{Tr}(\tilde{\mathbf{P}}^2) = \tilde{p}_{\pm 1}^2 + \tilde{v}_0^2$. Together, $\tilde{\mathbf{Q}}$ and $\tilde{\mathbf{P}}$ characterize a family of all defect-free homogeneously distorted (polar) helical/heliconical nematic phases (they are gathered in Table 1).

Generalized Landau-de Gennes expansion for 1D periodic nematics

In this section we introduce a generalized Landau-de Gennes free energy (GLdeG) expansion in $\tilde{\mathbf{Q}}$ and $\tilde{\mathbf{P}}$ capable of quantitative description of the systems with stable one-dimensional periodic nematics. The most important members of this family are the nematic twist-bend phase³ and recently discovered nematic splay phase.⁸ Our main effort in this and next section will concentrate on general characterization of GLdeG. An example of spatially homogeneous structures with its prominent representative - the N_{TB} phase - will be studied in great detail. Parameters entering the LdeG expansion will be estimated from experimental data

Table 1: Family of uniformly deformed nematic structures that can be constructed out of the fields $\tilde{\mathbf{Q}}$ and $\tilde{\mathbf{P}}$. Limiting cases of constant $\tilde{\mathbf{Q}}$ and $\tilde{\mathbf{P}}$ are also included.

Structure	Nonzero amplitudes	Abbreviation
Nonpolar structures		
(a) uniaxial nematic	$\tilde{x}_0$	N_{U}
(b) biaxial nematic	$\tilde{x}_0, \tilde{r}_1, \tilde{r}_2, \tilde{k} \rightarrow 0$	N_{B}
(c) (ambidextrous) cholesteric	$\tilde{x}_0, \tilde{r}_2, \tilde{k}_{N_C} = 2\tilde{k} \neq 0$	N_{C}
Locally polar structures		
(d) locally polar cholesteric	as in (c), $\tilde{p}_1$	N_{Cl}
(e) nematic twist-bend	$\tilde{x}_0, \tilde{r}_1, \tilde{r}_2, \tilde{p}_1, \tilde{k} \neq 0$	N_{TB}
Globally polar structures		
(f) polar (a)–(e)	any of (a)–(e), $\tilde{v}_0$	add subscript “ p ” to (a)–(e)

for the CB7CB compound in the uniaxial nematic phase. Then, the properties of the N_{TB} phase resulting from so constructed GLdeG expansion will be calculated and compared with available experimental data.

We assume that the stabilization of N_{TB} is due to entropic, excluded volume flexopolarization interactions,³³ induced by sterically polar molecular bent cores. The direct interactions between electrostatic dipoles will be disregarded³³ and long-range polar order will be attributed to the molecular shape polarity. With $\tilde{\mathbf{Q}}$ and $\tilde{\mathbf{P}}$ the general LdeG expansion then reads^{24,28}

$$\tilde{F} = \frac{1}{\tilde{V}} \int_{\tilde{V}} \tilde{f}_{tot} d^3\tilde{\mathbf{r}} = \frac{1}{\tilde{V}} \int_{\tilde{V}} \left(\tilde{f}_{b,Q} + \tilde{f}_{e,Q} + \tilde{f}_P + \tilde{f}_{QP} \right) d^3\tilde{\mathbf{r}}, \quad (10)$$

where $\tilde{\mathbf{r}}$ is the position vector, $\tilde{V}$ is the system's volume and where the free energy densities, $\tilde{f}_{x,X}$, are constructed out of the fields X . They involve the bulk nematic part $\tilde{f}_{b,Q}$, the nematic elastic part $\tilde{f}_{e,Q}$ and the parts $\tilde{f}_P$ and $\tilde{f}_{QP}$ responsible for the onset of chirality in the nematic phase. Although the general theory has plenty of constitutive parameters part of them, at least for CB7CB, can be estimated from existing experimental data for the N_U and at the $I - N_U$ and $N_U - N_{TB}$ phase transitions. One of the issues we would like to understand is whether the theory so constructed allows to account for the quantitative properties of the nematic twist-bend phase, below $N_U - N_{TB}$ phase transition.

Bulk nematic free energy

According to the phenomenological Landau-de Gennes (LdG) theory the equilibrium bulk properties of nematics can be found from a nonequilibrium free energy, constructed as an $SO(3)$ -symmetric expansion in powers of $\tilde{\mathbf{Q}}$. There are only two types of independent $SO(3)$ invariants that can be constructed out of $\tilde{\mathbf{Q}}$, namely $\text{Tr}(\tilde{\mathbf{Q}}^2)$ and $\text{Tr}(\tilde{\mathbf{Q}}^3)$. Hence $\tilde{f}_{Qb}$ is a polynomial in $\text{Tr}(\tilde{\mathbf{Q}}^2)$ and $\text{Tr}(\tilde{\mathbf{Q}}^3)$ with the only restriction on the expansion being that it must be stable against an unlimited growth of $\tilde{\mathbf{Q}}$. As we will show the experimental data for $\tilde{S}$ in the nematic phase of CB7CB fit well to a model where the expansion with respect to $\tilde{\mathbf{Q}}$ is taken at least up to sixth order terms. More specifically, in the absence of electric and

magnetic fields, introducing $\tilde{I}_2 = \text{Tr}(\tilde{\mathbf{Q}}^2)$ and $\tilde{I}_3 = \text{Tr}(\tilde{\mathbf{Q}}^3)$, we take for the bulk free energy density of the isotropic and the nematic phases

$$\tilde{f}_{Qb} = \tilde{f}_{Qb}[\tilde{I}_2, \tilde{I}_3] = a_Q \tilde{I}_2 - b \tilde{I}_3 + c \tilde{I}_2^2 + d \tilde{I}_2 \tilde{I}_3 + e \left(\tilde{I}_2^3 - 6 \tilde{I}_3^2 \right) + f \tilde{I}_3^2. \quad (11)$$

A full account of phases, critical and tricritical points that this theory predicts is found in.³²

The coefficients of the expansion (11) generally depend on temperature and other thermodynamic variables, but in Landau theory the explicit temperature dependence is retained only in the bulk part, quadratic in $\tilde{\mathbf{Q}}$. In what follows, as a measure of temperature we choose the relative temperature distance, Δt , from the nematic-isotropic phase transition, defined through the relation

$$a_Q = a_{0Q} \frac{(T - T^*)}{T_{NI}} = a_{0Q} \left(\frac{T - T_{NI}}{T_{NI}} + \frac{T_{NI} - T^*}{T_{NI}} \right) = a_{0Q} (\Delta t + \Delta t_{NI}), \quad (12)$$

where $a_{0Q} > 0$, T is the absolute temperature, T_{NI} is the nematic-isotropic transition temperature, T^* is the spinodal for a first-order phase transition from the isotropic phase to the uniaxial nematic phase, $\Delta t = (T - T_{NI})/T_{NI} \leq 0$ and $\Delta t_{NI} = (T_{NI} - T^*)/T_{NI} > 0$ is the reduced temperature distance of nematic-isotropic transition temperature from T^* . Additionally, $b, c, d, e > 0$ and $f > 0$ are the temperature independent expansion coefficients. The last two conditions for e and f guarantees that $\tilde{f}_{Qb}$ is stable against an unlimited growth of $\tilde{\mathbf{Q}}$.³² The expansion, Equation (11), generally accounts for the isotropic, uniaxial nematic and biaxial nematic phases.^{32,34}

We should mention that the fourth order expansion, where $c > 0$ and $d = e = f = 0$ predicts that the N_{TB} phase can be absolutely stable within the family of one-dimensional modulated structures,¹¹ but the theory does not give a quantitative agreement with the data for $\tilde{S}$ in the nematic phase of CB7CB unless unphysically large value of Δt_{NI} is taken.

Elastic free energy

A spatial deformation of the alignment tensor $\tilde{\mathbf{Q}}$ in the nematic phase is measured by the elastic free energy density $\tilde{f}_{Qel}$ of the Landau free energy expansion (10). For the description of elastic properties of nematic liquid crystals $\tilde{f}_{Qel}$ usually is expanded into powers of $\tilde{\mathbf{Q}}$ and its first derivatives $\partial\tilde{\mathbf{Q}} \equiv \partial\tilde{Q}_{ij}/\partial\tilde{x}_k = \tilde{Q}_{ij,k}$, where only quadratic terms in derivatives of the order parameter field are retained, in line with similar expansion for the director field, Equation (2).

This standard, the so called minimal-coupling Landau-de Gennes expansion for $\tilde{f}_{Qel}$, comprises of only two elastic terms: $[L_1^{(2)}] = \tilde{Q}_{\alpha\beta,\gamma}\tilde{Q}_{\alpha\beta,\gamma}$ and $[L_2^{(2)}] = \tilde{Q}_{\alpha\beta,\beta}\tilde{Q}_{\alpha\gamma,\gamma}$. Although again the theory, Equation (10), with $\tilde{f}_{Qel}$ containing only these two elastic terms accounts for absolutely stable N_{TB} among one-dimensional modulated structures¹¹ it is not sufficiently general to quantitatively reproduce, *e.g.* elastic properties of bent-core systems in the parent nematic phase for it implies equality of splay and bend Frank elastic constants, which so far is not an experimentally supported scenario with stable N_{TB} . Thus, we need to include higher-order elastic terms in the LdeG theory to account for experimentally observed elastic behaviour of bent-core mesogens. A general form of the LdeG elastic free energy density has been studied by Longa *et al.* in a series of papers.^{24,28,30} As it turns out the most important are third-order invariants of the form $\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}$, given explicitly in Supporting Information, because they are the lowest order terms removing splay-bend degeneracy of the second-order theory.²⁸ But with quadratic and cubic terms alone the elastic free energy $\tilde{f}_{Qel}$ is unbounded from below and, hence, cannot represent a correct theory of nematics. To assure the nematic ground state is stable against an unlimited growth of $\tilde{Q}_{\alpha\beta}$ and $\tilde{Q}_{\alpha\beta,\gamma}$ we need to add some fourth-order invariants.²⁸ In total, there are 22 deformation modes $[L_i^{(n)}]$ of $\tilde{\mathbf{Q}}$ up to the order $\tilde{\mathbf{Q}}\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}$ (*see* Supporting Information for details). The next step is to single out the relevant elastic terms $[L_i^{(n)}]$ that should enter the expansion $\tilde{f}_{Qel}$. A considerable reduction in the number of independent terms is obtained if we limit ourselves to a class of one-dimensional periodic structures $\tilde{\mathbf{Q}}(\tilde{z} + \tilde{p}) = \tilde{\mathbf{Q}}(\tilde{z})$.^{11,35} Then, the only relevant linearly

independent $[L]$ -terms are

- $\partial\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}$ terms: $[L_1^{(2)}], [L_2^{(2)}]$
- $\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}$ terms: $[L_2^{(3)}], [L_3^{(3)}], [L_4^{(3)}]$
- $\tilde{\mathbf{Q}}\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}$ terms: $[L_2^{(4)}], [L_3^{(4)}], [L_5^{(4)}], [L_6^{(4)}], [L_7^{(4)}], [L_{10}^{(4)}], [L_{11}^{(4)}]$.

As mentioned before the most important are third order terms $\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}$ linear in $\tilde{\mathbf{Q}}$ and quadratic in $\partial\tilde{\mathbf{Q}}$, because they remove splay-bend degeneracy.²⁸ Hence, in what follows we will keep the third-order terms and add three stabilizing terms of the order $\tilde{\mathbf{Q}}\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}$. More specifically, for the elastic free energy $\tilde{f}_{Qel}$ we take a sum of quadratic terms in deformations of the form:

$$\begin{aligned} \tilde{f}_{Qel} = & L_1^{(2)}\tilde{Q}_{\alpha\beta,\gamma}\tilde{Q}_{\alpha\beta,\gamma} + L_2^{(2)}\tilde{Q}_{\alpha\beta,\beta}\tilde{Q}_{\alpha\gamma,\gamma} + L_{14}^{(4)}\left(\lambda_2\tilde{Q}_{\mu\nu,\nu} + \tilde{Q}_{\alpha\beta}\tilde{Q}_{\alpha\mu,\beta}\right)^2 + \\ & L_6^{(4)}\left(\lambda_3\tilde{Q}_{\beta\nu,\nu} + \tilde{Q}_{\alpha\beta}\tilde{Q}_{\alpha\mu,\mu}\right)^2 + L_7^{(4)}\left(\lambda_4\tilde{Q}_{\beta\mu,\nu} + \tilde{Q}_{\alpha\beta}\tilde{Q}_{\alpha\mu,\nu}\right)^2 \end{aligned} \quad (13)$$

$$\begin{aligned} = & \left(L_1^{(2)} + \lambda_4^2 L_7^{(4)}\right) [L_1^{(2)}] + \left(L_2^{(2)} + \lambda_2^2 L_{14}^{(4)} + \lambda_3^2 L_6^{(4)}\right) [L_2^{(2)}] + \\ & L_2^{(3)} [L_2^{(3)}] + L_{14}^{(4)} [L_{14}^{(4)}] + L_3^{(3)} [L_3^{(3)}] + L_6^{(4)} [L_6^{(4)}] + L_4^{(3)} [L_4^{(3)}] + L_7^{(4)} [L_7^{(4)}] \end{aligned} \quad (14)$$

where the coefficients $L_i^{(n)}$ denote temperature-independent elastic constants that couple with the invariant $[L_i^{(n)}]$ and where $\lambda_2 = L_2^{(3)} / (2L_{14}^{(4)})$, $\lambda_3 = L_3^{(3)} / (2L_6^{(4)})$, and $\lambda_4 = L_4^{(3)} / (2L_7^{(4)})$. Use of the $[L_{14}^{(4)}]$ invariant, which is a linear combination of the invariants $\tilde{\mathbf{Q}}\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}\partial\tilde{\mathbf{Q}}$, allows to write the stability criteria for $\tilde{f}_{Qel}$ in a simple form (see Supporting Information). Indeed, the elastic free energy density $\tilde{f}_{Qel}$ is a sum of positive-definite terms if

$$\begin{aligned} L_1^{(2)} &> 0, \quad L_1^{(2)} + \frac{2}{3}L_2^{(2)} > 0, \\ L_6^{(4)} &> 0 \quad \vee \quad L_6^{(4)} = 0 \wedge L_3^{(3)} = 0, \\ L_7^{(4)} &> 0 \quad \vee \quad L_7^{(4)} = 0 \wedge L_4^{(3)} = 0, \\ L_{14}^{(4)} &> 0 \quad \vee \quad L_{14}^{(4)} = 0 \wedge L_2^{(3)} = 0. \end{aligned} \quad (15)$$

The conditions (15) are sufficient ones for $\tilde{f}_{Qel}$ to be positive definite ($\tilde{f}_{Qel} \geq 0$). For smooth tensor fields $\tilde{\mathbf{Q}}$ the ground state of $\tilde{f}_{Qel}$ ($\tilde{f}_{Qel} = 0$) corresponds to a constant, position-independent $\tilde{\mathbf{Q}}$, which represents an unperturbed uniaxial or biaxial nematic state. As we show later in the text, the elastic constants $L_m^{(n)}$ entering expansion (14) can all be estimated from the data for Frank elastic constants in the uniaxial nematic phase. To conclude, the free energy (14) is a thermodynamically stable expansion of the Landau-de Gennes free energy in the local alignment tensor, complete up to third-order for deformations realized in one spatial direction.

The elastic free energy (14) can still be written in a simpler form by further selecting terms that are relevant for UDS. Indeed, substitution of Equation (6) into expansion (14) induces extra relations between cubic and quartic elastic invariants, namely

$$\left[L_2^{(3)} \right] = -2 \left[L_3^{(3)} \right], \quad \left[L_{14}^{(4)} \right] = 4 \left[L_6^{(4)} \right]. \quad (16)$$

Thus, in seeking for a relative stability of UDS two elastic terms in (14) are still redundant. This redundancy becomes especially transparent in the parameterization where the elastic constants $L_2^{(3)}$, $L_3^{(3)}$, $L_6^{(4)}$ and $L_{14}^{(4)}$ are replaced by appropriate linear combinations of $L_7^{(3)}$, $L_8^{(3)}$, $L_{15}^{(4)}$ and $L_{16}^{(4)}$. They are given by

$$\begin{aligned} L_2^{(3)} &= L_8^{(3)} - L_7^{(3)}, & L_3^{(3)} &= 2 \left(L_8^{(3)} + L_7^{(3)} \right), \\ L_6^{(4)} &= 4 \left(L_{15}^{(4)} - L_{16}^{(4)} \right), & L_{14}^{(4)} &= L_{15}^{(4)} + L_{16}^{(4)}. \end{aligned} \quad (17)$$

where, in addition, the inequality $L_{15}^{(4)} > \left| L_{16}^{(4)} \right|$ is required to fulfill stability conditions (15). Substitution of (17) into (14) now yields

$$\begin{aligned} \tilde{f}_{Qel} &= \left(L_1^{(2)} + \lambda_4^2 L_7^{(4)} \right) \left[L_1^{(2)} \right] + \left(L_2^{(2)} + \lambda_2^2 L_{14}^{(4)} + \lambda_3^2 L_6^{(4)} \right) \left[L_2^{(2)} \right] + \\ &L_7^{(3)} \left[L_7^{(3)} \right] + L_{15}^{(4)} \left[L_{15}^{(4)} \right] + L_8^{(3)} \left[L_8^{(3)} \right] + L_{16}^{(4)} \left[L_{16}^{(4)} \right] + L_4^{(3)} \left[L_4^{(3)} \right] + L_7^{(4)} \left[L_7^{(4)} \right] \end{aligned} \quad (18)$$

where

$$\begin{aligned}
\left[L_7^{(3)} \right] &= 2 \left[L_3^{(3)} \right] - \left[L_2^{(3)} \right], \\
\left[L_8^{(3)} \right] &= 2 \left[L_3^{(3)} \right] + \left[L_2^{(3)} \right], \\
\left[L_{15}^{(4)} \right] &= \left[L_{14}^{(4)} \right] + 4 \left[L_6^{(4)} \right], \\
\left[L_{16}^{(4)} \right] &= \left[L_{14}^{(4)} \right] - 4 \left[L_6^{(4)} \right],
\end{aligned} \tag{19}$$

and where $\left[L_8^{(3)} \right]$ and $\left[L_{16}^{(4)} \right]$ terms vanish for UDS, given by Equation (6).

Coupling with steric polarization

According to the current understanding of the formation of stable twist–bend nematic phase its orientational order, being similar to that of smectic C^* ,¹ should be accompanied with a long-range polar order of molecular bent cores.^{36–40} As already pointed out the other direct molecular interactions, such as between electrostatic dipoles, are probably less relevant for thermal stability of this phase. Up to the leading order in $\tilde{\mathbf{P}}$ at least five extra terms must be included in $\tilde{f}_P$ and $\tilde{f}_{QP}$, Equation (10). They read^{11,12,28}

$$\tilde{f}_P = a_P \tilde{\mathbf{P}}^2 + A_4 (\tilde{\mathbf{P}}^2)^2 + b_P (\tilde{\nabla} \otimes \tilde{\mathbf{P}})^2, \tag{20}$$

$$\tilde{f}_{QP} = -\varepsilon_P \tilde{\mathbf{P}} \cdot (\tilde{\nabla} \cdot \tilde{\mathbf{Q}}) - \Lambda_{QP} \tilde{P}_\alpha \tilde{Q}_{\alpha\beta} \tilde{P}_\beta. \tag{21}$$

Here $a_P = a_{0P}((T - T_P)/T_{NI}) = a_{0P}(\Delta t + \Delta t_{NI,P})$, where $\Delta t_{NI,P} = (T_{NI} - T_P)/T_{NI} > 0$, $A_4 > 0$, $b_P > 0$, ε_P and Λ_{QP} are further temperature-independent constitutive parameters of the model. Again, limitations for A_4 and b_P stem from stability requirement of a ground state against unlimited fluctuations of $\tilde{\mathbf{P}}(\tilde{\mathbf{r}})$. The ε_P -term represents lowest-order flexopolarization contribution while the Λ_{QP} -term is the direct coupling between the polarization field and the alignment tensor. The presently existing experimental data seem in line with this minimal coupling expansion for the (flexo)polarization part of the free energy.^{11,12} A full structure

of the (flexo)polarization theory, along with some of its general consequences, can be found in.²⁴

Reduced form of generalized Landau de-Gennes expansion

For practical calculations it is useful to reduce the number of model parameters by rewriting Equation (10) in terms of reduced (dimensionless) quantities. It reveals the redundancy of four parameters in the expressions (11,14,20,21) and allows to set them to one from the start.^{12,24,28,29} This reduction is a direct consequence of the freedom to choose a scale for the free energy, $\tilde{F} = \Lambda_F F$, for the fields $\tilde{\mathbf{Q}} = \Lambda_Q \mathbf{Q}$ and $\tilde{\mathbf{P}} = \Lambda_P \mathbf{P}$, and for the position vector $\tilde{\mathbf{r}} = \Lambda_r \mathbf{r}$, where Λ_i are nonzero scaling parameters. Taking this freedom into account we introduce the reduced quantities F (f_{tot}), $\mathbf{Q}$ (equivalently S, x_0, r_1, r_2), $\mathbf{P}$ (equivalently p_1, v_0), $\mathbf{r}, \mathbf{k}, t_Q, \rho_{2,2} - \rho_{4,16}, t_P, a_d, e_P, \lambda, c_b, d_b$ and e_b with the help of equations

$$\begin{aligned}
\tilde{F} &= \frac{b^2}{f} F \quad (\tilde{f}_{tot} = \frac{b^2}{f} f_{tot}), \quad \tilde{\mathbf{r}} = \frac{\sqrt[6]{f} \sqrt{L_1^{(2)}}}{b^{2/3}} \mathbf{r}, \quad \tilde{\mathbf{Q}} = \sqrt[3]{\frac{b}{f}} \mathbf{Q}, \\
\tilde{\mathbf{P}} &= \sqrt[3]{\frac{b}{f}} \sqrt{\frac{L_1^{(2)}}{b_P}} \mathbf{P}, \quad a_Q = \sqrt[3]{\frac{b^4}{f}} t_Q, \quad a_P = \frac{b^{4/3} b_P t_P}{\sqrt[3]{f} L_1^{(2)}}, \\
L_2^{(2)} &= L_1^{(2)} \rho_{2,2}, \quad L_i^{(3)} = \sqrt[3]{\frac{f}{b}} L_1^{(2)} \rho_{3,i}, \quad L_i^{(4)} = \sqrt[3]{\left(\frac{f}{b}\right)^2} L_1^{(2)} \rho_{4,i} \\
\lambda_i &= L_1^{(2)} l_i, \quad l_2 = \frac{\rho_{3,2}}{2 \rho_{4,14}}, \quad l_3 = \frac{\rho_{3,3}}{2 \rho_{4,6}}, \quad l_4 = \frac{\rho_{3,4}}{2 \rho_{4,7}}, \\
A_4 &= \frac{\sqrt[3]{b^2 f} a_d b_P^2}{\left(L_1^{(2)}\right)^2}, \quad \varepsilon_P = \frac{b^{2/3} \sqrt{b_P} e_P}{\sqrt[6]{f}}, \quad \Lambda_{QP} = \frac{b b_P}{L_1^{(2)}} \lambda, \\
c &= \sqrt[3]{b^2 f} c_b, \quad d = \sqrt[3]{b f^2} d_b, \quad \tilde{\mathbf{k}} = \frac{b^{2/3}}{\sqrt[6]{f} \sqrt{L_1^{(2)}}} \mathbf{k}.
\end{aligned} \tag{22}$$

The remaining quantities (S, x_0, r_1, r_2) and (p_1, v_0) are connected with their tilted counterparts by the same relations as $\mathbf{Q}$ with $\tilde{\mathbf{Q}}$ and $\mathbf{P}$ with $\tilde{\mathbf{P}}$, respectively. In addition, the

definitions (19) now become reduced to

$$\begin{aligned}\rho_{3,2} &= \rho_{3,8} - \rho_{3,7}, & \rho_{3,3} &= 2(\rho_{3,7} + \rho_{3,8}), \\ \rho_{4,6} &= 4(\rho_{4,15} - \rho_{4,16}), & \rho_{4,14} &= \rho_{4,15} + \rho_{4,16}.\end{aligned}\quad (23)$$

Consequently, the generalized Landau-de Gennes free energy expansion in terms of reduced variables $\mathbf{Q}$ and $\mathbf{P}$ reads

$$F = \frac{1}{V} \int_V f_{tot} d^3\mathbf{r} = \frac{1}{V} \int_V (f_{b,Q} + f_{e,Q} + f_P + f_{QP}) d^3\mathbf{r}, \quad (24)$$

where

$$f_{Qb} = f_{Qb}[I_2, I_3] = t_Q I_2 - I_3 + c_b I_2^2 + d_b I_2 I_3 + e_b (I_2^3 - 6I_3^2) + I_3^2, \quad (25)$$

$$\begin{aligned}f_{Qel} &= (1 + \rho_{4,7} l_4^2) Q_{\alpha\beta,\gamma} Q_{\alpha\beta,\gamma} + (\rho_{2,2} + \rho_{4,14} l_2^2 + \rho_{4,6} l_3^2) Q_{\alpha\beta,\beta} Q_{\alpha\gamma,\gamma} + \\ &(\rho_{3,8} - \rho_{3,7}) Q_{\alpha\beta} Q_{\alpha\mu,\beta} Q_{\mu\nu,\nu} + 2(\rho_{3,8} + \rho_{3,7}) Q_{\alpha\beta} Q_{\alpha\mu,\mu} Q_{\beta\nu,\nu} + \\ &\rho_{3,4} Q_{\alpha\beta} Q_{\alpha\mu,\nu} Q_{\beta\mu,\nu} + \rho_{4,7} Q_{\alpha\beta} Q_{\gamma\beta} Q_{\alpha\mu,\nu} Q_{\gamma\mu,\nu} + \\ &4(\rho_{4,15} - \rho_{4,16}) Q_{\alpha\beta} Q_{\gamma\beta} Q_{\alpha\mu,\mu} Q_{\gamma\nu,\nu} + (\rho_{4,15} + \rho_{4,16}) Q_{\alpha\beta} Q_{\gamma\delta} Q_{\alpha\mu,\beta} Q_{\gamma\mu,\delta},\end{aligned}\quad (26)$$

$$f_P = t_P \mathbf{P}^2 + a_d (\mathbf{P}^2)^2 + (\nabla \otimes \mathbf{P})^2, \quad (27)$$

$$f_{QP} = -e_P \mathbf{P} \cdot (\nabla \cdot \mathbf{Q}) - \lambda P_\alpha Q_{\alpha\beta} P_\beta, \quad (28)$$

and where $I_2 = \text{Tr}(\mathbf{Q}^2)$ and $I_3 = \text{Tr}(\mathbf{Q}^3)$. In this parameterization terms proportional to $\rho_{3,8}$ and $\rho_{4,16}$ vanish for UDS.

The expansion (24-28) is our GLdeG theory of modulated nematics. If we limit ourselves to a family of periodic structures with periodicity being developed in one spatial direction the nonzero cubic and quartic couplings: $\rho_{3,4}$, $\rho_{3,7}$, $\rho_{4,7}$ and $\rho_{4,15}$ should admit the UDS states as global minimizers. The remaining two couplings: $\rho_{3,8}$ and $\rho_{4,16}$ are solely responsible for one-dimensional, *nonuniform* periodic distortions, which makes the corresponding elastic

terms vanish for UDS. This means that depending on the choice of $\rho_{3,8}$ and $\rho_{4,16}$ we should be able to eliminate inhomogeneously deformed structures from the ground states of GLdeG, leaving only UDS. In the remaining part of this paper we are going to concentrate exclusively on this simpler case.

Bifurcation scenarios for uniformly deformed structures

Here we limit ourselves to the UDS structures given in Table 1 and determine bifurcation conditions for various symmetry breaking transitions. Clearly, the isotropic-uniaxial nematic bifurcation temperature is given by T^* (12), which represents spinodal, while the $I - N_U$ phase transition takes place at T_{NI} , slightly above T^* . Likewise, T_P entering a_P , Equation (20), is transition temperature for a hypothetical phase transition from the isotropic to ferroelectric phase ($\mathbf{P} \neq 0$), in the absence of the nematic order ($\mathbf{Q} = 0$). Both, T^* and T_P are examples of bifurcation temperatures from less ordered phase (isotropic) - to more ordered one (nematic, ferroelectric). There are further bifurcations possible for UDS. Below, we give bifurcation conditions for all possible phase transitions between UDS given in Table 1. The procedure is found in¹² and we only briefly sketch it below. For given material parameters the equilibrium amplitudes $y_i \in \{ r_1, r_2, p_1, x_0, v_0 \}$ are found from the minimization of the free energy F , Equation (13), calculated for UDS (explicit formula for F is listed in the Supplementary Material). They are solutions of a system of polynomial equations $\psi_i(t_Q, t_P, \{y_\alpha\}) \equiv \partial F / \partial y_i = 0$. In order to employ a bifurcation analysis to $\{\psi_\alpha\}$ we expand y_i , t_Q and t_P in an arbitrary parameter ε :

$$\begin{aligned} y_i &= y_{i,0} + \varepsilon y_{i,1} + \varepsilon^2 y_{i,2} + \dots \\ t_m &= t_{m,0} + \varepsilon t_{m,1} + \varepsilon^2 t_{m,2} + \dots \quad m = Q, P, \end{aligned} \quad (29)$$

where non-vanishing $y_{i,0}$ define the reference, higher symmetric phase. For example, if the reference state is the N_U phase, only $y_{4,0} \equiv x_{0,0}$ is nonzero in Equation (29). By substituting

Equation (29) into $\{\psi_\alpha = 0\}$ and letting equations of the same order in ε vanish we find equations for $y_{i,\alpha}$ and t_m , ($m = Q, P$). The leading terms, proportional to ε^0 , are equations describing the high-symmetric reference state. Terms of the order ε^1 give conditions for bifurcation to a low-symmetric phase. An equivalent approach would be to construct from F the effective Landau expansion $\delta f(y_p)$ in a primary order parameter y_p of low-symmetric phase by systematically eliminating the remaining parameters $\{y_i\}$. A detailed procedure is given in Ref.²⁹ For example, in case of the $N_U - N_{TB}$ phase transition we could take for the primary order parameter either $y_1 \equiv r_1$ or $y_3 \equiv p_1$ with the final formulas being insensitive to the choice. Before we start it proves convenient to introduce auxiliary variables κ_1 and κ_2 :

$$\begin{aligned}\kappa_1 &= 1 + l_4^2 \rho_{4,7}, \\ \kappa_2 &= 2 \kappa_1 + \rho_{2,2} + l_2^2 \rho_{4,14} + l_3^2 \rho_{4,6},\end{aligned}\tag{30}$$

and relative phases χ_1, χ_2 :

$$\begin{aligned}\chi_1 &= \phi_1 - \phi_p, \\ \chi_2 &= \phi_2 - 2\phi_p,\end{aligned}\tag{31}$$

which simplify the free energy and consequently also bifurcation formulas.

Bifurcation condition for $I - N_{TB}$ phase transition

A bifurcation condition for a phase transition from the isotropic phase to the nematic twist-bend phase can be written down as an equation connecting t_P and t_Q :

$$a \equiv a(t_P, t_Q) = 2(k^2 + t_P) - \frac{e_P^2 k^2 \sin^2(\chi_1)}{2 \kappa_2 k^2 + 4 t_Q} = 0.\tag{32}$$

If we permit the k -vector and χ_1 to vary, then the bifurcation temperature $t_{P,I-TB}$ from the isotropic to nematic twist-bend phases will be the maximal t_P fulfilling the condition (32). Solving Equation (32) for t_P and maximizing with respect to k and χ gives the bifurcation values for k , $\sin(\chi_1)$ and t_P . They read

$$\begin{aligned} k_{I-TB}^2 &= \max \left(0, \frac{\sqrt{t_Q} |e_P|}{\sqrt{2} |\kappa_2|} - \frac{2t_Q}{\kappa_2} \right), \quad \text{for } t_Q > t_{NI} > 0, \quad \kappa_2 > 0 \\ \sin(\chi_{1,I-TB})^2 &= 1 \\ t_{P,I-TB} &= \begin{cases} 0 & \text{for } k_{I-TB} = 0 \\ \frac{e_P^2 + 8t_Q - 4\sqrt{2}\sqrt{t_Q}|e_P|}{4\kappa_2} & \text{for } k_{I-TB} > 0 \end{cases} \end{aligned} \quad (33)$$

where $t_{NI} > 0$ is the isotropic-uniaxial nematic transition temperature. Using formalism of Ref.²⁹ one can also show that the a -term, Equation (32), is actually the leading coefficient in the Landau expansion of the free energy of the N_{TB} phase about the reference I phase in the primary order parameter p_1 :

$$\Delta f_{I-TB} = \frac{1}{2!} a p_1^2 + \frac{1}{4!} b p_1^4 + \frac{1}{6!} c p_1^6 + \dots \quad (34)$$

Generally, nonzero value k_{I-TB} of the k -vector at the bifurcation point ($e_P^2 > 8t_Q$) indicates that the $I - N_{TB}$ phase transition is, at least weakly, first order. It can be classified as an example of a weak crystallization introduced by Kats *et al.*,⁴¹ with fluctuations that should be observed near the $k = k_{I-TB}$ sphere. Interestingly, for $k = k_{I-TB} = 0$ a direct inspection of higher-order terms of the expansion (34) shows that $b = 24a_d - \frac{\lambda^2}{t_Q}$ can change sign for sufficiently large λ . That is, for $c > 0$ the $I - N_{TB}$ transition can be first order ($a = 0$, $b < 0$), second order ($a = 0$, $b > 0$), or tricritical ($a = 0$, $b = 0$).

Bifurcation condition for $N_U - N_{TB}$ phase transtition

A bifurcation condition from N_U to N_{TB} , expressed in terms of an equation connecting t_P and x_0 reads:

$$a \equiv a(t_P, x_0) = 2 \left(k^2 + t_P + \frac{\lambda x_0}{\sqrt{6}} \right) - \frac{3 e_P^2 \sin^2(\chi_1)}{6 \kappa_2 + x_0 (\sqrt{6} \kappa_3 + \kappa_4 x_0)} = 0, \quad (35)$$

where $\kappa_3 = \rho_{3,4} - 4\rho_{3,7}$, $\kappa_4 = 5\rho_{4,7} + 8\rho_{4,15}$ and where x_0 is the nematic order parameter calculated from the minimization of f_{Qb} in the uniaxial nematic phase. For fixed t_Q (x_0) the bifurcation temperature corresponds to the maximal t_P fulfilling the condition of $a = 0$, Equation (35), where maximum is taken over k and χ_1 . It yields

$$t_{P,N-TB} = -\frac{\lambda x_0}{\sqrt{6}} + \frac{3e_P^2}{2(6\kappa_2 + \sqrt{6}\kappa_3 x_0 + \kappa_4 x_0^2)} \quad (36)$$

for $k = 0$ and $\sin^2(\chi_1) = 1$. As previously for the $I - N_{TB}$ phase transition, the a -term, Equation (35), is the leading coefficient in Landau expansion of the free energy of the N_{TB} phase about the reference N_U phase in the primary order parameter p_1 :²⁹ $\Delta f_{N-TB} = \frac{1}{2!} a p_1^2 + \frac{1}{4!} b p_1^4 + \frac{1}{6!} c p_1^6 + \dots$. A direct inspection of this expansion shows that the $N_U - N_{TB}$ transition can be first order ($a = 0$, $b < 0$, $c > 0$), second order ($a = 0$, $b > 0$, $c > 0$), or tricritical ($a = 0$, $b = 0$, $c > 0$). Our analysis in the next section shows that for the case of CB7CB the predicted $N_U - N_{TB}$ transition is weakly first-order. The tricritical conditions for $I - N_{TB}$ and $N_U - N_{TB}$ phase transitions will be studied in detail elsewhere.

Bifurcations to globally polar phases

In a similar way we can derive the bifurcation condition for phase transitions from I , N_U , N_{TB} to corresponding globally polar structures listed in Table 1. It reads

$$a = 2 t_P - 2\sqrt{\frac{2}{3}} \lambda x_0 + 4a_d p_1^2 = 0, \quad (37)$$

where $x_0 = p_1 = 0$ for $I - N_{U,p}$ bifurcation, $p_1 = 0$ for $N_U - N_{U,p}$ bifurcation, and where both x_0 and p_1 are non-zero when bifurcation takes place from N_{TB} to $N_{TB,p}$. Now the parameter a is the leading coefficient of Landau expansion $\Delta f_p = \frac{1}{2!}av_0^2 + \frac{1}{4!}bv_0^4 + \frac{1}{6!}cv_0^6 + \dots$ in v_0 - the primary order parameter for phase transitions to polar structures. Given the form of the expansion for f_P , Equation (20), the tricritical point can only be found for the $N_{TB} - N_{TB,p}$ phase transition.

Results and Discussion

Estimates of model parameters from experimental data for CB7CB

Before we explore relative stability of the nematic phases given in Table 1 we estimate some of the material parameters entering the expansion (10) from experimental data in the uniaxial nematic phase. This will allow us to study properties of N_{TB} with only a few adjustable parameters. Indeed, nearly all of the parameters of the purely nematic parts: the bulk $\tilde{f}_{Qb}$ and the elastic $\tilde{f}_{Qel}$ can be correlated with the existing data in the uniaxial nematic phase. The N_U phase usually appears stable at higher temperatures and $N_U - N_{TB}$ phase transition is observed as temperature is lowered.

The very first compound shown to exhibit stable nematic and twist-bend nematic phase was the liquid crystal dimer 1'',7''-bis(4-cyanobiphenyl-4'-yl)heptane, abbreviated as CB7CB.⁵⁻⁷ This compound is constituted of two 4-cyanobiphenyls (CB) linked by an alkylene spacer (C_7H_{14}). Currently, it is one of the best studied examples. In particular, Babakhanova *et al.*²⁰ have carried out a series of experiments for this mesogen in the uniaxial nematic phase. They determined the temperature variation of the nematic order parameter $\tilde{S}$ (see Equation (1)), the temperature variation of the Frank elastic constants K_{ii} ($i = 1, 2, 3$), the nematic-isotropic transition temperature T_{NI} , the nematic twist-bend-nematic transition temperature $T_{N_{TB}}$. An interesting fact is that twist-bend nematic phase formed by CB7CB can be supercooled to about 304.15 K⁵ and then there is a glass transition at ap-

proximately 277.15 K.⁴² We use the data presented in Table S1 to estimate some of the parameters of the extended LdeG theory.

Bulk part

Under the assumption that $\tilde{\mathbf{Q}}$ is uniaxial and positionally independent (Equation 1 with $\hat{\mathbf{n}}(\tilde{\mathbf{r}}) = \text{const.}$), the order parameter $\tilde{S}$ can be determined from the minimum of the free-energy density $\tilde{f}_{Qb}$, Equation 11, which becomes reduced to that of the uniaxial nematic phase

$$\tilde{f}_{Qb} = \frac{2}{3}a_{0Q}(\Delta t + \Delta t_{NI})\tilde{S}^2 - \frac{2}{9}b\tilde{S}^3 + \frac{4}{9}c\tilde{S}^4 + \frac{4}{27}d\tilde{S}^5 + \frac{4}{81}f\tilde{S}^6. \quad (38)$$

Now, from the necessary condition for minimum, $\partial\tilde{f}_{Qb}/\partial\tilde{S} = 0$, solved for $T(\tilde{S})$, we determine the ratios $b/a_0 = \tilde{b}$, $c/a_0 = \tilde{c}$, $d/a_0 = \tilde{d}$ and $f/a_0 = \tilde{f}$ by fitting $\{\tilde{S}, T(\tilde{S})\}$ to the experimental data of Babakhanova *et al.*²⁰ Independently, the scaling factor a_0 can be estimated from the latent heat per mole $\Delta H_{NI} = T_{NI} \left(\partial\tilde{f}_{Qb}/\partial T \right)_{T \rightarrow T_{NI}^-}$ for the nematic–isotropic phase transition.⁴³ It reads

$$a_0 = \frac{a_{0Q}}{T_{NI}} = \frac{3\Delta H_{NI}(2\tilde{S}_{NI}(24\tilde{c} + \tilde{S}_{NI}(15\tilde{d} + 8\tilde{f}\tilde{S}_{NI})) - 9\tilde{b})}{2\tilde{S}_{NI}T_{NI} \left(9\tilde{b}\tilde{S}_{NI} + 10\tilde{d}\tilde{S}_{NI}^3 + 8\tilde{f}\tilde{S}_{NI}^4 - 36T_{NI} + 36T^* \right)}, \quad (39)$$

where $\tilde{S}_{NI}$ is the nematic order parameter at the uniaxial nematic–isotropic phase transition. For overall consistency, a_0 has been onward multiplied by $\rho_C = \rho/M_w \approx 2.22 * 10^3 \text{ mol/m}^3$, which is the ratio of the mass density ($\rho \approx 10^3 \text{ kg/m}^3$) to the relative molecular weight of CB7CB ($M_w \approx 0.45 \text{ kg/mol}$) yielding the value $6.88 \cdot 10^4 \text{ J m}^{-3} \text{ K}^{-1}$. Thanks to this operation it was possible to express all expansion coefficients in units J/m^{-3} . Figure 2 depicts results of fitting to experimental data, whereas numerical values of the parameters are gathered in Table S2. Please observe that the expansion parameter e couples to a purely biaxial part and therefore it cannot be estimated from the data in N_U .

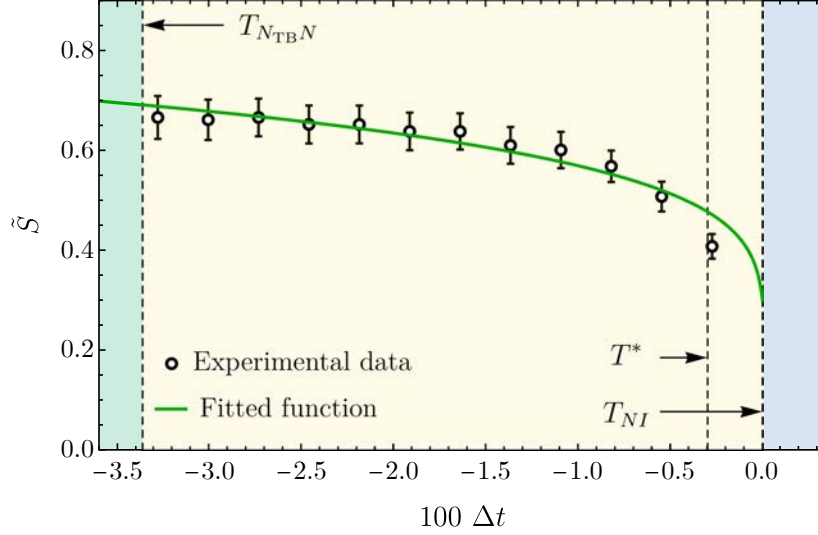


Figure 2: Experimental data from²⁰ representing the temperature dependence of $\tilde{S}$ in the uniaxial nematic phase of CB7CB. Green line illustrates the effect of fitting predictions of theory (38) to the data. T^* represents the maximal supercooling temperature of the isotropic phase. Our fit is carried out by taking as *ansatz* the experimentally known value of T_{NI} and T^* . Then $\tilde{S}_{NI}$ for CB7CB is estimated from our fitted function. If we compromise the agreement of T_{NI} and T^* with experimental data a better fit can be obtained for $\tilde{S}$ close to the transition temperature without affecting one in the vicinity of $N_U - N_{TB}$.

Flexopolarization renormalized elasticity of uniaxial nematics

It is important to realize that although (flexo)polarization terms (20,21) vanish in the uniaxial nematic phase any local deformation of the alignment tensor induces deformation of $\tilde{\mathbf{P}}$ due to the flexopolarization coupling $\varepsilon_P \neq 0$. Such deformations effectively renormalize elastic constants $L_m^{(n)}$ in ordinary nematic phases. The effect cannot be neglected if we intend to estimate $L_m^{(n)}$ from experimental data. A mathematical procedure of taking into account such deformations in the N_U phase is to minimize the free energy Equation (10) over Fourier modes of the polarization field for given, fixed Fourier modes of the alignment tensor. Assuming that deformation $\tilde{\mathbf{Q}}(\tilde{\mathbf{r}})$ is small and slowly varying we obtain with this procedure the $\tilde{\mathbf{Q}}$ -induced deformation of $\tilde{\mathbf{P}}(\tilde{\mathbf{r}})$ expressed in terms of Fourier modes which, when transformed back to the real space take the form of a series in $Q_{\alpha\mu}$, $Q_{\alpha\mu,\mu}$ and in higher-order derivatives

of $Q_{\alpha\mu}$. The relevant terms are

$$\tilde{P}_\alpha(\tilde{\mathbf{r}}) = \frac{\varepsilon_P}{2a_P} \tilde{Q}_{\alpha\mu,\mu} + \frac{\varepsilon_P \Lambda_{QP}}{2a_P^2} \tilde{Q}_{\alpha\beta} \tilde{Q}_{\beta\mu,\mu} + \frac{\varepsilon_P \Lambda_{QP}^2}{2a_P^3} \tilde{Q}_{\alpha\lambda} \tilde{Q}_{\lambda\beta} \tilde{Q}_{\beta\mu,\mu} + \dots \quad (40)$$

Substituting Equation (40) back to $\tilde{f}_P$ and $\tilde{f}_{QP}$ we obtain effective elastic contributions expressed in terms of only $\tilde{Q}_{\alpha\beta}$ and $\tilde{Q}_{\gamma\mu,\mu}$. When added to $\tilde{f}_{Qel}$ they give an effective elastic free energy of uniaxial and biaxial nematics with $L_m^{(n)}$ being replaced by $L_{m,eff}^{(n)}$, where relevant $L_m^{(n)}$'s are

$$\begin{aligned} L_2^{(2)} &\rightarrow L_{2,eff}^{(2)} = L_2^{(2)} - \frac{\varepsilon_P^2}{4a_P}, \\ L_3^{(3)} &\rightarrow L_{3,eff}^{(3)} = L_3^{(3)} - \frac{\Lambda_{QP} \varepsilon_P^2}{4a_P^2}, \\ L_6^{(4)} &\rightarrow L_{6,eff}^{(4)} = L_6^{(4)} - \frac{\Lambda_{QP}^2 \varepsilon_P^2}{4a_P^3}. \end{aligned} \quad (41)$$

An important physical distinction between the bare constant $L_m^{(n)}$ and the renormalized constant $L_{m,eff}^{(n)}$ is of the same sort as one between renormalized and bare Frank elastic constants, as discussed by Jákli, Lavrentovich and Selinger:³ $L_m^{(n)}$ gives the energy cost of $\tilde{Q}_{\alpha\beta,\gamma}$ deformations if we constrain $\tilde{P}_\alpha = 0$ during the deformation, while $L_{m,eff}^{(n)}$ relaxes to its optimum value during the the deformation. Assuming that major contribution to flexopolarization is of entropic, excluded volume type, any realistic experiment to measure elastic constants should not put constraints on the polar field $\tilde{\mathbf{P}}$, but rather allows it to relax. In this case, which is analysed here, $L_{m,eff}^{(n)}$ are the relevant contributions to the elastic constants in Equation (14).

Elastic part

In the hydrodynamic limit where spatial dependence of $\tilde{S}$ is disregarded and $\tilde{\mathbf{Q}}$ is given by (1) the elastic free energy $\tilde{f}_{Qel}$ turns into the Oseen-Frank free energy density of the director

field $\mathbf{n}(\tilde{\mathbf{r}})$, Equation (2), with K_{11} , K_{22} and K_{33} being polynomials in $\tilde{S}$ ²⁸

$$K_{ii} = K_{ii}^{(2)} \tilde{S}^2 + K_{ii}^{(3)} \tilde{S}^3 + K_{ii}^{(4)} \tilde{S}^4 \quad (i = 1, 2, 3). \quad (42)$$

The coefficients $K_{ii}^{(n)}$ are functions of $L_j^{(n)}$ ^{28,30} fulfilling the splay-bend degeneracy relation in the second order: $K_{11}^{(2)} = K_{33}^{(2)}$. For completeness, they are given in Supporting Information. As it turns out $K_{ii}^{(n)}$ with $n = 2, 3, 4$ along with flexopolarization renormalization (41) are sufficient to obtain a good fit of Equation (42) to experimentally observed K_{ii} for CB7CB.²⁰ Importantly, they also provide an estimate for the (flexo)polar couplings ε_P and Λ_{QP} . In finding $K_{ii}^{(n)}$ we use the $\tilde{S}(T)$ fit obtained from the analysis of the bulk free energy, which is a prerequisite to have a consistent theory of the uniaxial nematic phase for this compound. Results of fitting are gathered in Table S2. Finally, as the number of relevant couplings $L_\alpha^{(n)}$ ($n = 3, 4$), Equation (14), equals that of $K_{ii}^{(n)}$ we can correlate $L_\alpha^{(n)}$ with $K_{ii}^{(n)}$ using the results of Supporting Information and of Ref.²⁸ It yields

$$\begin{aligned} L_1^{(2)} + \lambda_4^2 L_7^{(4)} &= \frac{1}{4} K_{22}^{(2)}, \\ L_2^{(2)} + \lambda_2^2 L_{14}^{(4)} + \lambda_3^2 L_6^{(4)} - \frac{\varepsilon_P^2}{4 a_P} &= \frac{1}{2} (K_{11}^{(2)} - K_{22}^{(2)}), \\ L_2^{(3)} &= \frac{1}{2} (K_{11}^{(3)} - 3K_{22}^{(3)} + 2K_{33}^{(3)}), \\ L_3^{(3)} - \frac{\Lambda_{QP} \varepsilon_P^2}{4 a_P^2} &= \frac{1}{2} (2K_{11}^{(3)} - 3K_{22}^{(3)} + K_{33}^{(3)}), \\ L_4^{(3)} &= \frac{3}{2} K_{22}^{(3)}, \\ L_6^{(4)} - \frac{\Lambda_{QP}^2 \varepsilon_P^2}{4 a_P^3} &= \frac{3}{10} (4K_{11}^{(4)} - 3K_{22}^{(4)} - K_{33}^{(4)}), \\ L_7^{(4)} &= \frac{9}{10} K_{22}^{(4)}, \\ L_{14}^{(4)} &= -\frac{3}{10} (K_{11}^{(4)} + 3K_{22}^{(4)} - 4K_{33}^{(4)}). \end{aligned} \quad (43)$$

Results of fitting of $L_\alpha^{(n)}$, Equation (14), obeying stability ansatz (15) to experimental data for CB7CB are given in Table S2. Quality of fit is displayed in Figure 3.

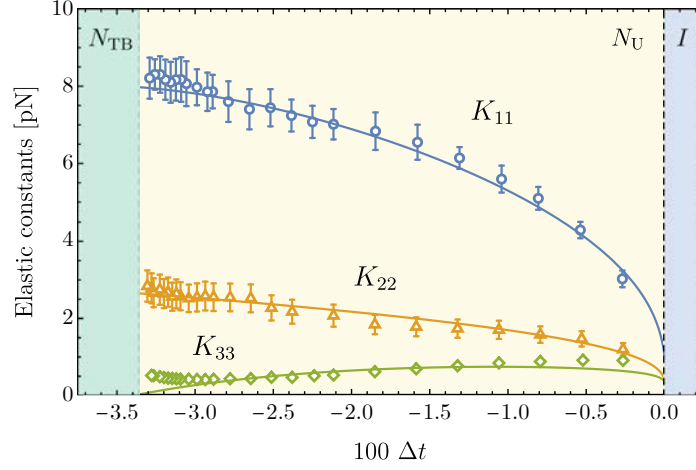


Figure 3: Temperature dependence of elastic constants acquired from.²⁰ Continuous lines depict adopted approach for elastic constants within the model. Note that the model cannot explain a slight increase of K_{33} in the vicinity of the $N_U - N_{TB}$ phase transition.

Predictions for nematic twist-bend phase of CB7CB-like compounds

Within this section, we explore the relative stability of the UDS structures, listed in Table 1, for the model Equation (24) with parameters (estimated in previous sections), which are gathered in Table S3. We limit ourselves to the temperature interval where the N_{TB} phase appears stable in the experiment (Table S4).

The temperatures t_P and t_Q are connected with absolute temperature T of the system studied (see Equation (12,20,22)). Since $a_P > 0$, $a_Q > 0$, $T^* > T_P$ and $T > T_P$ any straight line in $\{t_Q, t_P\}$ plane with positive slope and negative t_Q -intercept represents a permissible physical system with no polar order for $\tilde{\mathbf{Q}} = 0$. Thus, we present the phase diagrams in the general $\{t_Q, t_P\}$ plane for a broader view. In our case, the experimental-related line has the form:

$$t_P = 4.13t_Q + 8.29. \quad (44)$$

Results of our in-depth analysis, profoundly reduced the number of adjustable parameters for CB7CB-like compounds to solely four (λ , e_P , a_d , and e_b). From considerations related to the elastic constants, Table S2, it turns out that Λ_{QP} (*ipso facto* λ), responsible for globally

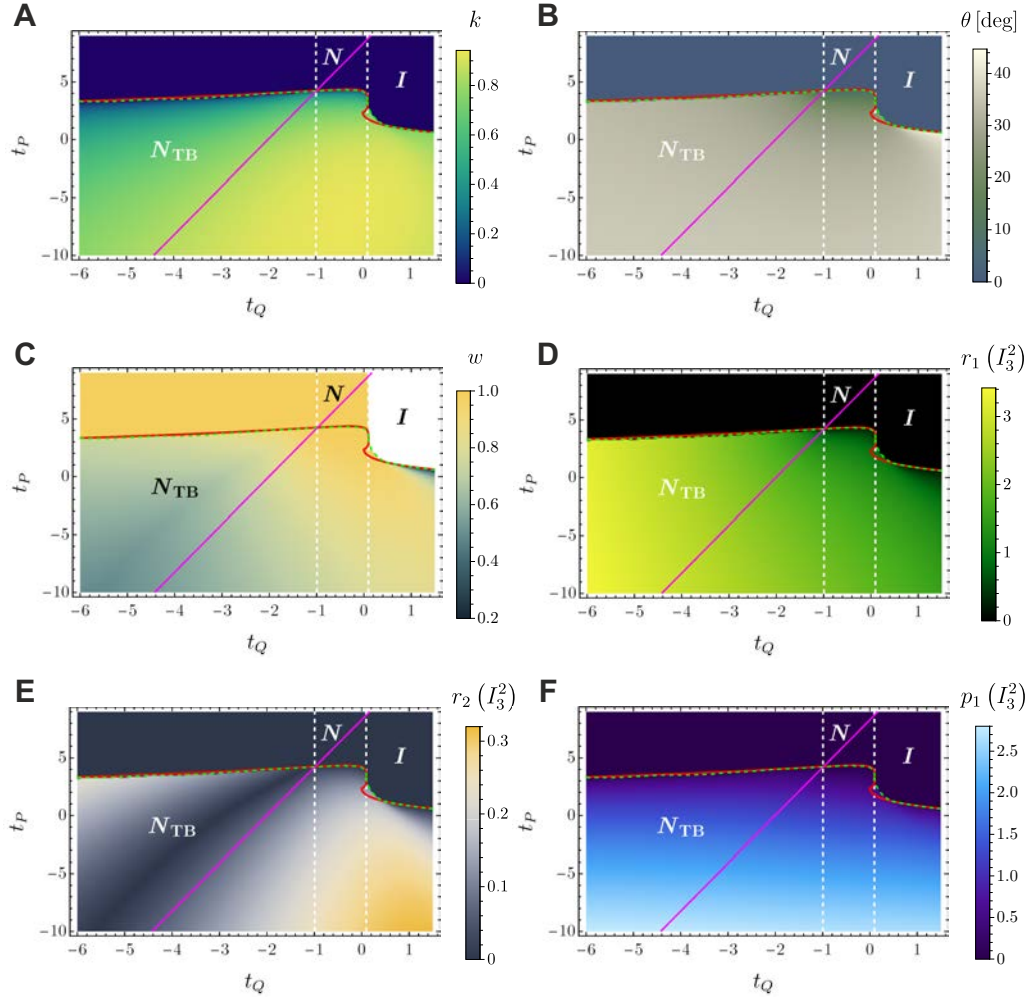


Figure 4: Phase diagram combined with density map of wave vector k (A), tilt angle θ (B), biaxiality parameter w (C) and mode's amplitudes: r_1 (D), r_2 (E) and p_1 (F) within theory (I_3^2). Red continuous curve marks the bifurcation between $N \leftrightarrow N_{TB}$ and $I \leftrightarrow N_{TB}$, whereas dashed green curve outlines the numerical results. Magenta line (described by Equation (44)) reflects the phase sequence associated directly with the experimental data for CB7CB. Vertical, dashed white lines designate the temperature span of N_U stability (experimental) mapped on t_Q (see Table S4).

polar structures, is negligible, i.e. $\sqrt{|\lambda|}/e_P \approx 10^{-13}$. Thus, we set $\lambda = 0$. Onward, we take $e_P = 7.1$ and $a_d = 0.75$ as the best values to reproduce the temperature dependance of k . For the bulk biaxial parameter e_b we take two values: $e_b = 0$ and $e_b = 1/6$. If we recall Equation (25), there is a term $e_b(I_2^3 - 6I_3^2) + I_3^2$. If we set $e_b = 0$, then it reduces to I_3^2 , on the other hand when we set $e_b = 1/6$ then we have only $I_2^3/6$. In the following discussion the first scenario ($e_b = 0$) will be referred to as theory (I_3^2) and second one as theory (I_2^3). The (I_3^2) theory will enhance phase biaxiality due to its tendency to lower equilibrium value of the w parameter, Equation (9), while the (I_2^3) theory is promoting the $w = \pm 1$ states through cubic and fifth-order terms in (25).³² In this latter case the biaxiality of N_{TB} can only be induced by the elastic terms.

Figure 4A-F depict phase diagrams combined with density maps of k, θ, w, r_1, r_2 and p_1 , respectively, which are outcomes of theory (I_3^2). In the analyzed case, being consistent with the experiment, stable, apart from isotropic, is the uniaxial nematic phase and the twist-bend nematic phase. Dashed green curve denotes numerically determined phase transitions and red continuous curve marks the results from the bifurcation analysis. Vertical, dashed white lines designate the temperature span of N_U stability (experimental) mapped on t_Q (see Table S4). The purple straight line described by the Equation (44) represents phase transition sequence: $I \leftrightarrow N_U \leftrightarrow N_{TB}$ based on the CB7CB data from.²⁰ From points lying on this line we have attained information about the behavior of pitch (p), tilt angle (θ) and nematic order parameter ($\tilde{S}$) in N_{TB} , alongside the insight into the N_{TB} 's biaxiality parameter (w) and the remaining order parameters (r_1, r_2, p_1) (see Figure 5A-E). With regard to the w parameter, in the literature there are not available any results concerning the biaxiality of N_{TB} , thus it is hard to compare. Nevertheless, our model permits to estimate the span and magnitude of affect on experimentally measurable parameters.

We set together results of our model with available experimental data concerning pitch p (Figure 5A^{7,44}), tilt angle θ (Figure 5B⁴⁵⁻⁵⁰) and nematic order parameter $\tilde{S}$ (Figure 5C^{20,49-51}). At the transition temperature from N_U to N_{TB} the pitch length is ca. 54 nm and with de-

creasing temperature it saturates at the level of ca. 8 nm (Figure 5A). As one can see, it goes fairly well with the experimental data. Within the literature the methodology regarding the pitch measurements for CB7CB are consistent, i.e. all indicate that the pitch value reaches the plateau at ca. 8 nm,^{6,7,44} in contradiction to measurements of θ and $\tilde{S}$.

Such span of experimental data for θ , Figure 5B, originate from the adopted method of determination and sample treatment. In Refs.,^{45,46} and⁴⁸ birefringence measurements were employed, however the choice of region in which they were taken varied across the aforementioned papers (*see discussion in*⁴⁶). In Refs.⁴⁹ and⁵⁰ the data regarding the conical tilt angle were extracted from X-ray methods, wherein in Ref.⁴⁹ it was small/wide angle X-ray scattering (SAXS/WAXS) and in Ref.⁵⁰ X-ray diffraction (XRD). In turn, conical tilt angle from Ref.⁴⁷ was determined *i.a.* from ²H Nuclear Magnetic Resonance (NMR) quadrupolar splittings of CB7CB-d₄. Similarly to tilt angle, discrepancies between the data related to order parameter, Figure 5C, arise from the method of acquisition. In Ref.²⁰ it was extracted from diamagnetic anisotropy measurements, in Ref.⁴⁹ from SAXS, in Ref.⁵⁰ from XRD and in Refs.^{50,51} from polarized Raman spectroscopy (PRS). As one can see data from Ref.²⁰ stands out from the rest of the data (Figure 5C), although it was the only source that provided simultaneously the data for the temperature dependence of orientational order parameter and elastic constants.

One can see that results of our model are generally in a very good agreement with experimental results, perhaps except an immediate vicinity of the $N_U - N_{TB}$ phase transition where fluctuations - not included in the present analysis - may play a role. Interesting seem predictions concerning the effect of intrinsic, molecular biaxiality on N_{TB} . While pitch, $\tilde{S}$ and p_1 are practically insensitive to w the remaining observables are affected. In particular, for tilt angle the green continuous line, associated with $e_b = 0$ fits well in between the data from Refs.⁴⁵ (blue circles) and⁴⁸ (yellow squares), whereas the red dashed line, associated with the weakly biaxial case, markedly departs from the above experimental data. Based on the results of Babakhankova *et al.*²⁰ we can conclude that biaxiality of N_{TB} , initially small

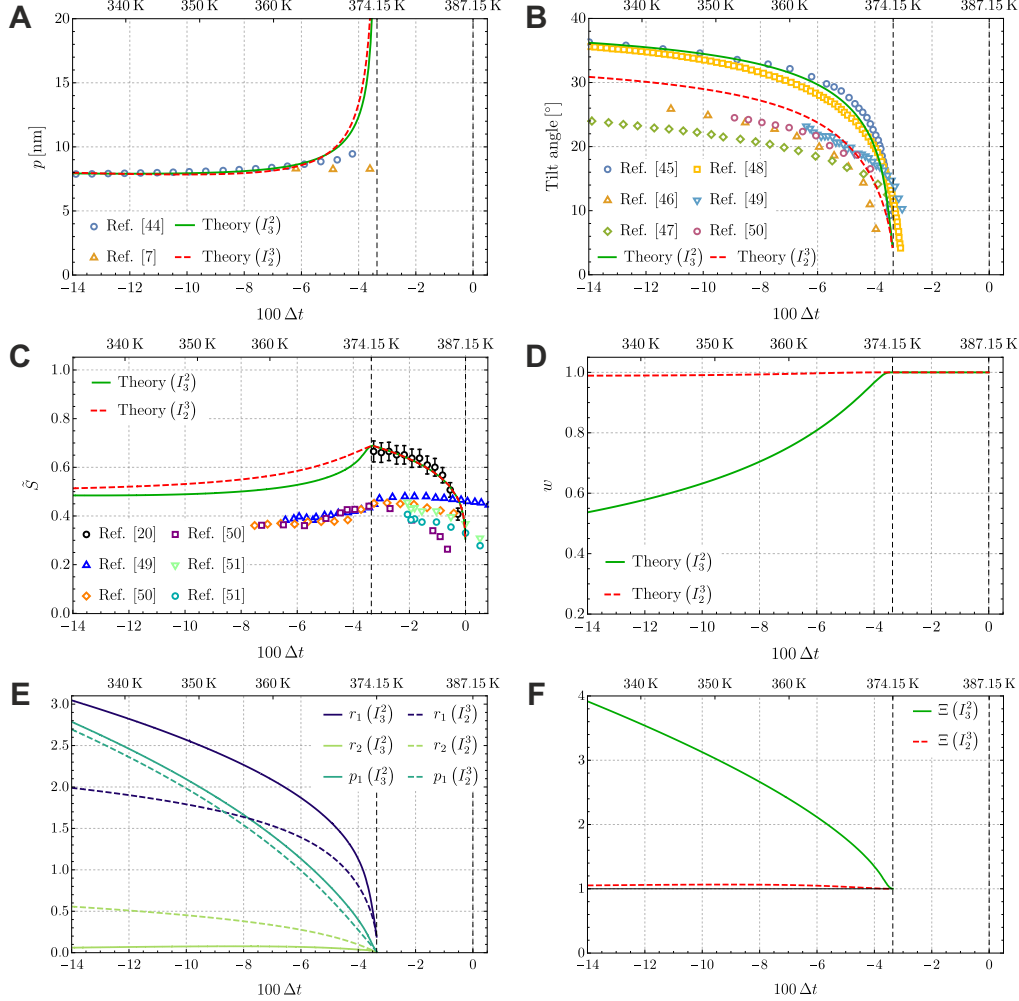


Figure 5: Comparison between experimental data (hollow points) and theoretical predictions (continuous green and dashed red line) for CB7CB's N_{TB} . (A) Temperature dependence of N_{TB} 's pitch p , (B) tilt angle θ and (C) order parameter $\tilde{S}$. (D) Plot depicts the behaviour of biaxiality parameter w and plot (E) mode's amplitudes: r_1 , r_2 and p_1 as a function of temperature in the range of N_{TB} stability. (F) Plot illustrates the temperature behaviour of the relevant factor parameterizing the relative magnitudes of intensities of two leading harmonics of the dispersion tensor that contribute to the resonant soft X-ray scattering (RSXS).⁵² All the data is drawn both with respect to the multiplied by factor 100 reduced temperature Δt , whereas key temperatures, corresponding to given Δt , are designated above each plot in absolute temperature T .

at the $N_U - N_{TB}$ phase transition, considerably increases on departing from the transition temperature (green line in Figure 5D). Figure 5E illustrates the behavior of the order parameters r_1 , r_2 and p_1 in N_{TB} phase of CB7CB, where the ratio $\sigma = r_1/r_2$ can be correlated with data acquirable from resonant soft X-ray scattering (RSoXS).^{44,53,54} In order to make this correlation, we translated our formalism into the one presented in.⁵² Thanks to that, we could tie the results for σ with experimentally measurable scattering intensities through following formula:

$$\Xi = -\frac{1}{2} + \frac{3\sigma}{2\sigma \cos(2\theta) + 4\sin(2\theta)}, \quad (45)$$

where $\Xi = f_1/f_2$ and θ is a conical tilt angle. The value of parameter Ξ determines the intensity of the $2q_0$ peak (half-pitch band) with the respect to the intensity of the q_0 peak (full pitch band) in the N_{TB} phase, where $q_0 = 2\pi/p$ is the magnitude of the wave vector of the heliconical deformation with the pitch p . As it was stated in,⁵² if $\Xi \geq 1$ then the intensity of the $2q_0$ peak is approximately two orders of magnitude lower than the intensity of the q_0 peak and further strongly decreases with increasing Ξ . On the other hand, if $\Xi < 1$ then the intensity of the $2q_0$ peak escalates rapidly. As one can see in Figure 5F, which illustrates the temperature dependence of Ξ for both theories I_3^2 and I_2^3 , all the data obeys the relation $\Xi \geq 1$ indicating a significant weakness of $2q_0$ peak. Interestingly, while for the I_2^3 theory the relative magnitude of the intensities should roughly differ by two orders of magnitude irrespective of the temperature the I_3^2 model predicts further strong reduction of the relative intensity with temperature. To our best knowledge, the $2q_0$ signal has not been detected so far in any of the examined N_{TB} forming compounds.^{44,53-55}

Conclusions

The understanding of self-organization in the twist-bend nematic (N_{TB}) phase is at the forefront of soft matter research worldwide. This new nematic phase develops structural chirality in the isotropic and the uniaxial nematic phases, despite the fact that the molecules

forming the structure are chemically *achiral*. Currently existing experimental data are in favor of the theory that the $N_U - N_{TB}$ phase transition is driven by the flexopolarization mechanism. According to this theory deformations of the director induce local polar order which, in turn, renormalizes the bend elastic constant to a very small value relative to other elastic constants, eventually leading to the twist-bend instability. It is dictated by the term coupled with $[L_2^2]$ (Equation 14), which changes sign from positive to negative at the bifurcation temperature between nematic and twist-bend nematic. What has to be also outlined is that grasping the true behavior of K_{33} at the $N-N_{TB}$ phase transition, where there is in fact a slight pretransitional increase, is elusive at the present level of theory, because fluctuations - not included in the present analysis - may play a role.

However, a fundamental description of orientational properties of nematics based on minimal coupling Landau-de Gennes theory of flexopolarization suggests that softening of K_{33} does not need to be a universal mechanism. Even when both K_{11} and K_{33} are simultaneously reduced due to splay-bend degeneracy (inherent to the minimal coupling LdeG expansion) the N_{TB} phase can still become absolutely stable among all possible one dimensional periodic structures. Since this case has not been observed experimentally to date an important question that arises is whether the flexopolarization mechanism is indeed sufficient to explain the experimental observations at the level of the “first principles” Landau-de Gennes theory of orientational order. To address this issue we proposed a generalization of the mesoscopic Landau-de Gennes theory of nematics, where higher-order elastic terms of the alignment tensor are taken systematically into account, in addition to the lowest-order flexopolarization coupling.

We demonstrated that the experimental observations involving the nematic twist-bend phase and the related uniaxial nematic phase can be explained if we generalize the minimal coupling theory to the level where the properties of high-temperature uniaxial nematic phase are properly accounted for. Especially, the constructed generalized free energy density is in line with experimentally observed temperature variation of the Frank elastic constants and

the orientational order parameter.

Our generalized theory of uniformly distorted nematics extends the elastic part of LdeG by additional two terms of third-order. The added elastic terms are the only independent ones for UDS and various UDS structures can become minimizers of the free energy, including the nematic twist-bend. This conclusion follows directly from the bifurcation analysis and the observation that the remaining four independent elastic terms of third-order, not included in the theory, can always be written in such a way that they vanish for UDS. It is worth noticing that only one more term is generally needed to extend the studies of the UDS class to *all possible* one-dimensional distortions of the alignment tensor. This sort of hierarchy between various elastic invariants indicates that the constructed theory can also serve as a starting point in seeking for different mechanisms of softening of the nematic elastic constants. This can potentially lead to a discovery of new classes of modulated nematic structures.

The numerical analysis of the model quite well reproduces measured quantities for the N_U and N_{TB} phases of the CB7CB-like mesogens and gives numerical estimates for its constitutive parameters including otherwise difficult to access (flexo-)polarization couplings. Overall, the N_{TB} phase is predicted to be biaxial with theoretical support that major contribution to the phase biaxiality can originate from the bulk term(s) in the free energy. Finally, although the phase transition to the N_{TB} is weakly first-order the theory permits the transitions to N_{TB} be second order with tricritical $I - N_{TB}$ and $N_U - N_{TB}$ points.

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Supporting Information Available

Helicity modes expansion (illustration), elastic free energy of nematic liquid crystals, effective elastic constants, a complete expression for free energy density of uniformly deformed structures (UDS) and experimental data, along with numerical results.

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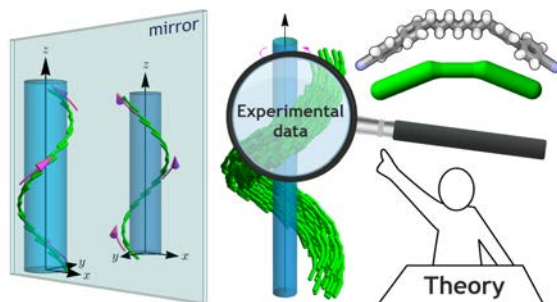
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Graphical TOC Entry



Supporting Information for

“Twist-Bend Nematic Phase from Landau-de Gennes Perspective”

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I. HELICITY MODES EXPANSION

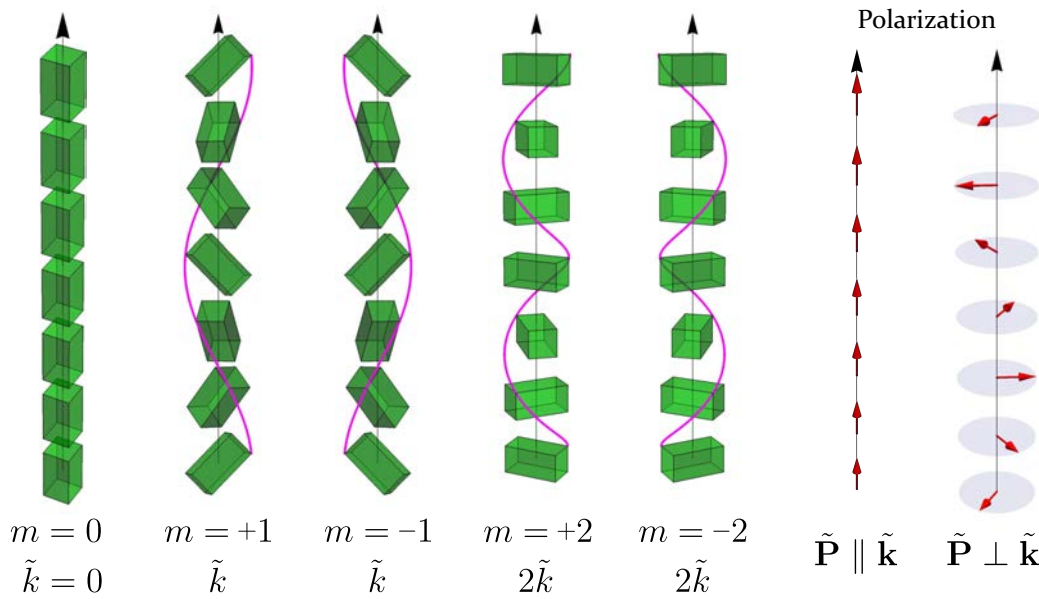


Figure S1. Visualization of helicity modes: $m = 0$, $m = \pm 1$ and $m = \pm 2$ (change of m into $-m$ corresponds to replacement of $\tilde{\mathbf{k}}$ by $-\tilde{\mathbf{k}}$). Bricks represent the tensor $\tilde{\mathbf{Q}}(\tilde{\mathbf{r}})$ where the eigenvectors of $\tilde{\mathbf{Q}}(\tilde{\mathbf{r}})$ are parallel to their arms, while the absolute values of eigenvalues are their lengths. Red arrows represent the polarization field $\tilde{\mathbf{P}}(\tilde{\mathbf{r}})$.

II. ELASTIC FREE ENERGY OF NEMATIC LIQUID CRYSTALS

The expansion of the free energy in powers of $\tilde{Q}_{\alpha\beta}$ and its derivatives up to the order $\tilde{Q} \tilde{Q} \partial \tilde{Q} \partial \tilde{Q}$ contains twenty-two terms. They are [1]:

$\partial \tilde{Q} \partial \tilde{Q}$:

$$\begin{aligned} [L_1^{(2)}] &= \tilde{Q}_{\alpha\beta,\gamma} \tilde{Q}_{\alpha\beta,\gamma}, \\ [L_2^{(2)}] &= \tilde{Q}_{\alpha\beta,\beta} \tilde{Q}_{\alpha\gamma,\gamma}, \\ [L_3^{(2)}] &= \tilde{Q}_{\alpha\beta,\gamma} \tilde{Q}_{\alpha\gamma,\beta}. \end{aligned} \tag{S1}$$

$\tilde{Q} \partial \tilde{Q} \partial \tilde{Q}$:

$$\begin{aligned} [L_1^{(3)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\alpha\beta,\mu} \tilde{Q}_{\mu\nu,\nu}, & [L_2^{(3)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\alpha\mu,\beta} \tilde{Q}_{\mu\nu,\nu}, \\ [L_3^{(3)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\alpha\mu,\mu} \tilde{Q}_{\beta\nu,\nu}, & [L_4^{(3)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\alpha\mu,\nu} \tilde{Q}_{\beta\mu,\nu}, \\ [L_5^{(3)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\alpha\mu,\nu} \tilde{Q}_{\beta\nu,\mu}, & [L_6^{(3)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\alpha\mu,\nu} \tilde{Q}_{\mu\nu,\beta}. \end{aligned} \tag{S2}$$

$\tilde{Q} \tilde{Q} \partial \tilde{Q} \partial \tilde{Q}$:

$$\begin{aligned} [L_1^{(4)}] &= (\text{Tr } \tilde{\mathbf{Q}}^2) \tilde{Q}_{\varrho\mu,\varrho} \tilde{Q}_{\mu\nu,\nu}, & [L_2^{(4)}] &= (\text{Tr } \tilde{\mathbf{Q}}^2) \tilde{Q}_{\mu\nu,\varrho} \tilde{Q}_{\mu\nu,\varrho}, \\ [L_3^{(4)}] &= (\text{Tr } \tilde{\mathbf{Q}}^2) \tilde{Q}_{\mu\nu,\varrho} \tilde{Q}_{\varrho\mu,\nu}, & [L_4^{(4)}] &= \tilde{Q}_{\alpha\varrho} \tilde{Q}_{\varrho\beta} \tilde{Q}_{\alpha\beta,\mu} \tilde{Q}_{\mu\nu,\nu}, \\ [L_5^{(4)}] &= \tilde{Q}_{\alpha\varrho} \tilde{Q}_{\varrho\beta} \tilde{Q}_{\alpha\mu,\beta} \tilde{Q}_{\mu\nu,\nu}, & [L_6^{(4)}] &= \tilde{Q}_{\alpha\varrho} \tilde{Q}_{\varrho\beta} \tilde{Q}_{\alpha\mu,\mu} \tilde{Q}_{\beta\nu,\nu}, \\ [L_7^{(4)}] &= \tilde{Q}_{\alpha\varrho} \tilde{Q}_{\varrho\beta} \tilde{Q}_{\alpha\mu,\nu} \tilde{Q}_{\beta\mu,\nu}, & [L_8^{(4)}] &= \tilde{Q}_{\alpha\varrho} \tilde{Q}_{\varrho\beta} \tilde{Q}_{\alpha\mu,\nu} \tilde{Q}_{\beta\nu,\mu}, \\ [L_9^{(4)}] &= \tilde{Q}_{\alpha\varrho} \tilde{Q}_{\varrho\beta} \tilde{Q}_{\alpha\mu,\nu} \tilde{Q}_{\mu\nu,\beta}, & [L_{10}^{(4)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\mu\varrho} \tilde{Q}_{\beta\mu,\alpha} \tilde{Q}_{\varrho\nu,\nu}, \\ [L_{11}^{(4)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\mu\varrho} \tilde{Q}_{\mu\nu,\alpha} \tilde{Q}_{\varrho\nu,\beta}, & [L_{12}^{(4)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\mu\varrho} \tilde{Q}_{\alpha\beta,\nu} \tilde{Q}_{\nu\varrho,\mu}, \\ [L_{13}^{(4)}] &= \tilde{Q}_{\alpha\beta} \tilde{Q}_{\mu\varrho} \tilde{Q}_{\alpha\beta,\nu} \tilde{Q}_{\mu\varrho,\nu}. \end{aligned} \tag{S3}$$

In defining stability conditions we will also use the $[L_{14}^{(4)}]$ invariant, which is a linear combination of $[L_1^{(4)}] \dots [L_{13}^{(4)}]$:

$$\begin{aligned} [L_{14}^{(4)}] &\equiv \tilde{Q}_{\alpha\beta} \tilde{Q}_{\gamma\delta} \tilde{Q}_{\alpha\mu,\beta} \tilde{Q}_{\gamma\mu,\delta} = \\ &= -\frac{[L_1^{(4)}]}{2} + \frac{[L_2^{(4)}]}{2} [L_3^{(4)}] - 2 [L_4^{(4)}] + [L_6^{(4)}] - [L_7^{(4)}] + [L_8^{(4)}] + 2 [L_9^{(4)}] + [L_{11}^{(4)}] \end{aligned} \tag{S4}$$

III. EFFECTIVE ELASTIC CONSTANTS

The effective elastic constants $K_{ii}^{(n)}$ for $i = 1, 2, 3$ and $n = 2, 3, 4$ expressed in terms of $[L_m^{(n)}]$, Equation (S1-S4). Included in decomposition is also $[L_{14}^{(4)}]$:

For $n = 2$:

$$\begin{aligned} K_{11}^{(2)} &= 2 \left(2L_1^{(2)} + L_2^{(2)} + L_3^{(2)} \right) \\ K_{22}^{(2)} &= 4L_1^{(2)} \\ K_{33}^{(2)} &= 2 \left(2L_1^{(2)} + L_2^{(2)} + L_3^{(2)} \right) \end{aligned} \tag{S5}$$

For $n = 3$:

$$\begin{aligned} K_{11}^{(3)} &= \frac{2}{3} \left(-L_2^{(3)} + 2L_3^{(3)} + L_4^{(3)} + 2L_5^{(3)} - L_6^{(3)} \right) \\ K_{22}^{(3)} &= \frac{2}{3} L_4^{(3)} \\ K_{33}^{(3)} &= \frac{2}{3} \left(2L_2^{(3)} - L_3^{(3)} + L_4^{(3)} - L_5^{(3)} + 2L_6^{(3)} \right) \end{aligned} \tag{S6}$$

For $n = 4$:

$$\begin{aligned} K_{11}^{(4)} &= \frac{2}{9} \left(6L_1^{(4)} + 12L_2^{(4)} + 6L_3^{(4)} + L_5^{(4)} + 4L_6^{(4)} + 5L_7^{(4)} + 4L_8^{(4)} + L_9^{(4)} - 2L_{10}^{(4)} - L_{11}^{(4)} + L_{14}^{(4)} \right), \\ K_{22}^{(4)} &= \frac{2}{9} \left(12L_2^{(4)} + 5L_7^{(4)} - L_{11}^{(4)} \right), \\ K_{33}^{(4)} &= \frac{2}{9} \left(6L_1^{(4)} + 12L_2^{(4)} + 6L_3^{(4)} + 4L_5^{(4)} + L_6^{(4)} + 5L_7^{(4)} + L_8^{(4)} + 4L_9^{(4)} - 2L_{10}^{(4)} + 2L_{11}^{(4)} + 4L_{14}^{(4)} \right) \end{aligned} \tag{S7}$$

**IV. A COMPLETE EXPRESSION FOR FREE ENERGY DENSITY OF UNIFORMLY
DEFORMED STRUCTURES (UDS)**

$$\begin{aligned}
f_{Qb} = & t_Q (r_1^2 + r_2^2 + x_0^2) - \frac{x_0 (x_0^2 - 3r_2^2)}{\sqrt{6}} - \frac{1}{4} r_1^2 \left(3\sqrt{2} r_2 \cos(2\chi_1 - \chi_2) + \sqrt{6} x_0 \right) \\
& + c_b (r_1^2 + r_2^2 + x_0^2)^2 \\
& + d_b (r_1^2 + r_2^2 + x_0^2) \left(\frac{1}{4} r_1^2 \left(3\sqrt{2} r_2 \cos(2\chi_1 - \chi_2) + \sqrt{6} x_0 \right) + \frac{x_0 (x_0^2 - 3r_2^2)}{\sqrt{6}} \right) \\
& + \left(\frac{1}{4} r_1^2 \left(3\sqrt{2} r_2 \cos(2\chi_1 - \chi_2) + \sqrt{6} x_0 \right) + \frac{x_0 (x_0^2 - 3r_2^2)}{\sqrt{6}} \right)^2 \\
& + e_b \left((r_1^2 + r_2^2 + x_0^2)^3 - \frac{1}{12} \left(3r_1^2 (3 \cos(2\chi_1 - \chi_2) r_2 + \sqrt{3} x_0) + 2\sqrt{3} x_0 (-3r_2^2 + x_0^2) \right)^2 \right)
\end{aligned} \tag{S8}$$

$$\begin{aligned}
f_{Qel} = & \frac{1}{12} k^2 \left[24 \rho_{4,7} r_2^4 + r_2^2 \left(48 \kappa_1 + 3 (9 \rho_{4,7} + 8 \rho_{4,15}) r_1^2 - 8\sqrt{6} \rho_{3,4} x_0 + 8 \rho_{4,7} x_0^2 \right) \right. \\
& + r_1^2 \left(6 \kappa_2 + 3 \rho_{4,7} r_1^2 + \sqrt{6} (\rho_{3,4} - 4 \rho_{3,7}) x_0 + (5 \rho_{4,7} + 8 \rho_{4,15}) x_0^2 \right) \\
& \left. + r_1^2 r_2 \left(9\sqrt{2} \rho_{3,4} - 12\sqrt{2} \rho_{3,7} + 2\sqrt{3} (3 \rho_{4,7} + 8 \rho_{4,15}) x_0 \right) \cos(2\chi_1 - \chi_2) \right]
\end{aligned} \tag{S9}$$

$$f_P = t_P (p_1^2 + v_0^2) + k^2 p_1^2 + a_d (p_1^2 + v_0^2)^2 \tag{S10}$$

$$f_{QP} = \frac{k p_1 r_1 e_P \sin(\chi_1)}{\sqrt{2}} - \frac{\lambda p_1^2 r_2 \cos(\chi_2)}{\sqrt{2}} - \sqrt{2} \lambda p_1 r_1 v_0 \cos(\chi_1) + \frac{\lambda p_1^2 x_0}{\sqrt{6}} - \sqrt{\frac{2}{3}} \lambda v_0^2 x_0 \tag{S11}$$

V. EXPERIMENTAL DATA AND NUMERICAL RESULTS

Table S1. Basic experimental data for CB7CB used to estimate some of the parameters of the extended LdeG theory, along with other crucial data based on aforementioned estimates.

Nematic				
Description	Parameter	Value	Unit	Source
Temperature of nematic-isotropic phase transition	T_{NI}	387.15	K	Ref. [2]
Supercooling temperature of the isotropic phase	T^*	386	K	acquired from $\tilde{S}(T)$
Enthalpy of nematic-isotropic phase transition	ΔH_{NI}	0.72	kJ/mol	Ref. [3]
Order parameter at T_{NI}	$\tilde{S}_{NI}$	0.3	-	acquired from $\tilde{S}(T = T_{NI})$
Twist-bend nematic				
Description	Parameter	Value	Unit	Source
Temperature of nematic-twist-bend nematic phase transition	$T_{N_{TB}N}$	374.15	K	Ref. [2]
Enthalpy of nematic-twist-bend nematic phase transition	$\Delta H_{N_{TB}N}$	0.83	kJ/mol	Ref. [3]

Table S2. Values of fitted coefficients of the bulk (38) and elastic constants (42) expansions, along with ones resulting from the flexopolarization renormalization. Additionally, according to (14) and (43) are provided $K_{ii}^{(n)}$ elastic constants.

Coefficient Value [$\times 10^7$ J/m ³]		Coefficient Value [pN]		Coefficient Value [pN]	
a_{0Q}	2.66	$K_{11}^{(2)} = K_{33}^{(2)}$	3.54	$L_1^{(2)}$	0.93
b	0.27	$K_{22}^{(2)}$	3.72	$L_2^{(2)}$	-0.0045
c	0.60	$K_{11}^{(3)}$	11.08	$L_2^{(3)}$	-11.16
d	-3.80	$K_{22}^{(3)}$	0.60	$L_3^{(3)}$	2.27
f	9.64	$K_{33}^{(3)}$	-15.80	$L_4^{(3)}$	0.90
		$K_{11}^{(4)}$	9.93	$L_6^{(4)}$	6.29
		$K_{22}^{(4)}$	1.77	$L_7^{(4)}$	1.59
		$K_{33}^{(4)}$	13.45	$L_{14}^{(4)}$	11.56
				$\frac{\varepsilon_P^2}{4a_P}$	0.08
				$\frac{\Lambda_{QP}\varepsilon_P^2}{4a_P^2}$	0.00013
$T_P = 362$ K					

Table S3. Dimensionless parameters related to bulk part, elastic constants and bifurcation equations. Below are provided converters for $\Delta t \leftrightarrow t_Q$, $\tilde{\mathbf{r}} \leftrightarrow \mathbf{r}$ and $\tilde{\mathbf{k}} \leftrightarrow \mathbf{k}$.

Parameter	Value	Parameter	Value	Parameter	Value
c_b	0.67	$\rho_{2,2}$	-0.0048	l_2	-1.58
d_b	-1.29	$\rho_{3,2}$	-3.64	l_3	0.59
Δt_{NI}	0.0029	$\rho_{3,3}$	0.74	l_4	0.93
		$\rho_{3,4}$	0.29	κ_1	1.13
		$\rho_{4,6}$	0.62	κ_2	5.38
		$\rho_{4,7}$	0.15	κ_3	-7.73
		$\rho_{4,14}$	1.14	κ_4	6.0054

$t_Q = 32.36(\Delta t + \Delta t_{NI}) \quad \tilde{\mathbf{r}} [\text{nm}] = 1.06 \mathbf{r} \quad \tilde{\mathbf{k}} [\text{nm}^{-1}] = 0.94 \mathbf{k}$

Table S4. Temperature ranges in Δt and t_Q units for stable liquid crystalline structures: nematic and twist-bend nematic from experiment [2]

Range of temperature parameter	Description
$-0.03 < \Delta t \leq 0$	nematic
$\Delta t \leq -0.03$	twist-bend nematic
$-0.99 < t_Q \leq 0.09$	nematic
$t_Q \leq -0.99$	twist-bend nematic

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Summary and outlook

There is no doubt that the discovery of N_{TB} phase become one of the most important milestones in the liquid crystalline science. The most fascinating feature of this phase is that this chiral superstructure is formed despite its constituent molecules being chemically achiral. Additionally, N_{TB} represents the first example of spontaneous chiral symmetry breaking in a liquid state with no support from long-range spatial ordering.

Thanks to the progress made both on experimental and theoretical grounds many ambiguities regarding N_{TB} were resolved. Within this thesis we have provided answers, based on theoretical models, to questions that embraced the key aspects behind the formation of the twist-bend nematic phase. By the means of generalized Maier-Saupe theory, we showed that alteration in molecules structure, namely in its bend angle and arms symmetry has a substantial impact on the stability of twist-bend nematic phase. Onward, within the framework of minimal coupling Landau-de Gennes theory, we have provided the insight into the role of chirality and polarity in the system where twist-bend nematic is present. Our last presented model, which goes beyond the minimal coupling, not only relates to experimental results in a qualitative manner but also in quantitative. What is more, on its basis we have provided a strong support that flexopolarization is a legitimate factor driving the emergence of the twist-bend nematic phase.

In the outlook of further research, the models formulated within this thesis can be extended and used to tackle the following issues:

- Starting point → [Article 4](#)
 - ◇ softening of other elastic constants: K_{22} or K_{11} ,
 - ◇ influence of electric/magnetic field - will theoretical results coincide with experimental data presented in [\[158\]](#) and [\[159\]](#)?,
 - ◇ confinement - regime where surface contributions become relevant,
- Starting point → [Article 3](#)
 - ◇ account for blue phases,
 - ◇ reformulate to add a temperature dependence of cholesteric's pitch,
 - ◇ influence of external shearing forces,

- Starting point → [Article 1](#) & [Article 2](#)
 - ◇ inherently chiral molecules,
 - ◇ addition of spatial modulation of mass density (smectic phases),
 - ◇ influence of electric/magnetic field and surfaces.

At the time, when work on this thesis was being completed, novel nematic phases were discovered: splay nematic [160–162] and ferroelectric nematic [163, 164], which is a vivid proof that liquid crystalline science is perpetually advancing and astonishing since 1888.

Additional achievements

This Appendix consists of authored and co-authored articles already published or being in preparation (which are out of the scope of this thesis), conference talks, posters, attended workshops, acquired awards, distinctions and scholarships within the time of PhD studies.

Published articles

- 1) *Phase behaviour and dynamics of the liquid crystal 4-ethyl-4'-octylazoxybenzene (4EOB)*
M. Gałązka, E. Juszyńska-Gałązka, A. Bąk, and W. Tomczyk, *Phase Trans.* **92**, 1098 (2019)
- 2) *Indication and discussion of flaws in "Properties of binary mixtures derived from hydrogen bonded liquid crystals" by M. Fouzai et al. [J. Mol. Liq. 249 (2018) 1279-1286]*
W. Tomczyk, *J. Mol. Liq.* **260**, 270 (2018)
- 3) *Comments on the published article "Electric field induced transformations and dielectric properties of ferroelectric smectic phase" by T. Soltani et al., Journal of Molecular Liquids, 199 (2014) 162-166*
W. Tomczyk, *J. Mol. Liq.* **251**, 92 (2018)
- 4) *Comment on the published article "Dichroic ratio and order parameters of some sudan dyes doped in nematic liquid crystalline matrix" by A. Maleki et al., Optik, 126 (2015) 5473-5477*
W. Tomczyk, *Optik* **141**, 146 (2017)
- 5) *Comments on the published article "The effect of optical purity on the coexistence phenomenon and on the polarization - electric field hysteresis behavior in SmC^* and SmC_A^* phases" by M. Chemingui et al., Journal of Molecular Liquids, 222 (2016) 1101-1108*
W. Tomczyk, *J. Mol. Liq.* **234**, 353 (2017)
- 6) *Comments on the published article "Dielectric anisotropy, refractive indices and order parameter of W-1680 nematic liquid crystal" by M. S. Zakerhamidi et al., Journal of Molecular Liquids, 181 (2013) 77-81*
W. Tomczyk, *J. Mol. Liq.* **230**, 59 (2017)

- 7) *Mesomorphic and physicochemical properties of liquid crystal mixture composed of chiral molecules with perfluorinated terminal chains*

W. Tomczyk, M. Marzec, E. Juszyńska-Gałązka, and D. Węglowska, *J. Mol. Struc.* **1130**, 503 (2017)

- 8) *Phase behaviour and dynamics of the liquid crystal 4'-butyl-4-(2-methylbutoxy)azoxybenzene (4ABO5*)*

E. Juszyńska-Gałązka, M. Gałązka, M. Massalska-Arodź, A. Bąk, K. Chłędowska, and W. Tomczyk, *J. Phys. Chem. B* **118**, 14982 (2014)

Article in Peer-Review

- 1) *Dipole-induced extraordinary conduction increase in poly(3-heksylthiophene)/(metal-complex cross linked) poly(4-vinylpyridine) bilayer system*

P. Dąbczyński, A. I. Pawłowska, A. M. Majcher-Fitas, O. Stefańczyk, A. Dłubacz, W. Tomczyk, M. M. Marzec, A. Bernasik, A. Budkowski, and J. Rysz

Conference contributions (only talks)

Conference name, date and place	Title
XXII Conference on Liquid Crystals: Chemistry, Physics and Applications CLC'2018, 17-21.09.2018, Jastrzębia Góra (PL)	The role of chirality and flexopolarization in the stability of twist-bend nematic and cholesteric phases
XXI Conference on Liquid Crystals: Chemistry, Physics and Applications CLC'2016, 18-23.09.2016, Krynica Zdrój (PL)	Twist-bend nematic phase under the influence of an external electric field: a mean-field approach
Twist-bend nematics and beyond, 07-08.04.2016, Southampton (UK)	Interplay between arm biaxiality and bend angle of bent-shaped molecules forming twist-bend nematic phase
Symposium doktoranckie Konsorcjum Warszawa-Fizyka-Kraków, 04-05.03.2016, Kraków (PL)	Model średniopolowy dla fazy nematycznej twist-bend zbudowanej z molekuł ze zgiętym rdzeniem i dwuosiowymi ramionami
The 13 th European Conference on Liquid Crystals, 07-11.09.2015, Manchester (UK)	Stability of nematic twist-bend phase formed by bent-core molecules with biaxial arms

Due to the COVID-19 pandemic my talk entitled “*More than meets the eye: twist-bend nematic phase from the phenomenological point of view*” at the 28th International Liquid Crystal Conference (ILCC 2020) in Lisbon (Portugal) was canceled, alongside my *Conference Fee Waiver Grant*, which I have been awarded by the Advanced Materials & Liquid Crystal Institute (AMLCI, Kent State University, USA).

Workshops

Date	Place	Name
02 - 06.12.2019	Vienna (AU)	New trends in the variational modeling and simulation of liquid crystals
07 - 08.04.2016	Southampton (UK)	Twist-bend nematics and beyond

Awards, distinctions and scholarships

Date	Name
10.2018 – 09.2020	Jagiellonian Interdisciplinary PhD Programme Scholarship
01.10.2018	3 rd in final ranking out of 75 accepted participants from all faculties at Jagiellonian University
10.2017 – 09.2018	ProQuality scholarship for the best PhD students in the academic year 2016/2017
10.2016 – 09.2017	M. Smoluchowski scientific scholarship for the best PhD students in the academic year 2015/2016
	Jagiellonian University Rector's scientific scholarship for the best PhD students in the academic year 2014/2015, 2015/2016 and 2016/2017
10.2014 – 10.2017	PhD scholarship (National Science Center in Poland project 2013/11/B/ST3/04247)
10.2014 – 09.2018	PhD scholarship (Jagiellonian University in Kraków)

Art - liquid crystalline textures

Some of my photos of liquid crystalline textures were distinguished as:

- Back Scatter Photo in *Physics Today*¹ (USA),
- Prefinalist in Wiki Science Competition 2017 (Photo competition)²,
- Winner of the photo contest 2015 organised by Soft Matter World³,
- Photo of August 2015 endorsed by the International Liquid Crystal Society⁴,
- Photo of January 2015 endorsed by the International Liquid Crystal Society⁵,

and used in a chapter of a book:

- G. A. DiLisi, *Phases of liquid crystals* in *An Introduction to Liquid Crystals* (Morgan & Claypool Publishers, 2019)⁶

¹ www.dx.doi.org/10.1063/PT.3.4052 [Accessed: 12th August 2020]

² www.bit.ly/2XAjila [Accessed: 12th August 2020]

³ www.softmatterworld.org/news/ [Accessed: 12th August 2020]

⁴ www.ilcsoc.org/art-contest/gallery/2015/#august [Accessed: 12th August 2020]

⁵ www.ilcsoc.org/art-contest/gallery/2015/#january [Accessed: 12th August 2020]

⁶ www.iopscience.iop.org/book/978-1-64327-684-7 [Accessed: 12th August 2020]

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