Twist–bend nematic phases of bent–shaped biaxial molecules

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How change in molecular structure can affect relative stability and structural properties of the twist–bend nematic phase (N_{TB})? Here we extend the mean–field model for bent–shaped achiral molecules, to study the influence of arm molecular biaxiality and the value of molecule’s bend angle on relative stability of N_{TB}. In particular we show that by controlling biaxiality of molecule’s arms up to four ordered phases can become stable. They involve locally uniaxial and biaxial variants of N_{TB}, together with the uniaxial and the biaxial nematic phases. However, the V–shaped molecule show 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.

Out of alternative theoretical approaches undertaken to tackle the nature of N_{TB} we will focus on a generic, mean–field model introduced by Greco, Luckhurst and Ferrarini (GLF). 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 the single local director \( \hat{n}(\mathbf{r}) \equiv \hat{n}(z) \) (see Figure 1):

\[
\hat{n}(z) = \left[ -\sin(\theta) \sin(\phi), \sin(\theta) \cos(\phi), \cos(\theta) \right],
\]

where \( \theta \) is the conical angle and \( \phi = k z = \frac{2\pi}{p} z \) with wave vector \( k = k z (k = \pm \frac{2\pi}{p}) \) and with period \( p \) of the phase. The wave vector, being parallel to the average direction of the main director over one period \( p \equiv \hat{k} \parallel \langle \hat{n}(z) \rangle \), can be identified with an effective optical axis.

Heliconal precession is assumed arbitrarily to take place around the \( z \)-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 the isotropic liquid can be stabilized by the GLF model.

The effective mean–field potential acting on molecular arms is defined by the well–known Maier–Saupe \( P_3 \) 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, weak temperature dependence of the pitch and consistent description of elastic properties of the N_{TB}. Tailoring molecules with particular shapes and interactions, it seems interesting to study extensions of the GLF model to molecules of more complex...
structure.

While there are many paths that can be followed, one obvious observation is that bent-shaped molecules, including the famous NTB-forming compound CB7CB, can acquire biaxiality not only due to their average "V" shape, but also as a results of biaxiality of molecule’s arms and conformational degrees of freedom. Importantly, they can form a stable biaxial nematic phase, and, hence, this structure should be included into theoretical analysis as a possible competitor of NTB.

Biaxiality is also regarded as a key factor to get spontaneous chiral symmetry breaking from first principles. These symmetry arguments are supported by recent phenomenological analysis of modulated nematic structures using generalized Landau–de Gennes–Ginzburg theory, where the key ingredients were couplings between the alignment tensor field and steric polarization. In this theory the N_{ TB} phase, described by a locally uniaxial distortion of the director field, appears less stable than its locally biaxial counterpart, i.e. where 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 stability of N_{ TB} and of competing nematic phases, including biaxial one. This extension allows to treat 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. Next we interpret 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 parametrization for molecular reference frames, where two mesogenic arms A and B, each of length L, are joined at the bend angle $\chi$ (Figure 1). At the midpoint of each arm a molecular basis is placed. The unit vector $\hat{w}$ at the center (C) of the particle describes molecular C_2 axis. In line with the present model of the N_{ TB} phase we generalize the local uniaxial ansatz, represented by the main director $\hat{\Omega}_i$, by its local biaxial counterpart (kept from the start in the variational ansatz for local environment of the molecule). That is, we assume two other directors to follow the precession of $\hat{n}(z)$ (Figure 1):

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

(2)

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

(3)

As for GLF the parametrization permits the N_{ TB} phase for $0^\circ < \theta < 90^\circ$ and finite pitch p, with wave vector $k$ being parallel to the 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 of the arms of the molecule, which is achieved via second–rank, $3 \times 3$, symmetric and traceless tensor $Q$. The basis of the Q tensors, defined with respect to the orthonormal right–handed tripod, say $(\hat{\xi}, \hat{\eta}, \hat{\zeta})$, comprises both uniaxial $Q_A$ and biaxial $Q_B$ parts, given in the general form as:

$$Q_{U}(\hat{\zeta}) \equiv \frac{1}{\sqrt{6}} (3\zeta \otimes \zeta - \mathbb{I}),$$

(4)

$$Q_{B}(\hat{\xi}, \hat{\eta}) \equiv \frac{1}{\sqrt{2}} (\zeta \otimes \zeta - \hat{\xi} \otimes \hat{\eta}),$$

(5)

where $\otimes$ denotes the tensor product and $\mathbb{I}$ is the identity matrix.

Taking linear combination of $Q_A$ and $Q_B$ the molecular tensors for each arm are now defined as:

$$Q(\Omega_i) \equiv Q_{U}(\hat{\xi}_i) + \lambda \sqrt{2} Q_{B}(\hat{a}_i, \hat{b}_i),$$

(6)

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

The next step is decomposition of the tensor $Q(\Omega_i)$:

$$\hat{Q}(R_j) = \hat{Q}_A(R_j) + \hat{Q}_B(R_j),$$

(7)

where $\hat{Q}_A(R_j)$ and $\hat{Q}_B(R_j)$ are the three local directors at the position $R_j$ of the midpoint of the $j$–th arm ($j = A,B$), and where
and where symbol \( \{ R_k \} \) stands for the right–handed tripod of 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:

\[
H_{\text{MF}}^{\text{GLF}} = -\epsilon \text{Tr} \left[ Q U (\hat{c}_A) \cdot Q_U (R_A) + Q U (\hat{c}_B) \cdot Q_U (R_B) \right].
\]  

\[ 15 \]

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

The difference between the two models lies in primary order parameters entering heliconical variational ansatz \( [7] \) on the \( N_{TB} \) structure. While in the GLF model the conical twist–bend helix \( Q_U \) is approximated by a locally uniaxial distortion of the director field weighted by \( q_0 \); our \( \bar{Q} \) tensor comprises 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 \( \hat{k} \parallel (\hat{m}) [18,19] \), which is an eigenvector of \( \langle Q \rangle_p \), where \( \langle \ldots \rangle_p \) denotes average over one period \( p \) along \( \hat{k} \). Indeed, the averaged alignment tensor \( \langle Q \rangle_p \) is diagonal, uniaxial and of zero trace, and the eigenvector \( \langle \hat{n} \rangle_p \) corresponds to the non–degenerate eigenvalue \( \Lambda_k \), given by a linear combination of \( q_0 \) and \( q_2 \):

\[
\Lambda_k = q_0 (3 \cos(2\theta) + 1) + q_2 \sin^2(\theta),
\]  

\[ 16 \]

Our extension is also important as it obeys two nematic phases, uniaxial and biaxial, both recovered for pitch \( p \to \infty \), while in the GLF model only a uniaxial nematic phase is present. 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 the bend angle \( \chi \), while our model permits molecular arms to be biaxial, with arm’s biaxiality controlled by \( \lambda \). 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 equations \( [1,3] \). Since in this limit directers become positionally independent, it implies that \( \bar{Q} (R_A) = \bar{Q} (R_B) \equiv \bar{Q} \) and

\[
H_{\text{MF,N}} (\Omega) = -\epsilon \text{Tr} \left[ (Q (\hat{c}_A) + Q (\hat{c}_B)) \cdot \bar{Q} \right].
\]  

\[ 17 \]

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

\[
Q_{\text{mol}} \equiv Q (\hat{c}_A) + Q (\hat{c}_B).
\]  

\[ 18 \]
The $Q_{\text{mol}}$ tensor is biaxial, also for the GLF model of $\lambda = 0$. The biaxiality of $Q_{\text{mol}}$ can be quantified by calculating the invariant, normalized biaxiality parameter $w = \sqrt{\text{Tr}[Q_{\text{mol}}^4]/\text{Tr}[Q_{\text{mol}}^2]^2}$ ($w^2 \leq 1$). It reads

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

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

![Figure 2](image)

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

For the GLF model ($\lambda = 0$) the V-shaped molecule exhibits effectively disc–like uniaxial shape at $\chi = 90^\circ$, which evolves to rod–like uniaxial one at $\chi = 180^\circ$. The curve in ($w; \chi$) plane passes through zero, the point of maximal molecular biaxiality, when the bend angle is equal to the tetrahedral value ($\chi = \arccos(-1/3) \approx 109.47^\circ$). 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 dependent on $\chi$ and already for $\lambda \gtrsim 0.15$ the arm–induced biaxiality starts prevailing over. In the limit of maximally biaxial arms ($\lambda = 1/\sqrt{6}$), the effective molecule becomes maximally biaxial irrespective of the angle between the arms. Hence, the simple mean–field model (8) with only two molecular parameters, $\lambda$ and $\chi$, allows to control almost independently molecular anisotropy and the angle between the arms. They both seem primary to liquid crystal behavior of bent–core, dimeric and trimeric mesogens, especially in view that compounds composed of these molecules are also candidates to exhibit the elusive biaxial nematic phase.

### 3 Results

In what goes after, we use the following notation for phases: $N_U$ for the uniaxial nematic, $N_B$ for the biaxial nematic, $N_{TB}$ for the twist–bend nematic with heliconial uniaxial ansatz ($Q_{TB}$), $N_{TB,B}$ for the twist–bend nematic with heliconical biaxial ansatz ($\hat{Q}$) and $I$ for the isotropic phase.

Phase diagrams for banana–shaped biaxial molecules for three typical values: 130°, 135° and 140° of the bend angle $\chi$ are presented in Figure 3. For $\chi = 130^\circ$ three phases: $N_{TB}$, $N_{TB,B}$, and $I$ become stable for $\lambda$ ranging from 0 to the so–called self–dual point (29) where $\lambda = 1/\sqrt{6}$. In Figure 3b the $N_{TB,B}$ phase becomes stable below the uniaxial $N_B$ with phase sequence: $I$ → $N_TB$ → $N_{TB,B}$, or directly below I through sequence: $I$ → $N_{TB,B}$. Widening the bend angle (see Figures 3b and 3c) leads to stable regions of $N_U$ and even $N_B$ phases, although $N_B$ is visible only in a very narrow region of $\lambda$ (in the closest vicinity of the self–dual point) and for $\chi = 140^\circ$. Apart from phase transitions that are present for $\chi = 130^\circ$ we can identify the following sequences: $I$ → $N_{TB}$ → $N_{TB,B}$, $I$ → $N_{TB}$ → $N_{TB,B}$ and $I$ → $N_{TB}$ → $N_{TB,B}$. Broadening of regions of the nematic phases, both uniaxial and biaxial, starts with further widening of the bend angle ($\chi > 140^\circ$), where the more ordered twist–bend nematics are moved to lower temperatures, similar to the tetrahedric nematic phases (23,24). Interestingly, for $\chi \lesssim 140^\circ$ the nematic 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 uniaxial ($q_0$) and biaxial ($q_2$) order parameters, tilt angle ($\Theta$) and pitch ($\rho$) for the selected cases. Additionally, we have calculated the order parameter ($\hat{\omega}, \hat{m}(z = R_C)$), which gives signature of polar order in the system, and hence allows to identify a nematic twist–bend phases. Figure 4 shows exemplary results for the $I$ → $N_{TB,B}$ phase sequence, where discontinuity in all parameters indicates on the first order phase transition between these phases. The tilt angle in $N_{TB}$ tends to $\Theta = 25^\circ$ and pitch is almost constant, smaller than the length of a stretched molecule.

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

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

Indeed, substitution of $\chi = 130^\circ$ gives 25° for $\Theta$ in this limit. The relation (20), being valid for arbitrary bend angle $\chi$, is also regained for $\Theta$ in the bottom panel of Figure 5. As concerning pitch of the twist–bend phase it should never exceed 4L in the ground state, but can be larger than this value for high temperatures. This is illustrated in Figure 5 where pitch becomes divergent in the vicinity of $N_{TB} \leftrightarrow N_{U}$ phase transition.

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

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The following averages need to be determined:

\[
\langle q_n \rangle = \frac{1}{2} \left( \langle q_n (\{ R_k \}, \Omega_A) \rangle + \langle q_n (\{ R_k \}, \Omega_B) \rangle \right), \quad n = 0, 2. \tag{21}
\]
Fig. 5 (Color online) Behavior of order parameters, tilt angle and pitch for Iso $\rightarrow$ N$_{U} \rightarrow$ N$_{TB}$ phase transitions when $\lambda = 0.36$ and $\chi = 140^\circ$. For further details see caption to Figure 4.

Fig. 6 (Color online) Behavior of order parameters, tilt angle and pitch for phase transitions Iso $\rightarrow$ N$_{TB} \rightarrow$ N$_{TB}$, when $\lambda = 0.1$ and $\chi = 130^\circ$. For further details see caption to Figure 4.

Fig. 7 (Color online) Behavior of order parameters, tilt angle and pitch for the sequence of phase transitions Iso $\rightarrow$ N$_{U}$, N$_{B} \rightarrow$ N$_{TB}$, when $\lambda = 0.408$ and $\chi = 140^\circ$. For further details see caption to Figure 4.

Fig. 8 (Color online) Behavior of order parameters, tilt angle and pitch for the successive phase transitions: Iso $\rightarrow$ N$_{B} \rightarrow$ N$_{TB}$, when $\lambda = 1/\sqrt{6}$ and $\chi = 140^\circ$. For further details see caption to Figure 4.
phases, it is possible to stabilize the $N_{B}$ phase, as well. The last plot (Figure 8) depicts a phase transition between $N_{B}$ and $N_{TB,B}$ at the self–dual point $(\lambda = 1/\sqrt{6})$ for the arms and $\chi = 140^{\circ}$. Here 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 order parameters (see Figures 7 and 8).

4 Summary

In conclusion, we analyzed an extension of the generic GLF mean–field model[1] to study the role biaxiality of 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 local biaxial ansatz for the alignment tensor. In the limit of uniaxial particles ($\chi = 0^{\circ}, 180^{\circ}$ and $\lambda = 0$) we recover 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 mean–field version of the well known Lebwohl–Lasher dispersion model.[39–50] As all bent–core molecules are biaxial[51] our generalization seems important for it allows to control intrinsic molecular biaxiality (by two molecular features: bend angle and arm anisotropy).

We showed that in our extended model, in addition to $N_{B}$ and $N_{TB}$, two extra phases: homogeneous $N_{B}$, and periodic $N_{TB,B}$ – the analog of $N_{TB}$ with local biaxial order of 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, like in the recently reported experiments.[15–52] Widening the bend angle opens the path for stabilization of standard nematics, where they start to dominate over less conventional phases as in.[53–55] However, the stable $N_{B}$ phase is not found for $\chi \lesssim 140^{\circ}$.

One can see from Figures 4–8 that the asymptotic relation for the tilt angle $\theta$ is actually the limit for $\theta$ in the $N_{TB,B}$ phase, as this structures 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).[56–58] Then, further nematic structures with one–dimensional modulation are also expected.[59–65]

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