

Soft Matter

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Molecular geometry, twist-bend nematic phase and unconventional elasticity: a generalised Maier-Saupe theory[†]

Cristina Greco,^a Geoffrey R. Luckhurst,^b and Alberta Ferrarini^{*a}

Received Xth XXXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXXXX 200X

DOI: 10.1039/b000000x

It has been found that bent-shaped achiral molecules can form a liquid crystal phase, called the Twist-Bend Nematic (N_{TB}), which is locally polar and spontaneously twisted having a tilted director, with a conglomerate of degenerate chiral domains with opposite handedness and pitch of a few molecular lengths. Here, using a major extension of the Maier-Saupe-like molecular field theory for V-shaped molecules, we can describe the transition from the nematic (N) to the N_{TB} phase. We provide a consistent picture of the structural and elastic properties in the two phases, as a function of the molecular bend angle, and show that on approaching the transition there is a gradual softening of the bend mode in the N phase. This points to the crucial role of the molecular shape for the formation of modulated nematic phases and their behaviour.

1 Introduction

Recently, a number of unusual features were identified in the second nematic phase formed by certain achiral bent-shaped liquid crystal dimers, which were interpreted as a signature of the Twist-Bend Nematic (N_{TB}) phase¹, where a periodically distorted director forms a conical helix with doubly degenerate domains having opposite handedness. The existence of a phase of this kind had been predicted earlier^{2,3}, and was suggested by Monte Carlo simulations of a small system of V-shaped particles formed from Gay-Berne units⁴. Such a picture was confirmed by different experimental techniques and valuable insights were reached by transmission electron and optical microscopy^{5,6} as well as electro-optical measurements⁷. From these and from the analysis of NMR experiments^{8,9} a remarkably short periodicity, of the order of a few molecular lengths, was identified. Although the structural features of the N_{TB} phase are becoming clear, there remain several open questions, the first of which concerns the origin of the director modulation. Either the flexoelectric coupling between bend deformation and electric polarization² or a negative bend elastic constant³ have been invoked as a potential causes of spontaneous bend distortions. Negative K_{33} values for nematics of bent molecules have been predicted either for purely steric reasons¹⁰ or as a result of flexoelectric renormalization¹¹. Another aspect which needs clarification is the sensitivity of the twist-bend phase formation to changes in the

molecular structure^{1,12–15}. The ability to address such a question would be particularly important in view of possible applications of the twist-bend phase in fast electro-optical devices⁷.

Here we present a molecular field theory for the N_{TB} phase. Considering the case of rigid, V-shaped molecules, a minimalist model is used, which can be seen as a generalization of the Maier-Saupe theory^{16–18}, suitable to take account of both the molecular architecture and the twist-bend spatial modulation of the director. Thus we obtain an expression for the free energy where the distinctive features of the system are introduced from the molecular level, rather than as *ad hoc* parameters. This allows us to obtain a consistent picture of the nematic (N) and N_{TB} phases, of their transitional and elastic behaviour, in relation to the molecular geometry.

In the next section we will give an overview of the model, then we will present the theoretical predictions and we will discuss them in the light of the available experimental data. Finally, we summarise the significant conclusions of our study and make comparisons with the other theories.

2 The molecular field model

The molecular model is sketched in Fig. 1: a molecule is made of two mesogenic arms (A, B), each of length L , joined at one end, with the bend angle χ . The following unit vectors are attached to the molecule: $\hat{\mathbf{w}}$ is parallel to the C_2 (molecular) symmetry axis and $\hat{\mathbf{u}}_A$, $\hat{\mathbf{u}}_B$ are along the arms. The classic N phase is characterised by a uniform director $\hat{\mathbf{n}}$, whereas, according to the customary description, each chiral domain of the N_{TB} phase features a director that undergoes a heliconical precession around an axis (parallel to the unit vector $\hat{\mathbf{h}}$), with conical angle θ_0 and pitch p , or wavenum-

^a Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35121 Padova, Italy E-mail: alberta.ferrarini@unipd.it; cristina.greco@studenti.unipd.it

^b School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK E-mail: G.R.Luckhurst@soton.ac.uk

ber $q = 2\pi/p$ (see Fig. 1). In a LAB frame with the Z axis parallel to the helix axis we can then write: $\hat{\mathbf{n}} = \hat{\mathbf{n}}(Z) = (\sin \theta_0 \cos \phi, \sin \theta_0 \sin \phi, \cos \theta_0)$, where $\phi = qZ$. The uniaxial nematic phase is recovered for pitch $p \rightarrow \infty$ and/or conical angle $\theta_0 = 0^\circ$, whereas the case with finite pitch and $\theta_0 = 90^\circ$ corresponds to the cholesteric* organization.

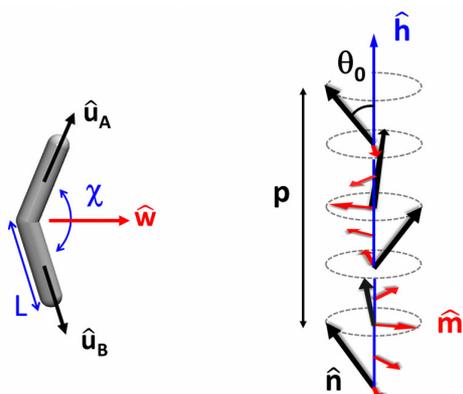


Fig. 1 On the left the molecular model, with χ the bend angle and L the length of one arm; $\hat{\mathbf{w}}$, $\hat{\mathbf{u}}_{A,B}$ are unit vectors parallel to the two-fold symmetry axis and to the arms, respectively. On the right the N_{TB} phase organization (one of the two degenerate helicoidal domains) with θ_0 the conical angle and p the helical pitch; $\hat{\mathbf{n}}$ and $\hat{\mathbf{h}}$ are unit vectors parallel to the local director and to the helix axis, respectively, and $\hat{\mathbf{m}} = \hat{\mathbf{h}} \times \hat{\mathbf{n}}$.

In the spirit of the Maier-Saupe theory, each arm is assumed to align preferentially to the local director $\hat{\mathbf{n}}$ at the position of the arm. Thus, the complete orientational potential experienced by the molecule, U , is the sum of the contributions of the two arms:

$$U = -\varepsilon \langle P_2 \rangle [P_2(\hat{\mathbf{u}}_A \cdot \hat{\mathbf{n}}(\mathbf{R}_A)) + P_2(\hat{\mathbf{u}}_B \cdot \hat{\mathbf{n}}(\mathbf{R}_B))], \quad (1)$$

where ε is a constant (with the dimension of energy) that quantifies the orienting strength, P_2 is the second Legendre polynomial, $\hat{\mathbf{n}}(\mathbf{R}_J)$ is the director at the position of the midpoint of the J th arm ($J = A, B$), and $\langle P_2 \rangle$ is the orientational order parameter of an arm. It is worth pointing out that the orientational potential $U = U(\Omega)$ defined in Eq. 1 depends on a microscopic order parameter ($\langle P_2 \rangle$) and two macroscopic order parameters (θ_0 and p) which characterize the position dependence of the director field. For the special case of rod-like molecules ($\chi = 180^\circ$) and uniform $\hat{\mathbf{n}}$ (*i.e.* $p \rightarrow \infty$), the Maier-Saupe expression is recovered^{16–18} (apart from a factor of 2, which results from considering the molecule as made of two mesogenic units). The molecular field potential defined in

Eq. 1 is a function of the molecular orientation: $U = U(\Omega)$, where $\Omega = (\alpha, \beta, \gamma)$ are Euler angles that define this orientation in a local frame with its Z' axis parallel to $\hat{\mathbf{n}}$. Orientational averages can then be defined as $\langle \dots \rangle = \int d\Omega f(\Omega) \dots$, where $f(\Omega)$ is the single molecule orientational distribution function, $f(\Omega) = (1/Q) \exp[-U(\Omega)/k_B T]$, with k_B the Boltzmann constant, T the temperature and Q the orientational partition function, $Q = \int d\Omega \exp[-U(\Omega)/k_B T]$.

By construction the potential $U(\Omega)$ reflects the symmetry of the molecule and that of its local environment. The N_{TB} structure has global D_∞ symmetry, with the C_∞ axis parallel to the helix axis ($\hat{\mathbf{h}}$ in Fig. 1), and local C_2 symmetry, with the twofold axis perpendicular to the plane containing the helix axis and the local $\hat{\mathbf{n}}$ director, *i.e.* along $\hat{\mathbf{m}}$ in Fig. 1. Therefore the N_{TB} phase is locally polar: it is compatible with the existence of odd-rank order parameters, defined with respect to the $\hat{\mathbf{m}}$ axis, which is the only principal direction common to any locally averaged property.

According to the molecular field procedure the Helmholtz free energy of the liquid crystal phase, taken as the difference with respect to that of the isotropic phase, is built as the sum of an entropy and an internal energy contribution, both expressed in terms of the molecular field orientational potential²¹. The N_{TB} phase, though non-uniform, is homogeneous; thus for both the N and the N_{TB} phases we can simply refer to thermodynamic properties per unit volume. The change in entropy density resulting from orientational order is given by: $\Delta s^{or} = -\rho k_B \int d\Omega f(\Omega) \ln[8\pi^2 f(\Omega)]$, where ρ is the number density, $\rho = N/V$, with N the number of molecules and V the volume. The change in internal energy density is simply related to the average value of the molecular field potential: $\Delta u^{or} = (\rho/2) \langle U \rangle$, where again the angular brackets denote the orientational averages defined previously. Then, we obtain for the entropic term: $\Delta s^{or} = -2\rho(\varepsilon/T) \langle P_2 \rangle^2 + \rho k_B \ln(Q/8\pi^2)$ and for the internal energy contribution: $\Delta u^{or} = -\rho \varepsilon \langle P_2 \rangle^2$. We can then define the scaled Helmholtz free energy density as:

$$\Delta a^* = \frac{\Delta a}{\rho k_B T} = \left\{ \frac{\langle P_2 \rangle^2}{T^*} - \ln \frac{Q}{8\pi^2} \right\}, \quad (2)$$

with the scaled temperature $T^* = k_B T/\varepsilon$. A key feature of the free energy density in Eq. 2 is that it implicitly contains the position dependence of the director, through the potential of mean torque, Eq. 1. Thus, it represents the free energy density of the nematic phase with the director field $\hat{\mathbf{n}}(\mathbf{R})$, relative to the isotropic phase. At a given scaled temperature, this difference is a function of the director deformation and of the $\langle P_2 \rangle$ orientational order parameter. Conversely, if a parametric form of the director field is used, the equilibrium state can be obtained by minimization of the free energy density see Eq. 2, with respect to $\langle P_2 \rangle$ and the director field parameters (θ_0 and p , or q , for the N_{TB} phase). We can define the deformation free energy density at a given temperature as the difference

* Unlike most literature, here "chiral nematic" will not be used as a synonym of cholesteric, since this could be ambiguous after the identification of other chiral nematic phases.^{19,20}

between the free energy density of the deformed (Δa^*) and the undeformed (Δa_u^*) system: $\Delta a_{def}^* = \Delta a^* - \Delta a_u^*$. Calculation of this difference as a function of the principal modes of deformation, defined with respect to the equilibrium state, allows us to determine the elastic constants, as will be shown later.

3 Results and discussion

We have investigated the phase behaviour of V-shaped molecules with different values of the bend angle χ . In our calculations the arm length L is taken as the unit of length. Fig. 2 shows a set of molecular orientational order parameters and the conical angle and pitch in the N_{TB} phase, calculated for $\chi = 140^\circ$, 135° and 130° . They are reported as a function of the reduced temperature $T_{red} = T/T_{NI}$, where T_{NI} is the nematic-isotropic transition temperature. In the two former cases we can see a first order transition from the isotropic to the uniaxial nematic phase, marked by a jump to a finite value of the $\langle P_2 \rangle$ order parameter, followed by a second order transition, from the N to the N_{TB} phase, at a lower temperature. This is evidenced by a discontinuous change in slope of $\langle P_2 \rangle$, and a simultaneous appearance of a conical angle and a finite pitch. Correspondingly, the onset of polar order is evidenced by the first rank order parameter $\langle P_1^{wm} \rangle$, with $P_1^{wm} = \hat{\mathbf{w}} \cdot \hat{\mathbf{m}}$. Both conical angle and pitch exhibit a steep change at the N_{TB} -N transition, reaching values that then remain almost constant with decreasing temperature: θ_0 around 30° and $p \approx 4 - 5L$. In the plots we also show the second rank order parameter $\langle P_2^h \rangle$, for the molecular arms with respect to the helix axis $\hat{\mathbf{h}}$. In the N phase, where there is no tilt, this is identical to $\langle P_2 \rangle$, but at the N_{TB} -N transition a difference appears, since the former exhibits a drop, which is a signature of the tilt of the $\hat{\mathbf{n}}$ director, and then increases very slowly with decreasing temperature. Surprisingly for $\chi = 130^\circ$ we can see a direct first order transition from the isotropic to the N_{TB} phase, denoted by a jump to finite values of the conical angle, the helical pitch and of all the orientational order parameters.

These results point to a strong sensitivity of the phase behaviour to the bend angle: as χ becomes smaller so the width of the N phase decreases and the N_{TB} phase is progressively stabilized. For χ larger than 150° the N_{TB} -N transition is predicted at a very low temperature ($T_{N-I}/T_{N_{TB}-N} > 2$), whereas for χ smaller than 130° the N phase disappears. Unlike the stability range of the N phase, the structural properties of the N_{TB} phase exhibit a weak dependence upon the χ value: interestingly in all cases a tight pitch is predicted, of the order of a few molecular lengths, which decreases only slightly with narrowing of the bend angle, whereas the conical angle tends to increase.

Fig. 3 shows the scaled deformation free energy density, Δa_{def}^* , as a function of helical wavenumber and conical angle, for $\chi = 140^\circ$ at three different reduced temperatures, on

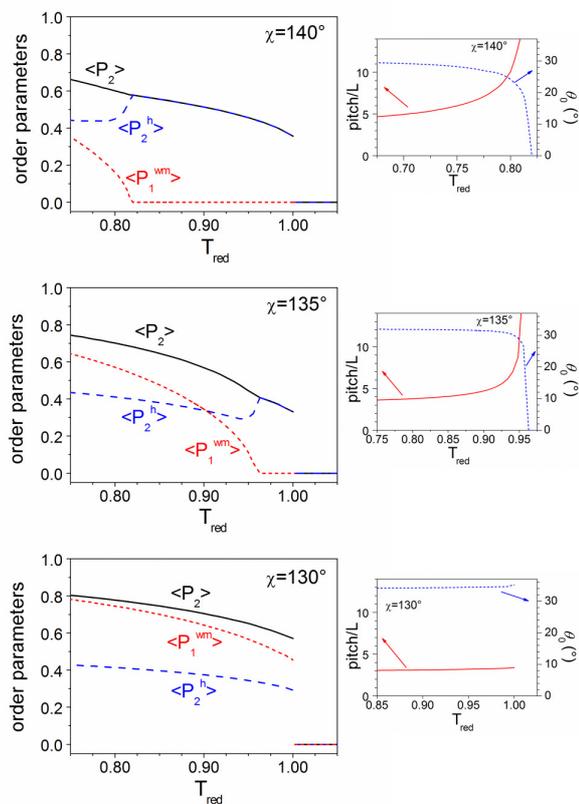


Fig. 2 Molecular order parameters (see text), on the left, and helical pitch p and conical angle θ_0 , on the right, as a function of the reduced temperature T_{red} , for V-shaped molecules with bend angle $\chi = 140^\circ$ (top), $\chi = 135^\circ$ (middle) and $\chi = 130^\circ$ (bottom).

either side of the N_{TB} -N phase transition. At the higher temperature the free energy exhibits a single minimum, at $q = 0$, $\sin \theta_0 = 0$, *i.e.* in the N phase, and increases as the deformation grows. On decreasing temperature the minimum becomes shallower until a new minimum appears, at finite values of q and $\sin \theta_0$. Then, on further decreasing temperature the minimum becomes deeper and moves toward higher θ_0 and q values.

According to the continuum elastic theory, the free energy density of the nematic phase in the presence of a twist-bend deformation ($q \rightarrow 0$) can be expressed as²²:

$$\Delta a_{def} = \frac{1}{2} K_{22} q^2 \sin^4 \theta_0 + \frac{1}{2} K_{33} q^2 \sin^2 \theta_0 \cos^2 \theta_0, \quad (3)$$

where K_{22} and K_{33} are the twist and bend elastic constants, respectively. For $\theta_0 = 90^\circ$ the deformation is a pure twist, whereas for $\theta_0 = 0^\circ$ the energetic cost is essentially that for bend. Therefore we can write: $\Delta a_{def} = \frac{1}{2} K_{22} q^2$, for $\theta_0 = 90^\circ$, and $\Delta a_{def} / \sin^2 \theta_0 = \frac{1}{2} K_{33} q^2$, for $\theta_0 \rightarrow 0^\circ$. Thus, from the

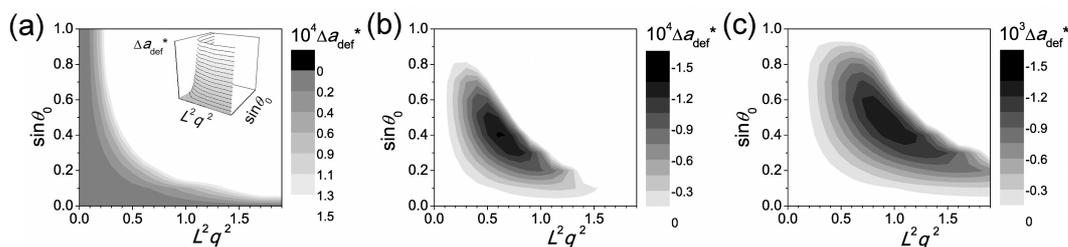


Fig. 3 Contour plots showing the scaled deformation free energy density Δa_{def}^* as a function of the wavenumber q (L is taken as the unit of length) and of $\sin \theta_0$, with θ_0 being the conical angle. Calculations are for molecules with bend angle $\chi = 140^\circ$, at three different reduced temperatures on either side of the N_{TB} -N phase transition: $T_{red}=0.83$ (a), 0.80 (b) and 0.77 (c). The inset in the (a) graph shows a 3D representation of the free energy surface.

initial slope ($q = 0$) of Δa_{def} vs q^2 we can obtain the twist and bend elastic constants of the N phase. This is different from the common methodology, in which explicit expressions for the elastic constants are used²³.

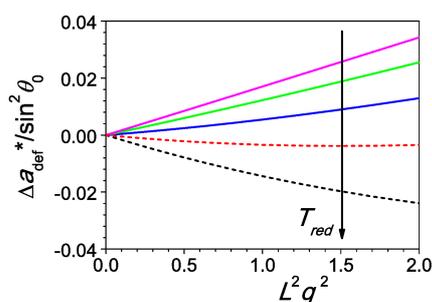


Fig. 4 Scaled deformation free energy density for pure bend as a function of the square of the wavenumber q (L is taken as the unit of length), for particles with bend angle $\chi = 140^\circ$ at different reduced temperatures ($T_{red}=0.90, 0.87, 0.83, 0.80, 0.77$).

For pure twist, the deformation free energy is an increasing function of q and its initial slope remains positive over the whole temperature range. For bend deformations we find a more complex behaviour, as illustrated in Fig. 4. This shows the ratio $\Delta a_{def}^*/\sin^2 \theta_0$ calculated for $\theta_0 \rightarrow 0^\circ$ as a function of q^2 for the case $\chi = 140^\circ$. Data for a set of temperatures are reported, on either side of the N_{TB} -N phase transition. Above the transition the deformation free energy for pure bend is positive and proportional to q^2 ; however, unlike the usual behaviour for rod-like nematics, the initial slope, and hence K_{33} , decreases with decreasing temperature. On going through the N_{TB} -N transition, the slope reverses its sign, simultaneously with the disappearance of the nematic minimum. Analogous results were obtained using a different methodology and a molecular field model with atomistic resolution^{10,24}, for both bent-core mesogens and odd liquid crystal dimers having an

average bent shape: the bend elastic constant K_{33} was found to decrease with increasing order, and then to take negative values. It is worth stressing that in this context K_{33} is meant as a synonym of 'second derivative of the free energy with respect to bend deformations', and only if positive does it have the meaning of a standard elastic modulus associated with a restoring force.

Our results are in keeping with the main experimental findings on the N_{TB} phase. These include the key role of the bend angle: the N_{TB} phase has been detected in liquid crystal dimers with an odd number of groups between the mesogenic units and its appearance exhibits a strong sensitivity to molecular modifications^{1,12,13,15}. In these systems the bend angle, taken as the angle between the mesogenic units, changes with the molecular conformation. The bend angle distribution for a given dimer has a subtle dependence on the nature of the linking group between the mesogenic units and the spacer, being shifted to larger values on moving from methylene to ether links^{1,10,14,25}. Up to now there is no evidence of a direct N_{TB} -I transition; according to our predictions good candidates would be systems with a small bend angle, for which however there could be other competing phases. From FFTEM and birefringence experiments^{5,6}, analysis of NMR spectroscopy data⁹ and measurements of an electroclinic effect⁷, conical angles between 11° and 30° , together with pitches in the range 5-10 nm and weakly dependent on temperature, have been determined for CB7CB and other odd liquid crystal dimers of similar structure (average molecular lengths $\sim 2.5 - 3$ nm). A slightly longer pitch, of 14 nm, was reported for a bent-core mesogen (average molecular length ~ 5 nm)²⁶. Another typical behaviour is exhibited by the birefringence, which in the N phase is found to increase with lowering temperature, but exhibits a decrease on entering the N_{TB} phase, which was interpreted as evidence for a tilt of the director. A strong decrease was observed at the N_{TB} -N transition for CB7CB and for a mixture of liquid crystal dimers^{5,27}, but for another odd mesogenic dimer a smoother decrease was found⁶. A qual-

itative comparison can be made with the temperature dependence of the $\langle P_2^h \rangle$ order parameter (Fig. 2). A great deal of information on the N_{TB} phase has been provided by NMR spectroscopy, however the molecular representation used in our present model is not sufficiently detailed to allow an accurate comparison with NMR data. Finally, we have to mention the anomalous behaviour of the bend elastic constant in the N phase: for odd liquid crystal dimers K_{33} has been found to be unusually small and to decrease on moving towards the transition with the N_{TB} phase, up to very small values in the proximity of the transition^{6,14}, although in one case a plateau was observed²⁸.

The ability to investigate on the same footing different phases and properties allows us to clarify some controversial issues. One is the relationship between the phase transition and the elastic properties. We have found that for sufficiently bent molecules, as the temperature decreases, the N free energy minimum broadens along the bend coordinate, until a new minimum appears, which corresponds to the N_{TB} phase. This behaviour can be described in terms of elastic constants, *i.e.* the principal curvatures of the free energy at its minimum: K_{33} in the N phase decreases, until vanishing, as the temperature is lowered. When $K_{33}=0$ the director can bend without cost and the twist-bend organization appears. With further decreasing of temperature the curvature of the free energy in the undeformed (N) state with respect to bend deformations becomes increasingly negative and the N_{TB} minimum becomes deeper. A few points are worth stressing. The N_{TB} phase has its own elastic properties, different from those of the N phase; thus, in principle the use of the classical Frank free energy to analyse experiments in the N_{TB} phase is not justified, and could lead to questionable conclusions²⁹. Recently, extensions of the Frank elastic theory to the N_{TB} phase have been proposed, one of which contains a quartic term³ whereas the other retains the quadratic form³⁰. Another issue that deserves attention is the concept of 'negative K_{33} ', which should be meant as negative curvature of the free energy in the undeformed N state with respect to bend deformations. As such it indicates that the N phase is unstable with respect to bend deformations^{10,14,23}.

4 Conclusions

We have shown that a generalized Maier-Saupe theory, modified to take into account the coupling between director field and molecular shape, predicts the existence of the N_{TB} -N transition. This means that, compared to the N phase, the N_{TB} organization allows a better interaction between the non-collinear mesogenic groups, which compensates for the loss of entropy due to the additional polar order. Differently from previous theoretical approaches^{3,11}, our model includes molecules explicitly, though in a rather basic form, so that we

can assess the effect of changes in the molecular structure on the phase behaviour. We show that this is especially sensitive to the molecular bend angle, with the N_{TB} -N transition occurring for a limited range of values. We predict the orientational and structural parameters of the N_{TB} phase and their temperature dependence; in particular, we obtain a pitch of the order of a few molecular lengths, weakly dependent on temperature or molecular details, in agreement with the available experimental data. We can also provide a consistent description of the elastic properties of the system, which allows us to discuss their relationship with the N_{TB} transition. In this regard, the scenario that we describe is in substantial agreement with the Dozov picture, which is based on a Landau theory. Elsewhere electrostatics, and in particular flexoelectric couplings, have been proposed as the main feature responsible for the formation of modulated phases^{2,31}. One cannot, of course, exclude that such couplings are present and may also be more significant than in conventional rod-like nematics, but this does not necessarily mean that they are the driving force for the phase transition. Interestingly, the N_{TB} phase has been observed experimentally even for mesogens that lack strong electric dipoles⁶. Indeed, the results predicted by our model point towards a primary role of the molecular shape, in line with the suggestion of early Monte Carlo simulations⁴ and also with more recent lattice simulations¹¹. In the latter the site interactions leading to the twist-bend modulation were denoted as 'dipolar' or 'flexoelectric' but, given the model used, this has to be taken more as a general indication of their symmetry, rather than of their physical nature.

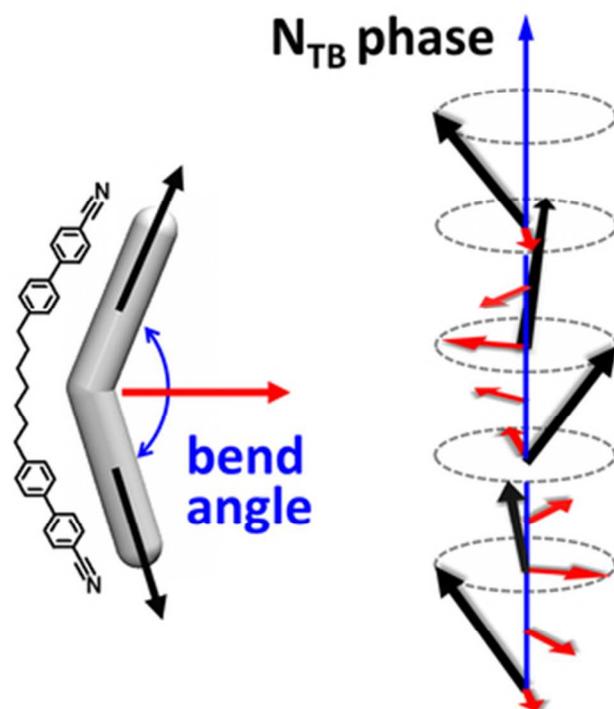
Our present study can be extended along various directions. One is the introduction of a more detailed molecular representation, along the lines shown in refs.^{10,24}, which will allow closer comparison of the predictions with experimental data, in particular with those from NMR spectroscopy^{8,9}. Another is the extension to different phases, having not only 1D periodicity, like the predicted splay-bend nematic³, but even 2D and 3D modulations.³² This is especially important in view of the well-known difficulties of molecular simulations of finite samples in handling non-uniform systems. Also the use of free energy calculations in the presence of director deformations, as proposed here, to evaluate the elastic constants, is a general methodology that clearly merits exploration.

5 Acknowledgments

A.F. acknowledges financial support from the Ateneo di Padova through ex 60%. C.G. thanks Merck Chemicals Ltd for a scholarship (PhD School in Materials Science and Engineering of Padova University).

Notes and references

- 1 M. Cestari, S. Diez-Berart, D. A. Dunmur, A. Ferrarini, M. R. de la Fuente, D. J. B. Jackson, D. O. Lopez, G. R. Luckhurst, M. A. Perez-Jubindo, R. M. Richardson, J. Salud, B. A. Timimi and H. Zimmermann, *Phys. Rev. E*, 2011, **84**, 031704.
- 2 R. B. Meyer, *Molecular Fluids (Le Houches Summer School on Theoretical Physics 1973)*, Gordon and Breach, New York, 1976, pp. 271–343.
- 3 I. Dozov, *Europhys. Lett.*, 2001, **56**, 247–253.
- 4 R. Memmer, *Liq. Cryst.*, 2002, **29**, 483–496.
- 5 D. Chen, J. H. Porada, J. B. Hooper, A. Klitnick, Y. Shen, M. R. Tuchband, E. Korblova, D. Bedrov, D. M. Walba, M. A. Glaser, J. E. Maclennan and N. A. Clark, *PNAS*, 2013, **110**, 15931–15936.
- 6 V. Borshch, Y.-K. Kim, J. Xiang, M. Gao, A. Jakli, V. P. Panov, J. K. Vij, C. T. Imrie, M. G. Tamba, G. H. Mehl and O. D. Lavrentovich, *Nat. Commun.*, 2013, **4**, 2635.
- 7 C. Meyer, G. R. Luckhurst and I. Dozov, *Phys. Rev. Lett.*, 2013, **111**, 067801.
- 8 L. Beguin, J. W. Emsley, M. Lelli, A. Lesage, G. R. Luckhurst, B. A. Timimi and H. Zimmermann, *J. Phys. Chem. B*, 2012, **116**, 7940–7951.
- 9 C. Greco, G. R. Luckhurst and A. Ferrarini, *PCCP*, 2013, **15**, 14961–14965.
- 10 M. Cestari, E. Frezza, A. Ferrarini and G. R. Luckhurst, *J. Mater. Chem.*, 2011, **21**, 12303–12308.
- 11 S. M. Shamid, S. Dhakal and J. V. Selinger, *Phys. Rev. E*, 2013, **87**, 052503.
- 12 P. A. Henderson and C. T. Imrie, *Liq. Cryst.*, 2011, **38**, 1407–1414.
- 13 R. J. Mandle, E. J. Davis, S. A. Lobato, C. C. A. Voll, S. J. Cowling and J. W. Goodby, *PCCP*, 2014, **16**, 6907–6915.
- 14 K. Adlem, M. Čopič, G. R. Luckhurst, A. Mertelj, O. Parri, R. M. Richardson, B. D. Snow, B. A. Timimi, R. P. Tuffin and D. Wilkes, *Phys. Rev. E*, 2013, **88**, 022503.
- 15 N. Sebastián, D. O. López, B. Robles-Hernández, M. R. de la Fuente, J. Salud, M. A. Pérez-Jubindo, D. A. Dunmur, G. R. Luckhurst and D. J. B. Jackson, *PCCP*, 2014, **16**, 21391–21406.
- 16 W. Maier and A. Saupe, *Z. Naturforsch.*, 1958, **13a**, 564–566.
- 17 W. Maier and A. Saupe, *Z. Naturforsch.*, 1959, **14a**, 882–889.
- 18 W. Maier and A. Saupe, *Z. Naturforsch.*, 1960, **15a**, 287–292.
- 19 E. Barry, Z. Hensel, Z. Dogic, M. Shribak and R. Oldenbourg, *Phys. Rev. Lett.*, 2006, **96**, 018305.
- 20 H. B. Kollí, E. Frezza, G. Cinacchi, A. Ferrarini, A. Giacometti and T. S. Hudson, *J. Chem Phys. Commun.*, 2014, **140**, 081101.
- 21 G. R. Luckhurst, *The Molecular Physics of Liquid Crystals*, Academic Press, 1979, ch. 4.
- 22 P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1993.
- 23 A. Ferrarini, *Liq. Cryst.*, 2010, **37**, 811–823.
- 24 C. Greco, A. Marini, E. Frezza and A. Ferrarini, *ChemPhysChem*, 2014, **15**, 1336–1344.
- 25 A. P. J. Emerson and G. R. Luckhurst, *Liq. Crystals*, 1991, **10**, 861–868.
- 26 D. Chen, M. Nakata, R. Shao, M. R. Tuchband, M. Shuai, U. Baumeister, W. Weissflog, D. M. Walba, M. A. Glaser, J. E. Maclennan and N. A. Clark, *Phys. Rev. E*, 2014, **89**, 022506.
- 27 P. K. Challa, V. Borshch, O. Parri, C. T. Imrie, S. N. Sprunt, J. T. Gleeson, O. D. Lavrentovich and A. Jakli, *Phys. Rev. E*, 2014, **89**, 060501(R).
- 28 R. Balachandran, V. P. Panov, J. K. Vij, A. Kocot, M. G. Tamba, A. Kohlmeier and G. H. Mehl, *Liq. Cryst.*, 2013, **40**, 681–688.
- 29 V. P. Panov, M. Nagaraj, J. K. Vij, Y. P. Panarin, A. Kohlmeier, M. G. Tamba, R. A. Lewis and G. H. Mehl, *Phys. Rev. Lett.*, 2010, **105**, 167801.
- 30 E. G. Virga, *Phys. Rev. E*, 2014, **89**, 052502.
- 31 N. Vaupotič, M. Čepič, M. A. Osipov and E. Gorecka, *Phys. Rev. E*, 2014, **89**, 030501.
- 32 S. M. Shamid, D. W. Allender and J. V. Selinger, *ArXiv:1405.5584*, 2014.



Just because of their geometry, bent mesogens can form the modulated twist-bend nematic phase, whose stability range is strongly sensitive to the bend angle.

39x32mm (300 x 300 DPI)