Opinion

The Ever Elusive, Yet-to-Be-Discovered Twist-Bend Nematic Phase †

Edward T. Samulski

Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA; et@unc.edu; Tel.: +1-919-425-4427
† Dedicated to Bob Meyer on the occasion of his 80th birthday (13 October 2023).

Abstract: The second, lower-temperature nematic phase observed in nonlinear dimer liquid crystals has properties originating from nanoscale, polar, and intermolecular packing preferences. It fits the description of a new liquid crystal phase discovered by Vanakaras and Photinos, called the polar-twisted nematic. It is unrelated to Meyer’s twist-bend nematic, a meta-structure having a macroscale director topology consistent with Frank–Oseen elastic theory.

Keywords: polar-twisted nematic; twist-bend nematic; biaxial nematic; dimer liquid crystal; nematic director field; Frank–Oseen elastic theory; molecular nematic; topological nematic

1. Are the $N_X$ and $N_{TB}$ Phases Equivalent?

Over the last decade or so, Robert Meyer’s elegant conjecture in the early 1970s about a twist-bend nematic director topology based on elastic continuum theory [1] has been conflated with another observed nematic phase, the $N_X$ phase, so named because its molecular organization was unfamiliar. In the $N_X$ phase, nonlinear dimer liquid crystals exhibit a very tight 1D twist modulation of the orientational ordering with a nanoscale pitch of ~10 nm. Meyer envisioned the twist-bend nematic phase ($N_{TB}$) specifically as a different kind of hierarchical meta-structure, a nematic having the apolar, uniaxial nematic director $n$ ($n \leftrightarrow -n$, $D_{max}$ symmetry) spontaneously bending on the macroscale (~1 μm). Nevertheless, Meyer’s $N_{TB}$ phase has been used by some [2–4] to explain the nanoscale roto-translation modulation exhibited by bent or V-shaped dimer mesogens (e.g., CB-7-CB) in the $N_X$ phase, a second, lower-temperature nematic phase discovered in 1991 [5]. This explanation suggests that Meyer’s twist-bend nematic phase has already been discovered. A growing body of literature has accumulated around the putative $N_X \approx N_{TB}$ equivalence without questioning it [3,4,6].

However, unbeknownst to many researchers, another theory about the $N_X$ phase, published in 2016, provides a closer match to the experimental values than the original 2011 article [2], claiming that $N_X$ is the sought-after $N_{TB}$ phase. This new theory proposed by Vanakaras and Photinos (VP) suggests that the $N_X$ phase is actually a novel liquid crystal (LC) phase—a new type of nematic that they call the polar-twisted nematic ($N_{PT}$). Initially described within a mean field approximation, the VP theory predicts spontaneous chiral symmetry breaking and the formation of chiral domains of opposite handedness [7]. Their predictions were corroborated by simulations using detailed modeling of dimer LCs [8].
Dunmur’s 2022 article, Anatomy of a Discovery: The Twist-Bend Nematic Phase, declares an intention to provide a comprehensive review of the subject, in his words, “to present as fair and documented account as possible” [4]. However, it includes no references to publications by Vanakaras and Photinos about their alternative model or to critiques of the $N_X = N_{TB}$ supposition [9–11]. Its sole reference to alternative views is to a critique of a critique [12], one that obscures Meyer’s coherent conjecture, relegating it to a genealogical affiliation with an ill-defined “family” of twist-bend nematics. Dunmur cites only research based on the assumption that $N_X$ and $N_{TB}$ are one and the same, and, in this regard, it is one-sided, not a comprehensive historical account. Much of the cited research is solid and has advanced the field, but the work of VP demonstrates that its underlying equation of $N_X = N_{TB}$ is erroneous. For that reason, the mass of papers (more than 600) citing the same 2011 base publication by Dunmur et al. [2] has had a twofold effect on the science of LCs: it has suppressed not only any investigation of the new polar-twisted nematic but also the search for Meyer’s twist-bend nematic via the claim that such a phase has already been found. While there have always been researchers who have been more circumspect about the $N_X = N_{TB}$ supposition (e.g., Chen et al., 2013 [13]), publications after 2016 should reference and fully address the advances in understanding made by the VP theory. Given that the VP theory is not mere speculation but a precise analysis and explanation of experimental findings, a failure to address the way it differentiates the $N_X$ and $N_{TB}$ phases in future will retard advances in the understanding of the nematic phases exhibited by nonlinear, achiral mesogens.

2. Achiral Mesogens with Chiral Nematic Phases

Meyer was the first to predict that nematics comprising achiral molecules could exhibit form chirality—the spontaneous adoption of left- and right-handed helical supramolecular structures. At the time Meyer proposed the twist-bend nematic phase, it was envisioned for rodlike (calamitic) mesogens, not nonlinear molecules. (Since the $N_{TB}$ phase has not been observed to date, little can be said about prerequisite mesogen chemical structures other than that the molecular symmetry should be $C_{2V}$ or lower.) Meyer’s so-called twist-bend nematic $N_{TB}$, derives from the interplay between the bend elasticity of the nematic director field $n(r)$ and its associated flexoelectric polarization $P(r)$ [1]. A half century later, Vanakaras’ and Photinos’ analysis of the nematic phase of nonlinear dimer molecules predicted spontaneous chiral symmetry breaking, the so-called polar-twisted nematic $N_{PT}$ [7]. Some have claimed that Vanakaras’ and Photinos’ new understanding of the $N_X$ phase only differs from prior interpretations semantically [12]; this is not the case, as was explained in 2020 [11].

Appreciating the VP modeling of the $N_X$ phase requires an understanding of the limitations of Meyer’s theory, namely, its foundation in continuum elasticity theory in nematics; my colleagues and I have published articles explaining the constraints imposed on Meyer’s conjecture by elasticity theory in 2020 [9] and 2021 [10].

There are two critical differences between Meyer’s $N_{TB}$ theory and the $N_X$ phase, which Vanakaras’ and Photinos’ $N_{PT}$ theory illuminates: (1) The pitch of the form chirality is measured in micrometers in $N_{TB}$ theory versus nanometers in the $N_X$ phase. (2) The twisting entity is qualitatively different in the two theories, a nematic director $n$ in $N_{TB}$ theory versus a polar director $m$ in the $N_X$ phase, as delineated by $N_{PT}$ theory.

2.1. The Polar-Twisted Nematic Phase

The polar-twisted nematic phase $N_{PT}$ is an orientationally ordered fluid phase without density modulations (i.e., it is nematic), and, like Marvin Freiser’s 1970 predicted biaxial nematic phase ($N_B$) [14], it is also derived from theory utilizing minimal molecular modeling [7]. The most striking property of the new $N_{PT}$ nematic is its nanoscale modulation of the local polar orientational order (Figure 1 Left), a prediction of the VP model that is in remarkable quantitative agreement with experimental observations in the $N_X$ phase (Figure 1 Center)—the pitch of the nanoscale orientational modulation is $\sim 3 \text{ L}$ (three dimer
lengths) \cite{13,15}. As Figure 1 emphasizes, the nominal pitch in the NTB phase (Right) is 100× larger than the observed pitch in the NX phase (Center); the difference is so large that the figure cannot accommodate it without the dotted blue lines leaving the page (Right).

![Figure 1. Molecular organization in nematic phases. Left: Schematic of the locally polar supramolecular structure of the polar-twisted nematic phase. The local polarization \( m \) spirals about a helix axis \( h \) and generates a 1D modulation of the polar orientational order with pitch \( L^{PT} \approx 10 \text{ nm} \). Center: Freeze-fracture transmission electron microscopy image of the \( NX \) phase of CB-7-CB, illustrating a 1D modulation pitch \( L^X = 8 \text{ nm} \), excerpted from Figure 4a in ref. \cite{15}. Right: The apolar director \( n(r) \) has a heliconical trajectory about \( h \) in the twist-bend nematic phase with an anticipated pitch \( L^{TB} \) of \( \approx 1000 \text{ nm} \). The magnified view in the insets showing that the microscopic structural organizations of average mesogen shapes are approximately to scale.

The nanoscale modulation of orientational ordering predicted by the VP polar-twisted nematic model \((L^{PT} \approx 10 \text{ nm})\) is much lower because it derives from the local, polar, molecular packing of dimer LCs. The dimers displaying the \( NX \) phase have a bent or V-shaped contour with associated polarity (electrostatic and/or shape) and a \( C_{2v} \) average molecular symmetry. In the VP simulations, the dimer \( C_2 \) symmetry axes locally align (Figure 1 Left magnified inset), generating a polar phase director \( m \) that roto-translates about a local axis \( h \), yielding a 1D modulation of orientational order with a pitch that is in agreement with experimental observations in the \( NX \) phase, i.e., \( L^{PT} = L^X \). The polar molecular packing in the polar-twisted phase defining \( m \) is unconstrained by elasticity theoretical considerations, and \( m \) is free to tightly spiral spontaneously about \( h \) to circumvent low-entropy, ferroelectric polarity \cite{7,8}. Polarity is averaged out over one pitch length in the direction of the modulation, and since both left- and right-handed chiral packing (spirals) are equally probable, in macroscopic regions, the \( N_{PT} \) phase is predicted to be uniaxial with balanced chirality as indeed observed experimentally in the \( NX \) phase.

2.2. The Twist-Bend Nematic Phase

The macroscopic director topology in Meyer’s twist-bend nematic minimizes the elastic energy associated with gentle perturbations of a uniaxial nematic’s director field—in the language of the Frank–Oseen elastic theory of nematics, the curvatures of the nematic director field are “soft” \cite{16}. The director \( n \) tilts with a constant cone angle \( \theta_c \), and spirals about a macroscopic direction \( z \) in the N\(_{TB}\) phase (Figure 1 Right). (The resulting N\(_{TB}\) structure is asymptotically related to that of a traditional cholesteric or chiral nematic N\(_c\) phase, where \( \theta_c = 90^\circ \).) Since the twist-bend structure must conform to the physics of Frank–Oseen elastic theory, continuum elasticity restricts the magnitude of such deformations. As a result, the lower bound on the pitch \( L^{TB} \) of the spiraling nematic director in the twist-bend phase is in the order of microns, i.e., in order for the 1D modulations of the orientational order in the N\(_{TB}\) phase to be consonant with Frank–Oseen theory, the \( L^{TB} \) pitch must be \( \geq 100L^X \) (Figure 1 Center).
Meyer’s $N_{TB}$ phase conforms to the limitations of Frank–Oseen theory. De Gennes carefully explained those limitations in his canonical text of 1974 [17], updated in 1993 [18]. Meyer certainly understood those limitations when he conjectured that (flexoelectric) polarization could spontaneously drive the formation of a space filling director topology that is labeled the twist-bend nematic:

“Although a state of uniform torsion is possible, a state of constant splay is not possible in a continuous three-dimensional object. A state of pure constant bend is also not possible, although a state of finite torsion and bend is possible. The latter is a modified helix in which the director has a component parallel to the helix axis. In laboratory coordinates,

$$n_z = \cos \varphi, \quad n_x = \sin \varphi \cos \theta_0 z, \quad n_y = \sin \varphi \sin \theta_0 z.$$ 

The magnitude of the bend is $t_0 \sin \varphi \cos \varphi$” [1] p. 320.

The “finite torsion and bend” are crucial in understanding the role of Frank–Oseen elastic theory in Meyer’s twist-bend conjecture for the twist and bend elastic deformations of the director $n$; $t_0$ is the helical wavenumber and in Figure 1 Right, $\theta_c = \varphi$. In fact, he prefaces his description of the $N_{TB}$ phase with language that parallels that of de Gennes [17] pp. 58, 61; [18] p. 100:

“Changes in the magnitude of the order parameters in a nematic phase are high energy local processes. However gradual changes in the orientation of the director are low energy processes capable of being induced by small external perturbations. A continuum elasticity theory has been developed to describe these curvature structures” [1] p. 291.

This quotation and the one above confirm that Meyer’s formulation of the twist-bend topology of the director field were established within Frank–Oseen theory of uniaxial nematics.

3. The Second Nematic Phase in Dimer LCs

Meyer’s proposed director topologies are constrained to the class of deformations having macroscale strains—slow splay, twist, and bend deformations of $n$. Such restrictions apply to all continuum elastic theories of nematics, even those with extreme elastic constants [19]. Those limitations effectively exclude Dunmur and collaborators’ original assumption that $N_X = N_{TB}$ [2]; that equivalence requires the director field $n(r)$ to twist through an angle of $\pi$ over a distance of approximately three molecular lengths ($\sim 9$ nm), a distance scale over which $n$ itself is undefined. In other words, there are not enough molecules in a volume element around $r$ to specify $n(r)$. As emphasized before, “The issue is not the mere definition of the director in some volume $v$, but the deformation of $n(r)$, described by the curvatures of the director field, i.e., it has to do with lengths. In order to describe the curvatures of $n(r)$, the director has to be definable over a small volume $v$ around $r$, and of course such a description is meaningful only if the length scale of the curvature of $n(r)$ is much larger than the dimensions of $v$.” [10]. Such constraints do not apply to the $N_{PT}$ phase, where the ferroelectric polarization associated with the molecular packing of V-shaped molecules is alleviated by nanoscale torsion—roto-translation of the polar director $m$ on the scale of a few molecular dimensions [7,8].

Despite the clear differences between the molecular organization in the $N_X$ and $N_{TB}$ phases, recent citation practices continue to assume they are identical. A 2023 report reviews a variety of dimer LCs exhibiting the $N_X$ phase, calls it the $N_{TB}$ phase, and appears to be exhaustively documented (100 references) [20]; yet, it does not cite Meyer’s original work. Instead, it relies on a 2001 elasticity-based model by Dozov [19], one sourced in visually inspiring simulations [21] that are, however, technically flawed [8]. Its claim that the Dozov model supports the $N_X = N_{TB}$ proposition stretches the limits of continuum elasticity; that model computes a twist pitch “$\leq 100 \text{ L} \equiv 300$ nm, rather small but still macroscopic” [19], a value $30 \times$ larger than the measured pitch in the $N_X$ phase. The VP model of the $N_{PT}$ phase requires no such gymnastics.
4. A New Heuristic

Perhaps the continuing propagation of the erroneous \( N_X = N_{TB} \) assumption can be rectified with a new heuristic, one that clearly differentiates the possible representations of nematics. To that end, we might consider a classification scheme delineating two length scales:

I. *Local* nematic ordering: local organization dictated directly by intermolecular attractive dispersion forces regulated by excluded volume considerations \([22]\), e.g., the uniaxial, biaxial, polar-twisted \((N_{LU}, N_B, N_{PT})\) nematic phases.

II. *Topological* nematic ordering: defined on a larger length scale by soft trajectories, reflecting analogously “soft residual” molecular interactions, of the (typically uniaxial) nematic director \( \mathbf{n} \), e.g., chiral, splay-bend, twist-bend \((N^{*}, N_{SB}, N_{TB})\) nematic phases.

There may even be a third category for disclination-mediated director topologies as well (e.g., the so-called blue phases \([23]\)).

In an effort to make clear the meaning of *topological* nematic ordering, an exaggerated example is shown below. It is a fictional “knot” nematic \( (N_X) \) phase comprising a contiguous (chiral) director field; it is displayed below for pedagogical purposes. It shows soft/slow changes in the trajectory of the uniaxial director \( \mathbf{n}(r) \); its associated flexoelectric polarization \( P(r) \) is aligned along the bend vector \( \mathbf{n}(\nabla \cdot \mathbf{n}) \). It is devised to communicate the unique, hierarchical, macroscale meta-structure in the types of phases Meyer predicted a half century ago (i.e., twist-bend and splay-bend nematics). A failure to differentiate these two types of nematic organizations, local molecular (I) and topological (II), will continue to obfuscate distinctions between nematic phases and to confound interpretations of new experimental findings (e.g., NMR \([24]\) and simulations \([25]\)) in bent-core and dimer liquid crystals.

![Diagram of topological knot nematic \( N_X \)](image)

5. Concluding Remarks

Vanarakas’ and Photinos’ prediction of the polar-twisted nematic \( N_{PT} \) phase is similar to Freiser’s predicted biaxial nematic \( N_B \) phase. The latter reaffirmed the notion that biased, intermolecular interactions (correlated azimuthal angles among board-shaped mesogens) could manifest on a macroscale, and its alleged discovery was greatly acclaimed \([26,27]\). The organization in \( N_{PT} \) similarly derives from unique intermolecular interactions (correlated polar ordering), but its predictions continue to be ignored \([4,20]\) even though the \( N_{PT} \) nematic phase perfectly describes the molecular organization in the \( N_X \) phase and may even account for incompletely understood behavior in other bent-core mesogens \([24]\). The V shape of the CB-7-CB dimers are inherently biaxial, and, in its \( N_X \) phase, the dimers assume ferroelectric packing arrangements. The low entropy of such configurations is averted by winding them into tight, right- and left-handed helices having a nanoscale pitch.

In summary, two decades after the \( N_X \) phase was discovered \([5]\), some thought that it represented the long-lost phase postulated by Meyer \([2]\). Then, Vanarakas and Photinos showed that, on the contrary, the \( N_X \) phase was a new phase, which they christened the \( N_{PT} \) phase. The nanoscale modulation of the orientational order in dimer LCs unequivocally precludes the second, lower temperature \( N_X \) phase from being Meyer’s (or Dozov’s) twist-
bend nematic. Those topological nematic models diverge from the observations in the $N_X$ nematic; the $N_{PT}$ model reveals this divergence.

**Funding:** This research received no external funding.

**Acknowledgments:** I am grateful to Oleg Lavrentovich for permission to reproduce a freeze-fracture TEM image, Demetri Photinos, Alexandros Vanakaras, Daphne Klotsa and Lou Madsen for clarifying conversations, and to Carol Shumate for editorial assistance.

**Conflicts of Interest:** The author declares no conflict of interest.

### References


7. Samulski, E.T.; Vanakaras, A.G.; Photinos, D.J. All structures great and small: Nanoscale modulations in nematic liquid crystals. *Nanomaterials* 2022, 12, 93–113. [CrossRef]


Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.