Article

Anatomy of a Discovery: The Twist–Bend Nematic Phase

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Abstract: New fluid states of matter, now known as liquid crystals, were discovered at the end of the 19th century and still provide strong themes in scientific research. The applications of liquid crystals continue to attract attention, and the most successful so far has been to the technology of flat panel displays; this has diversified in recent years and LCDs no longer dominate the industry. Despite this, there is plenty more to be uncovered in the science of liquid crystals, and as well as new applications, novel types of liquid crystal phases continue to be discovered. The simplest liquid crystal phase is the nematic together with its handed or chiral equivalent, named the cholesteric phase. In the latter, the aligned molecules of the nematic twist about an axis perpendicular to their alignment axis, but in the 1970s a heliconical phase with a tilt angle of less than 90° was predicted. The discovery of this phase nearly 40 years later is described in this paper. Robert Meyer proposed that coupling between a vector order parameter in a nematic and a splay or bend elastic distortion could result in spontaneously splayed or bent structures. Later, Ivan Dozov suggested that new nematic phases with splay–bend or twist–bend structures could be stabilised if the appropriate elastic constants became negative. Theoretical speculation on new nematic phases and the experimental identification of nematic–nematic phase transitions are reviewed in the paper, and the serendipitous discovery in 2010 of the nematic twist–bend phase in 1″,7″-bis(4-cyanobiphenyl-4′-yl)heptane (CB7CB) is described.

Keywords: liquid crystal; nematic; twist-bend phase

1. Introduction

Much has been written about the twist–bend nematic phase since its experimental identification was published more than 10 years ago. In a recent review [1], Rebecca Walker observed that:

"The prediction [2,3] and subsequent experimental discovery [4] of the twist–bend nematic phase, N_{TB}, is undeniably one of the most significant recent developments in the field of liquid crystals."

Like many advances in science, this particular discovery has not been without controversy [5], and there are still different views on the structure and nature of the twist–bend nematic phase. Additionally, there are differences of opinion as to who discovered what and when, and to whom any credit is due, if appropriate, for the scientific advance. Our knowledge of the natural world has accumulated through incremental steps due to the collaborative and interactive research of scientists, and this is true for the discovery of the twist–bend nematic liquid crystal phase. That is not to dismiss individual claims for the first or significant breakthrough, and not unnaturally we all want to be recognised for our ground-breaking discoveries. The case of the twist–bend nematic phase is no exception, and at one time there were three universities around the world all claiming the exclusive credit for the discovery of this new type of liquid crystal. Such stories are part of the process and deserve to be recorded, and this article reviews the development of the science behind the discovery of the twist–bend nematic phase. The author admits to an interest since he was one of those involved in the initial discovery, but it is the intention to present as fair and documented account as possible, recognising the work of many scientists who contributed to the initial discovery.

To set the discovery of the twist–bend nematic phase in context, traditionally liquid crystal phases were classified as nematic with no positional order, smectic with one degree of translational order, and columnar with two degrees of translational order. In recent times various sub-categories have been described, such as "banana" phases formed from bent-core shaped molecules, and our knowledge of the detailed structures of increasingly diverse liquid crystal phases has vastly increased. Within the established classes of liquid crystals, a variety of different structures have been identified, but for the nematic phase there have been only two types—the simple nematic formed from rod-like or disc-like molecules, and the chiral nematic or cholesteric phase formed from optically active or chiral (handed) molecules lacking a centre or plane of symmetry. There have been reports over the years of other nematic phases, of which the biaxial nematic phase with two optic axes but no translational order is one example. The optical differences between the nematic and chiral nematic phases are dramatically clear using a polarising microscope, and indeed it was the chiral nematic or cholesteric phase of cholesteryl benzoate that was the first liquid crystal to be identified [6]. The difference between a nematic phase and its chiral equivalent is that in the former, the orientation of the optic axis, or director, is distributed randomly through a non-aligned sample, whereas in a chiral nematic a helix forms, such that the director is at right angles to the helix axis. This rather remarkable structural difference does not seem to have much effect on the physical properties of the chiral and achiral nematic phases, but it does have a big effect on the optical properties.

The close packing of chiral or handed molecules inevitably produces a twist between adjacent molecules, and so the formation of a twisted structure for a chiral nematic phase is expected. Twisted structures are also found in some smectic phases formed from chiral molecules, such as twist–grain boundary phases and chiral tilted smectic C and related phases, and for such layered phases the director is not usually at 90° to the helix axis or layer normal but tilted at some smaller angle. Introducing another symmetry axis such as a helix raises the possibility of a biaxial phase. Such a biaxial nematic phase was proposed in 1970 by Freiser [7], and there has been a considerable research effort to identify such a phase. For a review, see [8]. A biaxial nematic phase should be distinguishable through various physical properties, and potentially has a number of applications.

For nematic phases there is no layer normal, but in chiral nematics there is a helix axis of molecular twist, to which the director axis is perpendicular. Macroscopically, the phase remains uniaxial, but locally, within a single period of the helix twist, the structure is biaxial. The essence of this local biaxiality is restricted rotation about the long axes of the molecules, which drives the formation of a macroscopic twist perpendicular to these long axes, but there is no reason to exclude a chiral structure in which the nematic director is tilted to the helix axis at less than 90°. The formation of twisted nematic phases seems to be dependent on the molecules being chiral, but the induction of twist through a local molecular tilt is an unanticipated development in the structure of fluid phases. The introduction of molecular tilt to a nematic phase is another way of lowering the symmetry and generating new and perhaps interesting properties. There are no clues as to how to engineer a molecule to tilt with respect to an axis of twist. Furthermore, the properties of such a structure are hard to fathom. It is perhaps for this reason that, in contrast to the biaxial nematic, there was no concerted research effort to find a tilted nematic phase, and its appearance had to await its serendipitous discovery. This is the story we wish to relate here.

2. Structures of Liquid Crystal Phases

A traditional approach to the understanding of the microscopic structure of liquid crystal phases is from the perspective of molecular shape. Thus, rod-like molecules result in nematic and smectic phases, while disc-like molecules can form nematic and columnar phases. Other molecular shapes can introduce new features to the molecular organisation, and in the recent past attention has focussed on bent-core molecules [9]. The latter have not disappointed, and a host of so-called "banana" phases B1 to B8 have been discovered with a variety of phase structures and properties. A banana shape representing a bent-

core molecule is of lower symmetry than rods and discs, and it can have an associated dipole, electric and/or steric, perpendicular to its major axis, which can influence the molecular assembly in condensed phases. The interactions driving molecular organisation in liquid crystals are a combination of repulsive (shape) forces and attractive forces of dispersion, electrostatic (polar) and hydrogen-bonding, and all of these are linked through the molecular structure, which may itself have intrinsic flexibility.

Molecules do not have to be polar, i.e., possess a dipole moment, to form a liquid crystal phase, though many are. The polar group or groups in a molecule have a direct effect on the dielectric properties, but in structurally organised phases such as liquid crystals, polar interactions can influence the local structure [10]. Intermolecular interactions may cause the dipole moments on adjacent molecules to favour a parallel or anti-parallel arrangement, and this can be dependent on the overall molecular shape. Thus, rod-like molecules with longitudinal dipoles favour anti-parallel correlations, while those with transverse dipoles have a tendency for a net parallel alignment of molecular dipoles [11]. The reverse arrangements apply to disc-like molecules, and for molecular shapes such as bent-core or flexible species, the situation becomes more complicated. These effects are often magnified in smectic phases where there can be monolayer or bilayer modulation of the molecular polarisation, and for some symmetries a macroscopic ferroelectric polarisation can develop.

It was Pierre Gilles de Gennes (Nobel Prize for Physics, 1993) who provided the basis for our physical understanding of liquid crystals through his publication in 1974 of "The Physics of Liquid Crystals" [12], in which the existence of different types of liquid crystal phases is discussed. As far as we know, there is only one type of gas, unless one counts an ionised gas, a plasma, as a different phase. Similarly, there is only one liquid phase, although many different liquids are immiscible, but their fluid properties are similar. Different crystalline structures are distinguishable by topological and optical symmetries, and for some materials there can be phase transitions between them. For liquid crystals, distinguishable types were identified in the earliest research, but until recently only two species of nematic phase have been experimentally acknowledged: the nematic phase and the chiral nematic phase. This article focuses on the theoretical background and experimental evidence for an additional nematic phase, which has been identified as a twist–bend nematic.

De Gennes, in the first edition of his book [12], discusses the possibility of another nematic phase with a biaxial symmetry, and also (p. 244) a transition to a conical phase from a cholesteric phase induced by a magnetic field. Such a transformation could be possible if the bend elastic constant is anomalously low, and this prediction of a conical phase in which there is a component of the director parallel to the helix axis is attributed to R. B. Meyer [13], although it is noted that such a phase had not been observed. The idea of a heliconical nematic phase is developed in a subsequent publication by Meyer [2], except that the driving force for the formation of a conical phase is identified as spontaneous polarisation. A perpendicular component of the polarisation couples with the bend distortion of the director to give a nematic state with non-zero bend. Meyer suggested that non-chiral bent molecules might be able to form a state of finite torsion and bend, and he identified this as a helical twist–bend nematic phase. A similar coupling between the parallel component of the polarisation with a splay distortion could result in a non-uniform splay–bend structure. Spontaneous splay or bend distortions can only exist in phases with vector order and the existence of polarisation can in principle stabilise splay–bend or twist–bend phases, as shown by Meyer.

A number of examples of nematic–nematic transitions have been experimentally identified. Such transitions were observed in liquid crystals formed from poly-ethers [14,15], but the structure of the nematic phases, labelled n_2, involved in the phase change were not fully characterised. The transition was tentatively attributed to a competition between the rigid and flexible parts of the polymer, which could result in two uniaxial nematic phases of different order parameters.

So-called dimeric liquid–crystal compounds consist of two rigid rod-like molecular fragments connected by a linking group and have been the subject of many investigations. The linking group may have a fixed molecular geometry, which gives rigid bent-core mesogens (molecules that form mesophases) or may be a flexible unit such as an alkyl chain, which allows the liquid crystal-like fragments to adopt a number of orientations. A study of dimeric phenyl alkoxybenzoates linked by flexible diiminoalkylene spacers [16] revealed a nematic–nematic phase transition in a single compound, which the authors attributed to changes in local structure resulting in the N_X phase, a precursor to forming a B6 phase. Further studies of structurally related rigid symmetric dimers of phenyl alkylbenzoates linked through an oxadiazole unit [17] suggested the existence of an unknown X phase. It was reported that these investigations using calorimetry, X-ray scattering, and optical microscopy provided evidence for the formation of molecular clusters, and their segregation into domains of opposite chiral handedness. This remarkable feature of symmetry-breaking was observed in an achiral fluid with chiral separation, such that domains of opposite chirality formed. Clark and others [18] had already shown spontaneous separation of equal and opposite chiral domains in an achiral bent core smectic C phase, but not in a nematic phase. Similarly, Lagerwall [19] proposed that achiral molecules could organise in domains of left- and right-handed helices in a smectic C phase to give a twist–bend structure. Spontaneous symmetry breaking has also been seen in a planar-aligned nematic device containing a bent-core liquid crystal [20].

The speculation of Meyer concerning other nematic phases has been added to by other predictions from theory. For nematic liquid crystals composed of bent-core molecules, Lubensky and Radzihovsky [21] predict a number of lower symmetry nematic and chiral nematic phases, but do not mention a heliconical nematic. Similarly, Mettout [22], using group theoretical arguments, proposes a variety of novel nematic phases of molecules of differing symmetries. Using Landau theory, a twisted conical phase following the melting of a hexagonal columnar phase of long polymer molecules was proposed by Kamien [23]. If the condition is satisfied that the twist elastic constant (k_2) is greater than the bend elastic constant (k_3) then the conical phase may be stabilised, but this experimental condition is rarely satisfied.

An asymmetric distribution of electric charge in a particle is conveniently quantified in terms of an electric dipole. Asymmetry in particle or molecular shape is sometimes described as a steric dipole, which represents a skewed structure having an imbalanced distribution of mass along a particular direction. This steric dipole is a vector, but there is no generally accepted definition of such a quantity. In 2001, Dozov [3] proposed that nematic phases of finite torsion and bend, or splay and bend, similar to those suggested by Meyer, could arise for achiral banana-shaped molecules if the bend elastic constant became negative. For these shapes, the steric dipole (***d***) can be represented by the radius of curvature (***r***) of the bent shape, $\boldsymbol{d} = (\ell/r^2)\boldsymbol{r}$ where ℓ is the length of the banana-shaped molecule. The steric dipole ***d*** can couple with the bend distortion of the director, giving rise to nematic states of permanent twist–bend or splay–bend, and for a negative bend elastic constant, these can become the stable ground states. The pathological behaviour of the bend elasticity constant for banana molecules approaching zero, or going negative, causes spontaneous symmetry-breaking and the "splay–bend" and "twist–bend" phases become stable. In achiral systems, the twist–bend is two-fold degenerate, and domains of left- and right-handed twist are expected to develop, but Dozov does not explore the details of the domain structure or the defects which might stabilise it.

Phase transitions are macroscopic phenomena, and so attract macroscopic interpretation rather than a molecular model. Phase properties are conveniently categorised by symmetry, of which the simplest, *O(3)*, is an isotropic fluid such as a gas or liquid. When two phases have the same symmetry, the transition between them must be first order with a non-zero entropy of transition. Liquid crystals are characterised by orientational phase transitions associated with rotational symmetry breaking. In the absence of external influences such as electric, magnetic, mechanical, or surface forces, spontaneous symmetry

breaking derives from molecular interactions resulting in structures with various degrees of orientational order. Changes of temperature and/or pressure may cause phase transitions between these phases, which are usually second order or weakly first order. One transition that is strictly symmetry forbidden is from a non-chiral state to a handed or chiral state, but it does happen with certain liquid crystals in which domain formation of opposite chirality preserves the overall achiral symmetry of the phase. Spontaneous deracemization in achiral smectic phases of liquid crystals has been observed, with domains of opposite chirality appearing as stripes tilting in different directions, and this has been compared [24] with the spontaneous deracemization of tartaric acid salts observed by Pasteur.

Fluid phases, and indeed mobile "crystal" phases, have structures which are subject to thermal fluctuations. Such changes in the local structure can be detected through a variety of physical properties, most especially through light scattering, and the opaqueness of liquid crystals is a consequence of these fluctuations. A convenient representation of the fluctuation modes is as "normal" modes, such that the normal coordinates represent squared terms in a free-energy expression. Under appropriate conditions, the equipartition of energy principle can be applied to determine the contributions of different normal modes to the free energy. In uniaxial nematics, the normal modes for director fluctuations are "splay–bend" and "twist–bend", while in chiral nematics they are "planar helical" and "heliconical modes". The contributions of the chiral fluctuation modes to optical properties have been evaluated theoretically [25,26]. Contributions of fluctuations to the free energy of phases will influence the stability of the phases and the nature of transitions between phases. For example, unfrozen fluctuations can prevent the formation of more asymmetric ordered states [22], and symmetry breaking second order phase transitions may become weak first order transitions [27].

For some researchers, the next best thing to a confirmatory experiment is a computer simulation. This is as true in liquid crystals as in other areas of condensed matter physics, and computer simulation studies [28] have been a valuable technique in understanding the structures and properties of different mesophases. The essence of computer simulations is a mathematical algorithm, which may be adaptable, that carries all the physics of local interactions responsible for the structures and properties of the phases of interest. Such studies can confirm experimental observations or theoretical predictions, but they cannot probe outside the limitations of the mathematical model that controls the simulation. Memmer [29] was the first to publish a simulated structure for the nematic twist–bend phase, using a model of two connected Gay–Berne particles with an included angle of 140° to represent a banana-shaped mesogen. There were no centres of charge, and so no dipole–dipole interactions, but Memmer notes that there is a steric dipole defined by the connected G–B particles. The computer simulation of twisted structures is influenced by the periodic boundary conditions and sample size, and Memmer states that the system studied generated a right-handed helix. For achiral particles, a left-handed structure should appear with equal probability, but could be separated by a large enthalpy barrier in the simulations.

3. The Discovery of the Twist–Bend Nematic Phase

The extensive introduction above records what, in a patent application, would be described as prior art up to around 2010. A number of publications had appeared that reported a new nematic phase, though structural studies and characterisations had not been sufficient for proper identification. In this section we will review claims of possible new nematic phases, and the serendipitous discovery of the twisted nematic phase at the end of the first decade of the 21st century.

Liquid crystal phases formed from bent-core or banana-shaped molecules have augmented the range of identified phase types, and many of these have layered structures and are related to the traditional smectic phases. In 2003, the famous liquid crystal group from Halle identified [30] a new nematic phase formed from asymmetric rigid bent-core mesogens, which they labelled as the N_X phase. This was thought to be a nematic columnar phase formed from bundles of bent-core molecules arranged in a nematic-like order. The N_X

phase exhibited a fan-like optical texture, and under some conditions displayed domains of opposite handedness, but no suggestion of a twisted structure was advanced. New nematic phases were reported in a number of other bent-core mesogenic compounds [31,32], and these were explained in terms of clusters or cybotactic groups forming with nematic order, often as a precursor to a smectic or columnar phase.

The existence of liquid crystalline order in biological systems has long been recognised, though the phase structures formed are much less studied than for low molecular weight materials. A suspension of helical flagella isolated from *Salmonella typhimurium* is reported [33] as forming a chiral conical nematic phase, though the twist is intrinsic to the flagella rather than formed through molecular interactions. The helices of the flagellae intermingle, and their polydispersity prevents the formation of layered structures. It is proposed that the director follows the helical structure set by the constituent molecules. Preparations of the flagella suspensions when viewed under a polarising microscope show a striped texture of alternating birefringence, and the authors concluded that their conical phase was similar to that proposed earlier by Meyer [2].

Dimeric liquid crystals are a class of compounds in which two mesogenic units are linked either through a rigid connecting unit or through a flexible alkyl or alkoxy chain of methylene units. For flexibly connected dimers there has been considerable focus on the effect of the parity of the alkyl chain, odd or even, on the liquid crystalline phase behaviour of the compounds [34]. In an extensive study of α, ω diiminoalkylene-linked alkoxyphenyl benzoates, Šepelj et al. [16] found that one compound exhibited a new monotropic nematic phase which was labelled N_X. The characteristic feature identified for this phase was an optical texture having spiral domains with alternating handedness, the origin of which could not be explained.

To establish a new liquid crystal phase requires the characterisation of its symmetry and its optical properties together with a model for the molecular arrangement in the ordered fluid, usually based on X-ray scattering. Studies of other physical properties can give an indication of the internal structure of a fluid, but invariably need some theoretical model to interpret the measurements. A review of the relationship between the dielectric properties of liquid crystals and the shapes of the constituent mesogens [35] revealed that the permittivity components of the dimeric mesogen 1″,7″-bis(4-cyanobiphenyl-4′-yl)heptane (CB7CB), the structure of which is represented in the figure below, showed a discontinuity at a temperature of 12 °C below the nematic to isotropic transition: this was interpreted as indicative of a phase transition to a new type of nematic phase.
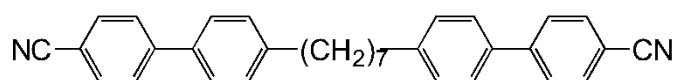

Chemical structure of CB7CB

The compound CB7CB was first synthesised in the Southampton liquid crystal group [36], who made a preliminary examination of the phase properties, noting a nematic phase and a lower temperature phase tentatively identified as a smectic C phase. Measurements of the dielectric relaxation in flexible dimeric liquid crystals [37] revealed unusual behaviour and were explained [38] in terms of a model that took account of different conformational states of the flexible dimeric molecules. It was found that lowering the temperature of the nematic phase of these dimers caused substantial changes to their average molecular shape, as represented by contributions from different conformations of the linking flexible alkyl chain. The observed transition to a lower temperature nematic phase could be attributed to shape changes of the flexible dimeric molecules. Further studies of the proposed new nematic phase of CB7CB were carried out, and a key observation [39] was made that the deuterium NMR quadrupole splitting measured for deuterated CB7CB d_4 bifurcated at the transition from the high temperature nematic phase to the lower temperature nematic phase. This result is indicative of a symmetry-breaking transition and the formation of equal domains of left- and right-handed chiral molecules. The liquid

crystal dimer investigated was on average achiral, but particular conformers stabilised by the flexible alkyl chain could be chiral with equal concentrations of left- and right-handed species. The origin of the symmetry-breaking was not apparent and clearly needed further investigation.

Every second year the liquid crystal community gathers for its International Conference, and in 2010 the 23rd such meeting was held in Kraków, Poland. There were about a dozen talks and posters on possible new nematic phases, including four posters on nematic–nematic phase transitions in flexible liquid crystal dimers. The author of this review contributed a talk entitled "A liquid crystal dimer with a bent nematic phase", which reported on a collaborative project involving 13 researchers working in six different institutions around Europe. The talk presented results on the identification and characterisation of a new nematic phase in CB7CB labelled as a twist–bend nematic phase. After the talk there were a few questions including one from J. K. Vij of Trinity College Dublin, Eire, concerning details of one of the optical textures presented. Vij had contributed a poster to the conference on a related compound CB11CB, which exhibited an additional phase at a lower temperature than the conventional nematic phase. The work by Vij was subsequently published later in 2010 [40], while the presentation on the twist–bend phase of CB7CB appeared in 2011 [4].

These publications gave slightly conflicting views of the structure of the new nematic phase observed in homologues of the α,ω-bis[(4-cyanobiphenyl)-4′]alkanes. The paper from Vij and collaborators from the Universities of Dublin and Hull confirmed the nematic nature of the phase in CB11CB using X-ray scattering and concluded from a Landau de Gennes calculation that the observed periodic deformation in thin films was a result of at least one of the elastic constants for splay or twist becoming negative. Their investigations failed to detect any evidence of symmetry breaking due to chirality. On the other hand, the paper [4] on CB7CB presented as a talk at the Kraków conference gave evidence from ^{2}H NMR that, for particular methyl protons in the alkyl chain, there were two non-equivalent sites in the oriented mesogen, consistent with the presence of chiral symmetry-breaking giving left and right enantiomers. Dielectric measurements indicated that at the transition from the high-temperature nematic to the unidentified lower temperature phase a macroscopic tilt developed with respect to the rubbing direction, and furthermore a calculation of the bend elastic constant of CB7CB predicted that it could be negative. The conclusion of the paper was that the low temperature nematic phase shared many of the characteristics of the twist–bend nematic phase proposed by Dozov [3] for materials of negative bend elastic constant. However, there were still unresolved questions concerning the identification of the twist–bend nematic phase. Although chiral symmetry breaking in CB7CB had been demonstrated as a possibility, further optical confirmation was lacking, and if the phase was heliconical, then it should be possible to determine the pitch of the helix and the tilt angle. Tilt had been observed at the transition from the nematic to the twist–bend nematic phase, but no estimate of its magnitude was given.

These and other outstanding questions concerning the new nematic phase were resolved to some extent in subsequent papers by a number of authors from different institutions. In the decade 2010 to 2020 there was an explosion of more than a thousand publications concerning many aspects of the twist–bend nematic phase. This is illustrated by the graph of numbers of papers containing "twist–bend nematic" in their titles. Because of the vagaries of titles, the total number of papers on the topic is much greater than the numbers given in graph. A few papers became identified as "highly-cited", and one [4] was selected by the editors of the American Physical Society Physical Review E as the milestone paper for 2011.

numbers of papers with "twist-bend nematic" in the title
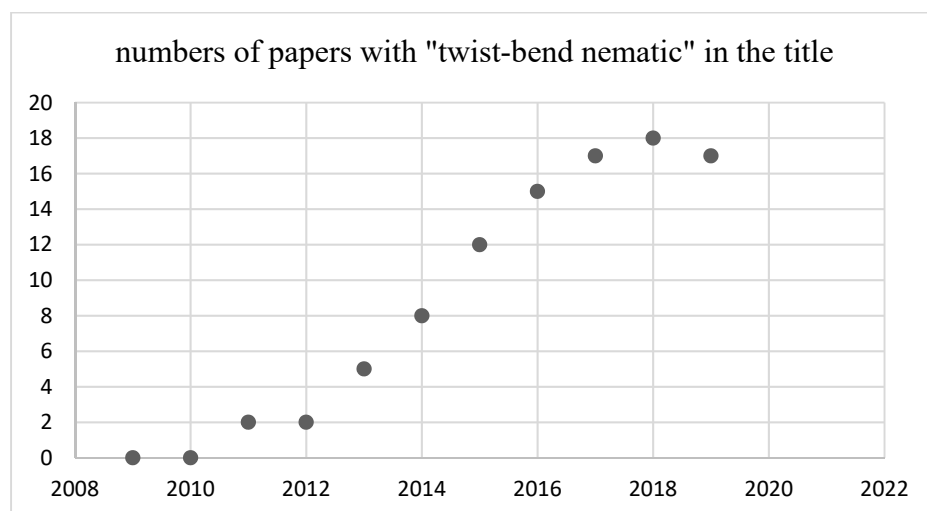
4. The Structure of the Twist–Bend Nematic Phase

The explosion of interest in the twist–bend nematic phase that followed from 2011 included key papers providing additional evidence for the proposed structure of the heliconical phase. In particular, a paper [41] from a large group at the University of Colorado Boulder presented freeze-fracture measurements on CB7CB, showing a periodic structure consistent with a helix having a pitch of 8.3 nm with a director cone angle of 25°. Freeze-fracture was also among the techniques used by a combined group of researchers from the Liquid Crystal Institute at Kent State University and the universities of Dublin, Aberdeen and Hull, who reported further results [42] on the twist–bend phases of CB7CB and a related mixture confirming the heliconical structure of the phase. Other examples of the twist–bend nematic phase also were reported [43] from studies of related homologues of CB7CB.

The absence of X-ray diffraction peaks corresponding to the helix is due to its glide symmetry, which means that there is no electron density modulation associated with the heliconical arrangement of molecules. However, diffraction can be observed from the periodicity of the helix for suitable samples using the method of resonant X-ray scattering which utilises polarised radiation. A group from the University of Colorado Boulder used the Advanced Light Source at the Lawrence Berkeley National Laboratory to confirm the helical structure of the twist–bend phase of CB7CB [44], and further demonstrated that the pitch increases rapidly as the transition to the normal nematic phase is approached from lower temperatures. A more detailed resonant X-ray scattering study of the twist–bend nematic phase of a mixture, the component molecules of which were structurally similar to CB7CB, gave measurements of the helical pitch [45], and demonstrated its increase with increasing temperature. Further analysis of the scattering pattern revealed that the flexible molecules modified their structure in the nematic twist–bend environment to adapt to the helical arrangement in the phase.

The chirality of the twist–bend phase is a consequence of its heliconical structure, but in an overall achiral system, symmetry-breaking must result in the formation of equal contributions from left- and right-handed helices. Optical textures of the twist–bend nematic phase provide some confirmation of domain formation of opposite handed structures, and in the characteristic striped textures, originally labelled as "rope-like domains", the birefringence of adjacent domains alternates, with the maximum axis of birefringence deviating alternately to the left and right by about 10°. Although consistent with optically chiral domains, these observations are not definitive. An indirect indicator of chirality in a sample can be revealed by NMR spectroscopy, since in a chiral phase of flexible molecules, the equivalence between certain nuclear sites can be removed by symmetry-breaking and detected through an appropriate NMR diagnostic. This was done for the material CB7CB, and the results demonstrated [46] that the twist–bend nematic phase of CB7CB was chiral,

with inequivalent C−H bonds in the alkyl chain related by left-right symmetry and contributing equal intensities to the NMR signal. Optical chirality in homeotropically aligned thin films of the twist–bend phase nematic phase of CB7CB and other homologues has been confirmed using circular dichroism [47].

Much of the investigative research on the structure of the twist–bend mesophase has been conducted on the material CB7CB, which was the first low molecular weight compound to be identified as exhibiting a twist–bend nematic phase [4]. However, it will be recalled that the first report of a nematic–nematic transition was described [14,15] in a series of main-chain liquid crystal copolyethers with semi-flexible biphenylethane groups linked by odd-numbered oligomethylene spacers. The structure of the liquid crystal phases of these materials has been reinvestigated [48] using techniques of grazing incidence X-ray diffraction and polarised infra-red spectroscopy. This work has unequivocally shown that the phases originally identified as low temperature nematic phases are in fact twist–bend nematic phases, and so were probably the first materials to be revealed exhibiting such a phase.

5. Features of the Twist–Bend Nematic Phase

This commentary on the discovery of the twist–bend nematic phase focuses only on a class of materials that exhibit the characteristic features identified in the low temperature phase of CB7CB. Thus, other low-temperature nematic phases that may or may not exist in other bent-core or banana-shaped molecules are not considered, neither are they excluded as possible new nematic phases. The main identifying feature of the twist–bend phase is a weak first order phase transition on lowering the temperature to a phase showing no X-ray scattering characteristic of long-range positional order. The higher temperature phase may be a normal nematic phase or sometimes an isotropic phase [49], and the low temperature phase should have features showing the tilt or twist of the director.

The compounds that have been identified in this article as having twist–bend nematic phases are dimers, oligomers, or polymers, with mesogenic units linked by flexible alkyl chains. The flexibility of the constituent molecules may be a stabilising aspect of the twist–bend phase which enables the molecular structure to adapt to the local environment, self-selecting conformations that result in director tilt or a preferred handed-twist (chirality). The importance of the molecular structure adapting to the twist–bend phase is signalled by the dielectric measurements on the material CB7CB, which has two dipolar groups linked by a methylene chain. In the isotropic phase, the mean permittivity (~10) is what would be expected of a fluid composed of monomer units of a short alkyl chain cyanobiphenyl, that is the mesogenic end groups are responding dielectrically as though they are not connected. On cooling into the normal nematic phase, over a small temperature interval there is a rise in the parallel permittivity and a fall in the perpendicular permittivity, which would be expected for a monomeric dipolar mesogen. Then, as the nematic order develops, there is a dramatic change in behaviour with both components and the average permittivity falling as the temperature decreases and the nematic order increases. This indicates that the flexible link is favouring an extended conformation of the connected mesogenic groups, and the average dipole moment of the mesogenic dimer falls. It continues to reduce on lowering the temperature until the transition to the twist–bend nematic is reached, when there is a sharp increase in the rate of decline of the average dipole moment. A few degrees into the twist–bend nematic, the dielectric anisotropy becomes zero. A careful X-ray study of a model dimer [45] has provided evidence that molecular conformations do adjust to the helical structure, such that the gain in translational entropy along the axis exceeds any enthalpy penalty from a change in the conformational distribution.

A key feature of the twist–bend nematic phase is chirality. Direct evidence of twist may be manifest by intrinsic optical chirality, but other techniques can observe evidence of tilt or twist. The optical textures or patterns shown by thin films of liquid crystal viewed under a polarising microscope have become valuable diagnostics for many phase types. Some phases show characteristic textures, and for the twist–bend nematic phase, stripped

textures having an apparent alternating twist, rope-like domains, have been frequently identified, although other textures can also be seen for different sample preparations. In achiral systems, the formation of the twist–bend phase results in equal left-handed and right-handed domains, but the matter of chiral separation has yet to be fully explored.

A model for a twist–bend nematic phase is easily imagined, and the driving force for its manifestation has been suggested as due to unusual elastic properties and/or ferroelectric organisation of constituent molecules. Understanding the formation of a twist–bend phase can only be obtained through careful measurement and interpretation of its physical properties. Since the materials to be studied are anisotropic fluids, their symmetry will determine the nature of the properties to be measured, and there is usually a requirement for samples to be macroscopically aligned. Being liquid crystals, elasticity and viscosity are key properties, but the complexity of the structure and symmetry of N_{TB} phase make definitive measurements and interpretation difficult.

The symmetry of a helix can be defined in various ways, but for a sample of achiral twist–bend nematic it is expected that both left- and right-handed helical structures will be present with defects between the different chiral domains. To define an elasticity or viscoelastic tensor for such a system is clearly difficult, and there is the added practical difficulty of ensuring a controlled alignment to provide measurement of appropriate components of the tensor properties. For these reasons, measurements of the physical properties of compounds forming twist–bend nematic phases have mostly been made in the nematic phases of the materials. There is some evidence that macroscopic alignment in the high-temperature nematic phase is preserved in the twist–bend phase, so it is possible to obtain information on the likely structure of the material.

The significance of the bend elastic constant in determining the formation of a twist bend nematic phase or heliconical phase really emerged from the work of Meyer [13,50,51]. He found that if a magnetic field is applied perpendicular to the helix axis of a chiral nematic phase, then the pitch increased. De Gennes expands on this [52] to suggest that for a small bend elastic constant, the orientation of the director could make an angle of less than 90° to the magnetic field, and so an induced heliconical phase could be formed. This was the basis of Meyer's original conjecture about the formation of a twist–bend phase. Dozov extended this idea to show that a negative bend elastic constant could, not surprisingly, result in a permanently bent structure, as represented by the twist–bend phase. Further theoretical work [53,54] established that a negative bend elastic constant (k_3) was not mandatory, only that k_3 was small and less than the twist elastic constant. As explained above, measurements of elastic properties in the twist–bend phase present difficulties, but it has been shown [55] that in CB7CB the bend elastic constant as measured in the nematic phase is smaller than both the splay and twist constants and decreases with temperature through the nematic phase as the transition to the twist–bend phase is approached. An alternative or additional driving force proposed for the formation of a twist–bend nematic phase was the local organisation of transverse molecular dipoles of bent-core molecules resulting in a macroscopic polarisation, and there have been a number of theoretical and experimental studies of related phenomena such as flexoelectricity. An electro-clinic effect has been observed [56] in the twist–bend phase of CB7CB, which proves the chirality of the phase, and analysis of the results provided an estimate of the short pitch of the helix and a value for the heliconical tilt angle.

Over the past 50 years, nematic liquid crystals have been transformational in the display industry, so it is natural to look for new applications of the twist–bend nematic phase in the area of opto-electronics. It is possible to electrically switch the optical appearance of thin films of N_{TB}, and preliminary measurements [57] indicate that Fréedericksz transitions occur, but the structures of the switched states need further study. It has been suggested [58] that the electric field-induced distortions of the twist–bend nematic phase are similar to those observed in chiral smectic A phases and include a sub-microsecond flexoelectric-induced rotation of the optic axis. There are many aspects of the structure and properties of the twist–bend nematic phase that remain to be understood, and as has

often been the case, a determining factor in the research will be the availability of suitable materials exhibiting the phase at convenient temperatures. However, this constraint on experiments does not inhibit theoretical studies. For example, a model for bend distortions in the twist–bend phase based on the Frank free energy has been developed [59], which might add to our understanding of complex structures in thin films.

6. Conclusions

A liquid crystal phase with a heliconical structure is a concept that follows from the models that we have for the chiral nematic phase. Robert Meyer recognized this around 1969 when investigating [50,51] the effect of a magnetic field on the structure of a chiral nematic phase formed from a mixture of *p*-azoxyanisole and cholesteryl acetate, as related in the book by de Gennes [52]. Such a field-induced heliconical phase occurring in a chiral material would require an anomalously small bend elastic constant. Meyer later proposed [2] that a helical state of finite torsion and bend is possible in a nematic if there is a non-zero polarisation perpendicular to the local director but noted that no helical structure had ever been reported in a non-chiral nematic. Thus, the factors identified for the stability of a heliconical nematic phase were a small bend elastic constant and/or a local perpendicular polarisation, yet the appearance of a chiral structure in an achiral material seemed unlikely.

In the decades following Meyer's observations, there was no research effort to find a heliconical nematic phase, although there were occasional reports of possibly novel but unidentified nematic phases [15–17]. In 2001, Dozov explored the consequences of a negative bend elastic constant in the context of Landau theory and predicted [3] that a state of continuous conical twist–bend could be stabilized with a two-fold degenerate twist left and right.

Like so many liquid crystal discoveries, the experimental identification of a twist–bend nematic phase was dependent on serendipitous studies of a particular material. A class of liquid crystals known as dimeric mesogens includes the compound CB7CB, which had presented some unexplained properties [37,38]. A careful study over a few years by a number of collaborating research groups through Europe established that this liquid crystal did indeed exhibit the features of a twist–bend nematic phase proposed by the theoretical work of Meyer and Dozov. The publication [4] of these results stimulated a flurry of research activity around the globe, and confirmation of the twist–bend structure was rapidly established by a number of research groups [41,42] in a variety of compounds. There followed a great increase in the investigation of novel nematic phases, a number of which were revealed to have characteristics of the twist–bend phase. Science does not provide a template for nature, and the structures of liquid crystal phase variants are determined by particular intermolecular interactions in different materials.

The emergence of the twist–bend nematic phase has been a consequence of the research of many scientists. Collaboration between groups has aided the evaluation of the structure of the new phase and should enhance the investigation of new properties with possible applications. Liquid crystals are examples of soft matter, and the variety of structures observed, including the twist–bend nematic phase, might be important in understanding the structure and growth of natural materials.

of the director away from the rubbing direction occurred at the phase transition to a twist–bend nematic. Confirmation of the nematic nature of the twist–bend phase was provided by the liquid crystal group of the HH Wills Physics Laboratory at the University of Bristol, which determined an intercalated structure with a weak tendency to layer formation i.e., not a smectic. The theory group from the Department of Chemical Science, University of Padua, used a surface interaction (SI) model to take account of molecular flexibility in the analysis of dielectric measurements, which showed the inadequacy of the rotational isomeric state model to describe the properties of flexible dimeric mesogens. This group also carried out calculations using the SI model to predict that the bend elastic constant of CB7CB could be negative. Evidence of chiral symmetry breaking came from magnetic resonance measurements for which selectively deuteriated samples of CB7CB were prepared by the group from the Department of Biophysics, Max-Planck Institute for Medical Research, Heidelberg. The compound CB7CB was originally prepared in the liquid crystal group of the School of Chemistry, University of Southampton. Magnetic resonance measurements, ESR and NMR, established that chiral symmetry breaking occurred at the phase transition from nematic to twist–bend nematic. This was dramatically illustrated by a bifurcation in the quadrupolar splitting for the 1″ and 7″ deuterons in CB7CB. Optical textures characteristic of the twist–bend nematic phase were identified in the Southampton group, which also coordinated the research from other contributing laboratories. Finally, the author would like to acknowledge the role of Professor Geoffrey Luckhurst as leader of the Southampton Liquid Crystal Group, the research of which resulted in the discovery of the twist–bend nematic phase.

References

1. Walker, R. The twist-bend phases: Structure–property relationships, chirality and hydrogen-bonding. *Liq. Cryst. Today* **2020**, *29*, 2–14. [CrossRef]
2. Meyer, R.B. *Structural Problems in Liquid Crystal Physics, in Molecular Fluids*; Balian, R., Weill, G., Eds.; Vol. XXV-1973 of Les Houches Summer School in Theoretical Physics; Gordon and Breach: New York, NY, USA, 1976; pp. 273–373.
3. Dozov, I. On the spontaneous symmetry breaking in the mesophases of achiral banana-shaped molecules. *Eur. Lett.* **2001**, *56*, 247–253. [CrossRef]
4. Cestari, M.; Diez-Berart, S.; Dunmur, D.A.; Ferrarini, A.; de la Fuente, M.R.; Jackson, D.J.B.; Lopez, D.O.; Luckhurst, G.R.; Perez-Jubindo, M.A.; Richardson, R.M.; et al. Phase behaviour and properties of the liquid crystal dimer 1″,7″-bis(4-cyanobiphenyl-4′-yl)heptane: A twist-bend nematic liquid crystal. In Proceedings of the 23rd International Liquid Crystal Conference, Kraków, Poland, 11–16 July 2010; Volume 84, p. 031704. [CrossRef]
5. Dozov, I.; Luckhurst, G.R. Setting things straight in "The twist-bend nematic: A case of mistaken identity. *Liq. Cryst.* **2020**, *47*, 2098–2115. [CrossRef]
6. Reinitzer, F. Contributions to the understanding of cholesteryls. *Monat. f. Chem.* **1888**, *9*, 421–441. [CrossRef]
7. Freiser, M.J. Ordered States of a Nematic Liquid. *Phys. Rev. Lett.* **1970**, *24*, 1041–1043. [CrossRef]
8. Luckhurst, G.R.; Sluckin, T.J. (Eds.) *Biaxial Nematic Liquid Crystals*; Wiley: Chichester, UK, 2015.
9. Jákli, A.; Lavrentovich, O.D.; Selinger, J.V. Physics of liquid crystals of bent-shaped molecules. *Rev. Mod. Phys.* **2018**, *90*, 045004. [CrossRef]
10. Dunmur, D.A. Dielectric studies of intermolecular and intramolecular interactions in nematic liquid crystals. *Proc. SPIE* **2002**, *4759*, 196–208.
11. Dunmur, D.A.; Palffy-Muhoray, P. A mean field theory of dipole-dipole correlation in nematic liquid crystals. *Mol. Phys.* **1992**, *76*, 1015–1024. [CrossRef]
12. De Gennes, P.G. *The Physics of Liquid Crystals*; Oxford University Press: Oxford, UK, 1974.
13. Meyer, R.B.; University of Harvard, Cambridge, MA, USA. Personal communication, 1969.
14. Ungar, G.; Percec, V.; Zuber, M. Liquid crystalline polyethers based on conformational isomerism. 20. Nematic-nematic transition in polyethers and copolyethers based on 1-(4-hydroxyphenyl)2-(2-R-4-hydroxyphenyl)ethane with R = fluoro, chloro and methyl and flexible spacers containing an odd number of methylene units. *Macromolecules* **1992**, *25*, 75–80. [CrossRef]
15. Ungar, G.; Percec, V.; Zuber, M. Influence of molecular structure on the nematic-nematic transition in polyethers based on 1-(4-hydroxy-phenyl)-2-(2-R-4-hydroxyphenyl ethane where R = CH3 and Cl, and flexible spacers with an odd number of methylene units. *Polym. Bull.* **1994**, *32*, 325–330. [CrossRef]
16. Šepelj, M.; Lesac, A.; Baumeister, U.; Diele, S.; Nguyen, H.L.; Bruce, D.W. Intercalated liquid-crystalline phases formed by symmetric dimers with an α,ω-diiminoalkylene spacer. *J. Mater. Chem.* **2007**, *17*, 1154–1165. [CrossRef]
17. Görtz, V.; Southern, C.; Roberts, N.W.; Gleeson, H.F.; Goodby, J.W. Unusual properties of a bent-core liquid-crystalline fluid. *Soft Matter* **2009**, *5*, 463–471. [CrossRef]
18. Link, D.R.; Natale, G.; Shao, R.; Maclennan, J.E.; Clark, N.A.; Körblova, E.; Walba, D.M. Spontaneous Formation of Macroscopic Chiral Domains in a Fluid Smectic Phase of Achiral Molecules. *Science* **1997**, *278*, 1924–1927. [CrossRef]

19. Lagerwall, S.T. Ferroelectric Liquid Crystals. In *Handbook of Liquid Crystals*, 1st ed.; Demus, D., Goodby, J.W., Gray, G.W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: New York, NY, USA, 1999; Volume 2B, p. 515.

20. Salter, P.S.; Benzie Reddy, R.A.; Tschierske, C.; Elston, S.J.; Raynes, E.P. Spontaneously chiral domains of an achiral bent-core nematic liquid crystal in a planar aligned device. *Phys. Rev. E* **2009**, *80*, 031701. [CrossRef] [PubMed]

21. Lubensky, T.C.; Radzihovsky, L. Theory of bent-core liquid-crystal phases and phase transitions. *Phys. Rev. E* **2002**, *66*, 031701. [CrossRef]

22. Mettout, B. Macroscopic and molecular symmetries of unconventional nematic phases. *Phys. Rev. E* **2006**, *74*, 041701. [CrossRef]

23. Kamien, R.D. Liquids with Chiral Bond Order. *J. Phys. II* **1996**, *6*, 461–475. [CrossRef]

24. Takezoe, H. Spontaneous Achiral Symmetry Breaking in Liquid Crystalline Phases. *Top. Curr. Chem.* **2011**, *318*, 303–330. [CrossRef]

25. Filev, V.M. Temperature-induced inversion of rotation of the polarization-plane of light in liquid crystals. *JETP Lett.* **1983**, *37*, 703–706.

26. Dolganov, V.K.; Demikhov, E.I. Pretransitional effects near blue phases of a cholesteric liquid-crystal. *JETP Lett.* **1983**, *38*, 445–447.

27. Kats, E.I.; Abalyan, T.V. Ordering and phase transitions in liquid crystals. *Phase Transit.* **1991**, *91*, 237–268. [CrossRef]

28. Pasini, P.; Zannoni, C. (Eds.) *Advances in the Computer Simulations of Liquid Crystals*; Kluwer: Dordrecht, The Netherlands, 1998.

29. Memmer, R. Liquid crystal phases of achiral banana-shaped molecules: A computer simulation study. *Liq. Cryst.* **2002**, *29*, 483–496. [CrossRef]

30. Schröder, M.W.; Diele, S.; Pelzl, G.; Dunemann, U.; Kresse, H.; Weissflog, W. Different nematic phases and a switchable SmCP phase formed by homologues of a new class of asymmetric bent-core mesogens. *J. Mater. Chem.* **2003**, *13*, 1877–1882. [CrossRef]

31. Tamba, M.G.; Baumeister, U.; Pelzl, G.; Weissflog, W. Banana-calamitic dimers: Unexpected mesophase behaviour by variation of the direction of ester linking groups in the bent-core unit. *Liq. Cryst.* **2010**, *37*, 853–874. [CrossRef]

32. Keith, C.; Lehmann, A.; Baumeister, U.; Prehm, M.; Tschierske, C. Nematic phases of bent-core mesogens. *Soft Matter* **2010**, *6*, 1704–1721. [CrossRef]

33. Barry, E.; Hensel, Z.; Dogic, Z.; Shribak, M.; Oldenbourg, R. Entropy-Driven Formation of a Chiral Liquid-Crystalline Phase of Helical Filaments. *Phys. Rev. Lett.* **2006**, *96*, 018305. [CrossRef]

34. Imrie, C.T.; Luckhurst, G.R. Liquid Crystal Dimers and Oligomers. In *Handbook of Liquid Crystals*, 1st ed.; Demus, D., Goodby, J.W., Gray, G.W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: New York, NY, USA, 1999; Volume 2B, Chapter X; p. 801.

35. Dunmur, D.A.; de la Fuente, M.R.; Perez-Jubindo, M.A.; Diez, S. Dielectric studies of liquid crystals: The influence of molecular shape. *Liq. Cryst.* **2010**, *37*, 723–736. [CrossRef]

36. Barnes, P.J.; Douglass, A.; Heeks, S.K.; Luckhurst, G.R. An enhanced odd-even effect of liquid crystal dimers orientational order in the α,ω-bis(4′-cyanobiphenyl-4yl) alkanes. *Liq. Cryst.* **1993**, *13*, 603. [CrossRef]

37. Dunmur, D.A.; Luckhurst, G.R.; De La Fuente, M.R.; Diez, S.; Jubindo, M.A.P. Dielectric relaxation in liquid crystalline dimers. *J. Chem. Phys.* **2001**, *115*, 8681–8691. [CrossRef]

38. Stocchero, M.; Ferrarini, A.; Moro, G.J.; Dunmur, D.A.; Luckhurst, G.R. Molecular theory of dielectric relaxation in nematic dimers. *J. Chem. Phys.* **2004**, *121*, 8079. [CrossRef] [PubMed]

39. Luckhurst, G.R.; Tropea, Italy. Personal communication, 2009.

40. Panov, V.P.; Nagaraj, M.; Vij, J.K.; Panarin, Y.P.; Kohlmeier, A.; Tamba, M.G.; Lewis, R.A.; Mehl, G. Spontaneous Periodic Deformations in Nonchiral Planar-Aligned Bimesogens with a Nematic-Nematic Transition and a Negative Elastic Constant. In Proceedings of the 23rd International Liquid Crystal Conference, Kraków, Poland, 11–16 July 2010; Volume 105, p. 167801. [CrossRef] [PubMed]

41. Chen, D.; Porada, J.H.; Hooper, J.B.; Klittnick, A.; Shen, Y.; Tuchband, M.R.; Korblova, E.; Bedrov, D.; Walba, D.M.; Glaser, M.A.; et al. Chrial heliconical ground state of nanoscale pitch in a nematic liquid crystal of achiral molecular dimers. *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 15931–15936. [CrossRef] [PubMed]

42. Borshch, V.; Kim, Y.-K.; Xiang, J.; Gao, M.; Jakli, A.; Panov, V.P.; Vij, J.K.; Imrie, C.T.; Tamba, M.G.; Mehl, G.H.; et al. Nematic twist-bend phase with nanoscale modulation of molecular orientation. *Nat. Commun.* **2013**, *4*, 2635. [CrossRef] [PubMed]

43. Henderson, P.A.; Imrie, C.T. Methylene-linked liquid crystal dimers and the twist-bend nematic phase. *Liq. Cryst.* **2011**, *38*, 1407–1414. [CrossRef]

44. Zhu, C.; Tuchband, M.R.; Young, A.; Shuai, M.; Scarbrough, A.; Walba, D.M.; Maclennan, J.E.; Wang, C.; Hexemer, A.; Clark, N.A. Resonant CarbonK-Edge Soft X-Ray Scattering from Lattice-Free Heliconical Molecular Ordering: Soft Dilative Elasticity of the Twist-Bend Liquid Crystal Phase. *Phys. Rev. Lett.* **2016**, *116*, 147803. [CrossRef] [PubMed]

45. Stevenson, W.D.; Ahmed, Z.; Zeng, X.B.; Welch, C.; Ungar, G.; Mehl, G.H. Molecular organisation in the twist-bend nematic phase by resonant x-ray scattering at the Se K-edge and by SAXS, WAXS and GIXRD. *Phys. Chem. Chem. Phys.* **2017**, *19*, 13449. [CrossRef]

46. Beguin, L.; Emsley, J.W.; Lelli, M.; Lesage, A.; Luckhurst, G.R.; Timimi, B.A.; Zimmermann, H. The Chirality of a Twist–Bend Nematic Phase Identified by NMR Spectroscopy. *J. Phys. Chem. B* **2012**, *116*, 7940–7951. [CrossRef] [PubMed]

47. Stevenson, W.D.; Zeng, X.; Welch, C.; Thakur, A.K.; Ungar, G.; Mehl, G.H. Macroscopic chirality of twist-bend nematic phase in bent dimers confirmed by circular dichroism. *J. Mater. Chem. C* **2020**, *8*, 1041–1047. [CrossRef]

48. Stevenson, W.D.; An, J.; Zeng, X.B.; Xue, M.; Zou, H.X.; Liu, Y.S.; Ungar, G. Twist-bend phase in biphenylethane-based copolymers. *Soft Matter* **2018**, *14*, 3003. [CrossRef]

49. Dawood, A.A.; Grossel, M.C.; Luckhurst, G.R.; Richardson, R.M.; Timimi, B.A.; Wells, N.J.; Yousif, Y.Z. On the twist-bend nematic phase formed directly from the isotropic phase. *Liq. Cryst.* **2016**, *43*, 2–12. [CrossRef]

50. Meyer, R.B. Effects of electric and magnetic fields on the structure of cholesteric liquid crystals. *Appl. Phys. Lett.* **1968**, *12*, 281–282. [CrossRef]

51. Meyer, R.B. Distortion of a cholesteric structure by a magnetic field. *Appl. Phys. Lett.* **1969**, *14*, 208–209. [CrossRef]

52. De Gennes, P.G.; Prost, J. *The Physics of Liquid Crystals*, 2nd ed.; Oxford University Press: Oxford, UK, 1993; p. 292.

53. Virga, E.G. Elasticity of Twist-Bend Nematic Phases. In *Differential Geometry and Continuum Mechanics*; Chen, G.Q., Grinfeld, M., Knops, R., Eds.; Springer Proceedings in Mathematics & Statistics; Springer: Cham, Switzerland, 2015; Volume 137, pp. 363–380.

54. Barbero, G.; Evangelista, L.R.; Rosseto, M.P.; Zola, R.S.; Lelidis, I. The Physics of Liquid Crystals. *Phys. Rev. E* **2015**, *92*, 030501. [CrossRef] [PubMed]

55. Babakhanova, G.; Parsouzi, Z.; Paladugu, S.; Wang, H.; Nastishin, Y.A.; Shiyanovskii, S.V.; Sprunt, S.; Lavrentovich, O.D. Elastic and viscous properties of the nematic dimer CB7CB. *Phys. Rev. E* **2017**, *96*, 062704. [CrossRef] [PubMed]

56. Meyer, C.; Luckhurst, G.R.; Dozov, I. Flexoelectrically Driven Electroclinic Effect in the Twist-Bend Nematic Phase of Achiral Molecules with Bent Shapes. *Phys. Rev. Lett.* **2013**, *111*, 067801. [CrossRef]

57. Panov, V.; Song, J.-K.; Mehl, G.; Vij, J. The Beauty of Twist-Bend Nematic Phase: Fast Switching Domains, First Order Fréedericksz Transition and a Hierarchy of Structures. *Crystals* **2021**, *11*, 621. [CrossRef]

58. Meyer, C.; Dozov, I.; Davidson, P.; Luckhurst, G.R.; Dokli, I.; Knezevic, A.; Lesac, A. Electric-field effects in the twist-bend nematic phase. *Proc. SPIE Emerg. Liq. Cryst. Technol.* **2018**, *10555*, 105550Z. [CrossRef]

59. Binysh, J.; Pollard, J.; Alexander, G.P. Geometry of Bend: Singular Lines and Defects in Twist-Bend Nematics. *Phys. Rev. Lett.* **2020**, *125*, 047801. [CrossRef]