Mirror symmetry breaking in liquids and liquid crystals

Carsten Tschierske
Department of Chemistry, Martin Luther University Halle-Wittenberg, Halle, Germany

ABSTRACT
In the recent two decades liquid crystal science has contributed significantly to the understanding of mirror symmetry breaking and spontaneous emergence of chirality in fluids. This account tries to summarise the current state of understanding of mirror symmetry breaking in the liquid and liquid crystalline mesophases, ranging from isotropic liquids, via cubic, columnar and tetragonal SmQ phases of polycatenar compounds, the twist bend nematic phases of bent dimers to the heliconical and conglomerate type smectic phases of bent-core mesogens. Especially, the importance of dynamic chirality synchronisation of molecular conformers, cooperativity, helical superstructures, layer chirality, network formation, as well as chiral and achiral surface effects is discussed. At the end the transition from local to absolute symmetry breaking, chirality amplification and the relevance for the emergence of uniform chirality in prebiotic fluids and biosystems are considered.

1. Introduction
In the recent two decades liquid crystal science has contributed significantly to the contemporary subject of mirror symmetry breaking and spontaneous emergence of chirality. This is of fundamental scientific interest for the understanding of the mechanisms of development of homogeneous chirality in biological systems [1], as well as it is of significance for the future technological applications of LCs [2–5]. Herein an attempt is made to summarise the current status of understanding of reflection symmetry breaking in fluids with some focus on the contribution of the EU financed Project BIND to the progress in this field. It was a pleasure to participate in this consortium of leading European scientists in the field of LC research, involving our jubilee Prof. Claudio Zannoni, together with P. Raynes S. Elston (Oxford), H. Finkelmann (Freiburg), G. Mehl (Hull) and J. Vij (Dublin) as PIs, and D. Photinos (Patras) as project leader [6]. Claudios group provided important insights into the organisation of molecules with formation of locally
ordered domains and how this and other molecular parameters contribute to the development of phase biaxiality. I am indebted to Claudio for the numerous discussions we had and the insights they provided and therefore was honoured when I was asked to write an article for this Festschrift. As shown further below in more detail, the research in the BIND project, though targeted to biaxial nematic phases, provided numerous insight into cybotaxis, cooperativity and different aspects of spontaneous emergence of chirality, so that I decided to write an account on the present state of understanding of spontaneous mirror symmetry breaking in fluids.

Molecules are usually divided into chiral and achiral, where chiral is commonly used for permanently chiral molecules (lacking mirror symmetry) and all others are considered as achiral. However, strictly speaking, all molecules involving at least four atoms can assume chiral conformations. Common organic molecules, including those forming LC phases, are significantly above this limit and thus can be divided into permanently chiral, transiently chiral and prochiral, depending on the relative energies of chiral and achiral conformations/configurations [7,8]. Molecules are considered as transiently chiral if enantiomorphic conformations/configuration represent the energy minima in an equilibrium, and the enantiomerisation barrier is low with respect to $kT$ that they coexist in a thermodynamic equilibrium. If the enantiomerisation barrier becomes sufficiently high ($\gg kT$) that no enantiomerisation takes place at the given temperature and in the considered time frame, then these molecules are permanently chiral. Prochiral molecules have non-chiral lowest energy conformations, but can adopt chiral conformations after application of an external twisting force [7,8].

Because enantiomeric conformations and configurations have identical scalar properties, and thus identical energies, they can only be distinguished under chiral conditions, as the combinations of like and unlike enantiomers provide different energies (diastereoisomerism). If interaction between like enantiomers is preferred, then chirality discrimination leads to the

![Figure 1](image_url)

**Figure 1.** (Colour online) Modes of mirror symmetry breaking. (a) Chirality discrimination of permanently chiral molecules leads to conglomerates by self-sorting (local mirror symmetry breaking); (b) chirality synchronisation of transiently chiral molecules (fast equilibrating enantiomers or conformers) leads either to conglomerates (local symmetry breaking) or to uniform chirality with equal probability of either enantiomer (stochastic symmetry breaking). (c) Chirality amplification leads to uniform chirality governed by a weak applied external chiral force or chiral dopand [7,8].
segregation of the enantiomers into distinct domains (Figure 1(a)). This local breaking of mirror symmetry by spontaneous resolution of racemic mixtures of permanently chiral molecules into a conglomerate of crystals with opposite handedness has been well-known since the groundbreaking work of Pasteur which marked the birth of stereochemistry [9]. In the meanwhile chiral segregation of permanently chiral molecules (Figure 1(a)) and chirality synchronisation of transiently chiral molecules or supramolecular assemblies (Figure 1(b)) during phase transitions to solid-state crystals or self-assembled crystalline fibres and gels has developed to a prosperous field which is extensively reviewed [10–12]. Chiral (in most cases helical) aggregates can in principle, be formed by achiral, prochiral, transiently chiral or permanently chiral molecules, i.e. chirality observed on a higher level of self-assembly does not require chirality at a lower level, but any lower level chirality affects the higher level by the diastereomeric relations.

Major investigated molecular systems forming chiral (helical) self-assembled aggregates are provided by amphiphiles, either polar–apolar amphiphiles [13,14], bolaamphiphiles [15], π-conjugated molecules bearing hydrophobic/hydrophilic chains, or combining π–π-interactions and solvophobic interactions [16,17]. Different helical modes can be distinguished, which in most cases result from the helical deformation of self-assembled ribbons (Figure 2(b)) [18]. Twisted ribbons (b) involve Gaussian curvature (saddle splay), whereas in helical ribbons (c) there is only mean curvature and these helical ribbons can easily fuse to tubules which still retain helical markings and finally become achiral after these markings (d) have disappeared (e) [19]. The helical twist is favoured by torsion due to steric packing frustration occurring during self-assembly if incompatible segments with different size are combined in simple amphiphiles or rod-like, star-shaped and disc-like molecules (Figure 2(a)) [20,21]. In addition, these chiral or achiral columnar aggregates can spontaneously buckle and twist into single, double [22] and multiple stranded helical structures (Figure 2(c)) [10,12,13], which is an entropy supported process, especially for soft columns [23,24]. Formation of uniform helix sense usually requires permanently chiral molecules either with uniform chirality or as scalemic (non-racemic) mixtures (majority rule [25]). In contrast, for achiral, prochiral or transiently chiral molecules helices of both handedness are formed in equal ratio. Uniform chirality of helical fibres and gels was in these cases only observed along individual aggregates often interrupted by helix reversal defects. For development of uniform chirality the growths in a chiral environment, for example, provided by chiral solvents or dopands (Sergeant and soldier principle [25]) is required [26]. Only recently spontaneous macroscopic mirror symmetry breaking by synchronisation of the helix sense and spontaneous formation of macroscopic chiral conglomerates in the absence of any chiral source was observed for some gels [12,27–32]. However, chiral segregation in the fluid state was generally thought to be impossible until the late 1990s,
when fluid conglomerates were discovered in certain liquid-crystalline phases formed by achiral bent-core molecules [33–36].

2. Layer chirality and helical nanofilaments with bent-core molecules

Bent-core mesogens organise in densely packed layers with uniform tilt and polar direction and thus the molecular tilt (with respect to the layer normal), the polar direction and the layer normal, which are all perpendicular to each other, define either a right-handed or a left-handed Cartesian coordinate system (Figure 3(a)) [34]. The liquid-crystalline phases of these bent-core molecules either segregate into a conglomerate of homochiral domains with layers of the same layer chirality (SmC_sP_F and SmC_aP_A), or form racemic domains with alternating layer chirality (SmC_aP_A or SmC_sP_F, see Figure 3(b)), representing energetically different diastereomeric structures combining layers with like or unlike chirality [34].

This ‘layer chirality’ (Figure 3) represents a new mode of spontaneous reflection symmetry breaking in self-assembled systems, adding to the common helical modes of molecular self-assembly shown in Figure 2 [10,12–14,20,22,25]. The unique feature of layer chirality is that macroscopic chirality can develop spontaneously in flat lamellar phases without the need of any helical superstructure. Nevertheless, formation of homochiral lamellae and development of polar order in the layers is often associated with the development of helical superstructures on different lengths scales. On a macroscopic scale helical features can be found in the spectacular optical textures of the B7 phases [37] and on a much smaller nanometer-sized scale the layers break into twisted ribbons (Figure 2(b)) in the helical nanofilament (HNF) phases, also designated as B4 phases. The HNF phases are formed by helical filaments of twisted lamellar ribbons with in-plane crystalline order and phase coherent twist, similar to the twisted ribbons known for crystalline amphiphilic self-assembly. Typically these HNF phases form conglomerates of domains with opposite sign of optical rotation [32,36,38–40]. Due to the crystalline order of parts of the molecules these mirror-symmetry broken mesophases are not considered as LC phases herein, but as soft crystalline mesophases. Due to the crystalline aggregates the HNF phases can be swollen by isotropic or liquid crystalline solvents and gels are formed which retain the conglomerate structure in many cases [36,39,41–44]. HNF phase formation is obviously not restricted to bent-core molecules, it has also been reported for different kinds of di-and trimesogens [45–49]. As well there are soft crystalline conglomerate phases composed of much smaller and disordered helical aggregates (helical nanocrystallite phases = HNC) [48–52] and related mesophases with hexatic in-plane order, i.e. having an order of the aromatic cores between crystalline in the HNF/HNC phases and liquid-like in the fluid symmetry broken smectic LC phases (DC phases, see below) [53]. These crystalline and hexatic mesophases have recently been reviewed [36,39]. The focus of this account will therefore be exclusively on mirror symmetry breaking in true fluid mesophases without any fixed positions of the individual molecules as indicated by the diffuse wide angle scattering in the XRD patterns.

Figure 3. (Colour online) Layer chirality and the structures of the polar SmC phases of bent-core mesogens. (a) The orthogonal combination of tilt and polar order leads to reduced C_{2v} symmetry and superstructural chirality of the layers; and (b) the four subtypes of tilted polar smectic phases resulting from the correlation of tilt direction and the polar direction of bent-core molecules in adjacent layers (colour indicates chirality sense, dots and crosses indicate the polar direction) [34,35,127],(a) was reproduced from ref. [35] by permission of The Royal Society of Chemistry and (b) was used under CC BY 4.0 from ref.[127].
3. Dark conglomerate (DC) type isotropic lamellar phases of bent-core mesogens

There is a large number of reports about fluid mirror symmetry broken smectic LC phases of bent-core molecules that are optically isotropic and form macroscopic chiral domains, therefore designated as dark-conglomerate (DC) phases (Figures 4(b,c) and 5(b,c)) [35,36,39,54,55]. Though also the HNF/HNC phases can form optically isotropic (dark) conglomerates we reserve the designation ‘DC’ here for the fluid DC phases. Though the optical appearance can be quite similar, the crystalline and the fluid conglomerates can be distinguished by the WAXS patterns which only for the DC phases is completely diffuse. Moreover, DC phases appear directly on cooling from the isotropic liquid state as high temperature phases, while the crystalline HNF phase represent low temperature phases. Another difference is the sensitivity of DC phases to electric fields that can easily induce birefringent smectic phases [35,56–58]. In some cases it is the other way around, the birefringent smectic phase is replaced by the DC phase under an applied field [59–67] and occasionally the sign of optical rotation of the chiral domains can be flipped by reversing the direction of an applied electric field [62–64].
The chiral domains can be identified by polarising optical microscopy by rotating the analyser by a small angle out of the precise 90° position, where domains with different brightness appear; rotating the analyser in the opposite direction inverts the brightness of the domains (Figures 4(b,c) and 5(b,c)). Thus, the polarising microscope is used as a polarimeter with spatial resolution. However, by rotating the sample between fixed polarisers the brightness must not be inverted that would indicate a tilt alignment as origin of this effect. This check is especially important if the considered phase is not completely isotropic, because in this case the linear birefringence is in competition with the effects of optical rotation.

Probably the first report about such a fluid DC phase came in 2000 from Heppke et al., who observed a chiral domain texture after application of an electric field to a B7 phase [65]. In the same year Thisayukta et al. reported a fluid smectic phase with chiral domains and bluish structural colour as a ground state structure (Figure 4) [66]. The bluish colour can be attributed to a selective reflection of circularly polarised light by a larger helical superstructure, probably similar to that proposed for some HNF phases [67]. We entered this field in 2002 with bent-core mesogens having nano-segregating siloxane units (Figure 5(a)) [56, 68, 69]. We found an optically isotropic DC phase without any selective reflection in the visible range (Figure 5(b,c)) [56]. In the same year Sadashiva et al. reported a similar phase for non-silylated bent-core molecules with a fluorinated core [70]. In both cases formation of the DC phases appeared to be associated with the enhanced stability of the ferroelectric states in the tilted polar smectic phases (SmCPF phases). The DC phases were replaced by birefringent smectic phases on decreasing the size of the silyl group, which simultaneously leads to antiferroelectric switching (SmCP,A) [56, 69]. The segregation of sufficiently large silyl groups into distinct sublayers was assumed to inhibit out-of-plane interlayer fluctuations, thus supporting the polar correlation between the layers for entropic reasons; this provided the first ferroelectric switching achiral bent-core mesogens [56]. Similarly, the alternation of spacer parity in bent-core dimesogens has lead to an alternation between ferroelectric switching DC phases and birefringent antiferroelectric B2 phases [68]. This concept of nano-segregation by silyl groups to stabilise ferroelectric and chiral states was extended to oligomesogens, dendritic molecules [71–73] and polymers [74, 75] and from siloxanes to different kinds of carbosilanes [68, 76–78].

The phase structure of the DC phases remained unclear for a long time and was explained in 2009 by Hough et al. as a disordered lamellar phase resembling the lyotropic sponge phases, formed by layers with saddle-splay curvature (Figure 5(f,d)) [58]. This smectic phase is globally disordered on a short length scale (~100 nm) and therefore appears optically isotropic. Basically, the formation of saddle splay was explained by a geometrical frustration due to the different tilt of the two arms of the bent-core mesogens in the smectic layers, so that the short range lattices formed by these two arms cannot match with the lattice provided by the molecular centres (Figure 5(d,e)). Therefore, the layers bend with saddle-splay curvature, which relieves some of the resulting strain [58].

Despite of being principally understood there are still details, which are not yet completely clear and require additional investigations. For example, an anticlinic and antiferroelectric SmCP,A structure, instead of the synclinic ferroelectric SmCP,F structure, was suggested for DC phases formed by some oxadiazole based LC compounds (e.g. compound 3 in Figure 6(a)) [55]. Low twist and bend elastic constants (K22 and K33, respectively, see Figure 6) [79] appear to be responsible for layer distortion in oxadiazole based DC phases, whereas for the silylated compounds layer distortion by steric effects, layer decoupling by the formation of nano-segregated silyl layers and developing polar order appear to be more important [69].

Another point of discussion concerns the origin of optical activity. The optical rotation in the chiral domains is in the range of about 1 deg μm⁻¹, which is huge compared to the optical rotation measured for chiral molecules in solutions, being only in the range of saddle-splay curvature (Figure 5(f,d)) [58]. This smectic phase is globally disordered on a short length scale (~100 nm) and therefore appears optically isotropic. Basically, the formation of saddle splay was explained by a geometrical frustration due to the different tilt of the two arms of the bent-core mesogens in the smectic layers, so that the short range lattices formed by these two arms cannot match with the lattice provided by the molecular centres (Figure 5(d,e)). Therefore, the layers bend with saddle-splay curvature, which relieves some of the resulting strain [58].

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~1 deg cm\(^{-1}\), i.e. only about one promille of the effect observed in the DC phases \([80,81]\). These large values cannot be explained with layer chirality alone \([2,82]\) and indicate that optical rotation is due to the presence of a chiral (helical) supramolecular structure \([36,39,80,81]\). Another important observation was made by Jakli et al. who have shown that the opposite tilt domains (at least in the reported case) do not correlate with the much larger optically active domains \([83]\). This raises the question if there is any coupling between layer chirality and the optically observed superstructural chirality. This supports the conformational chirality hypothesis, which assumes that spontaneous segregation of helical molecular conformers, leading to a denser packing, is responsible for conglomerate formation, optical activity and layer distortion \([8,35,36,66,84]\). This hypothesis is controversially discussed \([85–88]\) since the first reports of mirror symmetry breaking in LC systems and recently got some support by the discovery of chiral conglomerate formation in the isotropic liquid phases in the completely different class of polycatenar mesogens. For these isotropic liquid mesophases neither layer chirality nor surface induced director alignment are possible sources of chirality (see Sections 5 and 15) \([8,89]\). This requires a rethinking of the origins of mirror symmetry breaking in LC phases in general and especially in the fluid type of DC phases.

### 4. Optically inactive isotropic lamellar phases of bent-core mesogens

There are also occasional reports about optically inactive lamellar phases without visible conglomerate structure. A distorted lamellar structure similar to the DC phases is deduced from the reduced lamellar correlation length, concluded from the line widening of the layer reflection and its random orientation in 2D patterns (closed ring around the primary beam), features which are also typical for the DC phases.

Uniformly chiral isotropic lamellar phases can be found if an internal (chiral molecules) or external chiral influence (chiral dopands, surface effects, etc.) makes the DC phase homochiral, so that no domains can be distinguished by polarising microscopy and uniform optical rotation is observed, which is more difficult to detect \([90]\).

However, there are also cases of isotropic lamellar phases without measurable optical activity. In some cases a broad single polarisation current peak is observed under an applied triangular wave field, indicating a ferroelectric switching of sufficiently large polar domains \([91]\). There are at least two possible phase structures under discussion; (i) a distorted achiral anticlinic Sm\(_{C_a}P_F\) layer structure \([91]\) and (ii) a chiral domain structure without long-range chirality synchronisation, i.e. the connectivity between the chiral clusters is below the critical value required for macroscopic chirality synchronisation. This is in line with the appearance of these achiral isotropic mesophases immediately below a cybotactic nematic phase (N\(_{cybC}\)), meaning that a domain structure is retained, and twisted layer fragments remain only loosely connected. Thus, network formation by random connections between the clusters is essential for macroscopic chirality synchronisation \([92]\), as it is also the case for macroscopic symmetry breaking in gels \([28]\) and, as shown in the next section, for the Isom-

Another example of an achiral isotropic smectic phase, also occurring below a nematic phase, was reported by Nagaraj et al. \([93]\). In this case an electric field induced transition of the achiral isotropic mesophase to a DC phase is observed, i.e. the critical network connectivity required for macroscopic chirality synchronisation appears to be achieved under a sufficiently strong field. Interestingly, with further increasing field strength the chiral domain size increases whereas optical rotation decreases, finally ending in an achiral and slightly birefringent state \([93]\).

![Figure 7](crystallisation_of_connectedwebs.png)  
**Figure 7.** Crystallisation of connected webs \([92]\). The 10 dots are connected at random by an increasing number of lines. As a certain threshold ratio of dots/lines most points become connected in one net.
The developing flat lamellar organisation would only be compatible with longitudinal twist, leading to heliconical phases (Figure 8(a,d)). Even if a heliconical smectic phase would develop, the helical pitch would have to be close to the wave length of visible light to show optical rotation (see below).

5. Chirality synchronisation in mirror-symmetry broken isotropic liquids and the issue of conformational chirality

The discovery of chirality and spontaneous symmetry breaking in the polar smectic phases of bent-core LCs had a huge impact and stimulated intensive research, leading to further examples of spontaneous mirror symmetry breaking in other LC phases of bent-core molecules [94–96], as well as in LC phases of other achiral molecules, including rod-like, polycatenar and disc-like, thus leading to chirality in columnar [97], cubic [98,99], low temperature smectic [100], tilted smectic [94,96,101–105] and nematic phases [94,106–110], in the ground state or under the influence of external electric fields [111–113].

In 2014 we reported the first experimental observation of an isotropic liquid conglomerate (Iso*) formed by achiral polycatenar molecules (Figure 9) and suggested cooperative chirality synchronisation of molecular conformations and coupling of these helical conformers with a cybotactic helical superstructure as origin of this observation [89]. As already mentioned, the question of contribution of molecular conformational chirality to spontaneous symmetry breaking in fluid LC phases is a highly controversial discussed issue [85–88]. There is no doubt that in the crystalline HNF phases the helical packing is associated with a fixation of helical conformers of the involved molecules. In contrast, it is usually argued that in the liquid state the energetic difference between the conformers is too small to give rise to any significant bias of molecular conformations and that the entropy of mixing disfavours enantiomeric segregation [36,85,105]. However, there is simulation work suggesting that spontaneous synchronisation of the helix sense of helical conformers (‘ferrochirality’) is possible in polymers [114], as well as in liquids [115,116], provided that the molecules are transiently chiral (see for example compound 4 in Figure 9(a)). Chirality synchronisation was previously suggested as origin of chirality in some nematic phases of bent-core molecules [84] though it turned out later that in this case director rotation by surface pinning of the nematic director appears to be more important (see Section 9) [117,118].

Figure 8. Helical self-assembly in LC phases of transiently and permanently chiral molecules. (a,b) Chiral molecules considered as short helicoids, the helical properties and even the handedness depend on the direction of view parallel or perpendicular to the molecular long axis [204], providing distinct helix couplings in (a) longitudinal and (b) transversal direction. (c–h) Chiral superstructures known for (e,f,h) permanently and (c,d,g) transiently chiral molecules; (c–e) heliconical organisations as found in the (c) N* phase and (e) SmC*, SmC, P_{hel} and SmC_{TB} phases; (f–h) helical organisations in the (f) N* phase, (g) HNF phases and (h) in the TGB phases; the helix sense and pitch length were arbitrarily chosen and the molecules used in the phase models are simplified and shown without bend. (c,f) were used under CC BY 3.0 from ref. [168], published by the RSC.
The situation is different in the Iso\textsuperscript{*} phases lacking any long range order. As there is no long range orientational order in the isotropic liquid state, chirality due to surface induced chiral/helical director orientation cannot be the reason for this chirality. Moreover, the Iso-Iso\textsuperscript{*} transition can be observed optically by a reversible spinodal decomposition of the optically inactive isotropic liquid into a conglomerate of domains with opposite optical activity (Figure 9(e)), associated with clear DSC features (Figure 9(f)), i.e. it is associated with a phase transition. The Iso\textsuperscript{*} phase shows the same conglomerate texture of areas with opposite chirality (Figure 9(b,d)) as known from the DC phases (Figure 5(b,c)), but in contrast to the DC phases that represent smectic phases, the Iso\textsuperscript{*} phase is a true liquid. This is indicated by the circular shape of the chiral domains (see Figure 9(b,d)) and the easy flow under gravity (see videos attached to ref. [89]), as well as by the presence of only a weak and diffuse small angle scattering, similar as found in cybotactic nematic phases [119,120], but being much broader and weaker than in the DC phases. It was postulated that the chirality in these liquids results from a synchronisation of the helix sense of molecular conformers, which allows a slightly denser packing of molecules with uniform helix sense, thus leading to an enthalpy gain for homochiral packing [8,89]. This chirality synchronisation [7,8] requires that the weak interactions are not exclusively nearest neighbour type but that there is cooperativity [121–123], as in this case a large number of molecules has to change its twist sense simultaneously. This is provided by a locally ordered structure in the cybotactic liquids and sets in at a certain temperature when the cybotactic clusters exceed a certain critical size. Below this temperature the enthalpy gain of chirality synchronisation exceeds the entropic penalty of the separation of the enantiomorphic conformers. Chirality synchronisation is additionally favoured by a coupling between the molecular conformational chirality and the chirality provided by the helical organisation of the molecules in the cybotactic clusters (diastereomerism).

Macroscopic chirality results from network formation by random connections between the clusters (Figure 7) [92]. Network formation in the liquid state is dynamic, i.e. there are no fixed connection points, only an increased attraction mediated by non-covalent interactions and supported by the cooperativity of intermolecular interactions, thus retaining the liquid state. This dynamic mode of chirality synchronisation in the fluid state retains a large part of the (conformational, rotational and translational) entropy of the system and therefore is observed at high temperatures directly below the achiral isotropic liquid phase (often around 200°C) [8]. In contrast, chirality synchronisation in the crystalline state is
associated with a much stronger restriction of molecular and conformational motions, leaving mainly thermal vibrations and thus leading to a larger entropic disadvantage of this process. As the contribution of entropy increases with temperature, the classical non-dynamic mode of chirality synchronisation requires low temperatures and is typically observed in low temperature crystalline or semicrystalline mesophases, like HNF phases [36,38,39], crystalline smectic phases [36,100] and fibrous crystalline assemblies (gels [10,12-14,16,20,27,42-44] and HNF+ N systems [39,41,42]).

In the liquid conglomerates the zero-crossing of the CD curve coincides with the position of the UV-vis absorption maximum of the chromophore (Cotton effect), similar to the conglomerates in the cubic phases (see Section 13). This excludes an anomalous optical rotation around the selective reflection of a larger structural chirality as origin of optical activity. However, a locally twisted organisation of the rod-like π-conjugated core units on a much smaller molecular length scale leads to exciton coupling, which is known to give large values of the optical rotation if the absorption maximum of the chromophore is in the visible range or close to it [124,125]. It is noted that the major contribution to exciton coupling arises from twisted pairs and little difference arises on going to larger helical aggregates (Figure 10(a,b)). Therefore, optical rotation and CD do not give information about the helical coherence length, though there must be a uniform twist sense to observe optical activity. The helical twist of the chromophores in the helical conformers is also known to give high values of molecular optical rotation values, though intermolecular exciton coupling is usually the dominating effect [126].

More details of the structure of these liquid conglomerates will be discussed after describing chirality in columnar, cubic and tetragonal LC phases (Sections 12–14). In the next sections we will return to the spontaneous mirror symmetry breaking phenomena in nematic and smectic phases of bent molecules.

6. Heliconical SmC_p_F^hel phases

Another spontaneously mirror symmetry broken smectic phase is a weakly tilted helical smectic phase. This phase is found at the transition from paraelectric to ferroelectric polar order, but in this case for weakly tilted polar SmC phases having weakly coupled layers (SmC_p_F^hel phase). It is a heliconical smectic phase with the helix axis perpendicular to the layers as in SmC* phases (Figures 8(e) and 11) [127]. The helix pitch is short (14 nm corresponding to three layers), leading to an isotropic appearance of the homeotropic aligned polar SmC_p_F^hel phase (inset in Figure 11(d)). In planar cells a fan texture as typical for SmA or anticalinic SmC phases is observed (Figure 11(d)). Neither a layer distortion nor domains with opposite chirality, as typical for DC phases could be observed. This heliconical SmC_p_F^hel phase occurs only for weakly tilted SmC phases at the transition from paraelectric to ferroelectric switching as an intermediate structure at the transition from the optically uniaxial tilt-randomised (de Vries like) paraelectric SmA phase (Figure 11(b)) to the polar SmCP_A phases, when layer coupling is still weak. The SmC_p_F^hel phase shows V-shaped switching by helix deformation and therefore can be used for fast gray scale switching [128].

In a phenomenological theory developed by Pikin and Indenbom the pitch in a SmC* phase can be expressed as \( q = \frac{(A + \mu P_s \theta)}{K} \), where \( \mu \) is the flexoelectric coefficient, \( P_s \) the spontaneous polarisation, \( \theta \) is the molecular tilt angle, \( K \) is the relevant elastic constant and \( A \) the Lifshitz invariant, which is responsible for the formation of a helix of fixed sense due to the permanent (SmC*) or transient molecular chirality (SmC[s]°) [129]. Accordingly, this phase can be formed if the effects of chirality or polar order, or a combination of both, are sufficiently large to exceed the elastic energy required for helix formation. Interestingly, a related heliconical SmC* phase with a longer 10 layer helix was induced by doping an achiral polar smectic phase of a bent-core mesogen with a homochiral dopand [130]. This indicates that besides polar order also chirality (A) is required for helix formation.

The SmCP_F^hel phase can be considered as a polar smectic version of the twist bend nematic phase \( N_{TB} \) (see Section 10). A similar phase (SmC_{TB}) without measurable polar response was recently observed for mesogenic dimers as an intermediate phase structure at the transition between \( N_{TB} \) and SmA [131]. Though this phase appears to be apolar in this case, there are recent indication of polar order in the \( N_{TB} \) and related phases (see Section 10) [132].

That no optical activity or chiral domains could be detected in the uniaxial SmC_p_F^hel phase by polarising microscopy is due to the very small pitch of only 14 nm, which is outside the range of visible light. In addition the π-conjugated cores retain an almost parallel organisation between each other in the layers so that also no significant exciton coupling (Figure 10) could be expected in the heliconical phases; the twist occurs only between the chromophores located in adjacent layers that are decoupled from each other by the fluid alkyl chain layers. Overall, it appears that heliconical organisation, which retains an undistorted layer structure, requires small tilt and weak layer coupling.
The discovery of the SmC$_{P_F}^{hel}$ phase was initiated by the work on phase biaxiality and cybotaxis carried out in the above mentioned BIND project [6]. The work in this project was actually targeted towards an understanding of the cybotactic cluster formation for development of phase biaxiality in nematic phases of bent-core mesogens [119,133,134]. An extension of the concept of cybotaxis to polar and chirality synchronised domain formation in smectic phases provided an improved understanding of the importance of cooperativity for development of polar order [135–137] and chirality in smectic phases of bent molecules [95,96,135–138]. This project also lead to the discovery of conglomerate formation in paraelectric SmC phases (see next Section 7) [95,96] and contributed significantly to the contemporary field of mirror-symmetry breaking in nematic phases of bent molecules [117], especially it provided the first indications for the existence of a new type of mirror symmetry broken nematic phase [107] and thus initiated the presently most prosperous field of twist-bend nematic phases (see Section 10).

7. Chirality in paraelectric SmC phases

Recently, formation of chiral domains was also observed for paraelectric SmC phases of bent-core mesogens (SmC$_{P}^{s}$ and SmC$_{P_R}^{s}$), i.e. in biaxial tilted smectic phases with uniform tilt but only local polar order [95,96]. Homeotropically aligned thin films between glass substrates (~10 μm) show chiral segregation into domains with opposite rotation of the plane of polarised light (Figure 12(a,c)), very similar to the DC phase. The formation of these domains requires a certain strength of the dielectric permittivity, i.e. size of the polar domains and therefore appears for paraelectric SmC or polarisation randomised SmC$_{P_R}$ phases close to the transition to the SmCP$_A$ phases with macroscopic polar order in the layers [135–137]. These chiral domains cannot be observed in free standing films and therefore it appears that in this case chiral segregation is not spontaneous, but surface assisted.

Due to the presence of orientational order any twist between two surfaces can lead to chiral configurations, even if the surfaces and the molecules are achiral. The simplest example is the Mauguin effect; if a nematic LC is confined between two rubbed glass plates and the rubbing directions of the two plates is adjusted at exactly 90° to each other, the nematic director adopts a continuous twist configuration, which can be left or right (Figure 13 (a,b)) [139,140]. As the resulting macroscopic helix acts as a polarising wave guide a conglomerate of macroscopic domains with opposite twist sense can be observed after cooling from the isotropic liquid. Though the exact 90° condition is very special and unlikely to be observed by chance, there are numerous other confinement induced reflections symmetry breaking conditions, especially if flow is involved, as for example observed for lyotropic nematic phases (Figure 13(c,d)) [17,141,142]. Similar to these nematic phases, director alignment, topological defects or vortex flow can provide sources of chirality in the SmC$_{P}^{s}$($P_R$) phases. The induced twist can be amplified in the LC phases with local chirality synchronisation of the transiently chiral molecules, thus leading to the macroscopic chiral domains (chiral surface supported symmetry breaking) [143].

On the other hand, surfaces can exclusively stabilise and increase the size of chiral or polar domains in the
paraelectric SmC\textsubscript{s}(P\textsubscript{R})\textsuperscript{[\ast]} phases and thus reinforce cooperativity without providing any source of chirality. This effect supports the spontaneous chirality synchronisation and macroscopic symmetry breaking in the surface layers or even in the bulk (achiral surface supported symmetry breaking) \cite{95,96}. In the SmC\textsubscript{s}(P\textsubscript{R})\textsuperscript{[\ast]} phases the tilt is small and flat layers are retained. Therefore, any helical twist can only be heliconical (helix axis perpendicular to the layers, see Figure 8(a,d)) with a much longer pitch than in the SmC\textsubscript{s}P\textsubscript{F}\textsuperscript{hel} phase, exceeding the wave length of light.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{(Colour online) Heliconical smectic phase. (a) Molecular structure and (b–d) textures of the 4-cyanoresorcinol based bent-core mesogen 5 showing the phase sequence (b) SmA, (c) SmC\textsubscript{s}P\textsubscript{a}, (d) SmC\textsubscript{s}P\textsubscript{F}\textsuperscript{hel} on cooling. (b–d) The textures in planar cells (\textit{R} is the rubbing direction) with the insets showing homeotropic alignment \cite{127}; used under CC BY 4.0 from ref. \cite{127}.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{(Colour online) Chiral paraelectric SmC\textsubscript{s}(P\textsubscript{R})\textsuperscript{[\ast]} phase. (a–c) Chiral domains in the SmC\textsubscript{s}(P\textsubscript{R})\textsuperscript{[\ast]} phase of compound 6 (\textit{n} = 20) as observed by rotating the direction of the analyser clockwise or anticlockwise out of the exact 90° position with respect to the polariser; (d,e) rotation of the sample between the crossed polarisers does not change the domain brightness, indicating that this observation is not due to a simple director alignment \cite{137}; reprinted with permission from ref. \cite{137}, copyright 2015, VCH-Wiley.}
\end{figure}
represent transiently chiral mesogens with significant helicity [86], as for example evident from the observation of strengthening of the chirality (shortening of the helical pitch) of chiral nematic phases by addition of the transiently chiral bent-core mesogens [144]. A similar phenomenon was also observed in the chiral smectic C phases mixed with bent-core molecules [145]. Because there is still birefringence in the homeotropic conglomerate textures of the SmC(P_R)^[x] phases (Figure 12), it appears that the pitch is much longer than the wave length of light and it is likely that the heliconical superstructure itself acts as a polarising wave guide, and optical activity is not due to exciton coupling in this case.

8. Mirror symmetry breaking in SmC phases of rod-like molecules

Chiral domains were also observed in SmC phases of simple rod-like molecules [101–104], lacking any polar packing. In this case surface induced chiral modes of director alignment appear to be mainly responsible for the observed effects [36,85,105]. Nevertheless, easy formation of chiral conglomerates under weak surface confinement indicates transiently chiral molecules or aggregates being sensitive to weak chiral perturbations and easily providing synchronisation of conformational chirality in these LC phases, being also expressed by small or negative twist elastic constants K_{22} (Figure 6(c)). The COO groups involved in all investigated molecules are assumed to significantly contribute to transient conformational chirality of the mesogens [36].

9. Nematic conglomerates

Chiral conglomerate formation was even observed in nematic phases of some bent-core mesogens (N^[x]) first reported by Weissflog et al. [94,146], by Niori et al. [147], and later also found in oxadiazole based mesogens reported by Goodby et al. [84,118]. It appears that these chiral domains result from director alignment at the surfaces [117,118] as discussed above for the SmC phases. Reflection symmetry breaking is
10. Twist-bend nematic phases

Another remarkable spring-off of the BIND project [6] is the indication of a new nematic phase with negative bend elastic constant $K_{33}$ in dimesogens with odd-numbered spacers, showing a typical stripe pattern and indications of chirality ($N_x$ phase) by Mehl and Vij et al. [107,148], later assigned to the $N_{TB}$ phase [149–151] and previously predicted by B. Meyer [152], Dozov [153] and Memmer [154]. This discovery has motivated a great deal of study into the properties of this intriguing state of matter by a wide range of techniques [155–201], especially freeze fracture EM techniques [151,164,165], resonant X-ray scattering [155,156,166,193] and solid-state NMR [157,158]. Though there were previous reports about apparent $N-N_x$ transition in mesogenic dimers and bent-core molecules, these were attributed to $N-N_{Col}$ transitions [159,160] or transitions to smectic phases [161]. Also for main chain polymers a $N-N_x$ transition was actually observed much earlier [162], and later attributed to a $N-N_{TB}$ transition [155]. This field has in the meanwhile spread out and developed to a prosperous new field of LC research conducted by several groups [163–173] and comprehensively reviews have appeared [163,174–178]; here we focus the discussion on some chirality related issues.

Synthetic work has shown that $N_{TB}$ phase formation is not restricted to mesogenic dimers with different types of odd-numbered aliphatic spacers (for example compounds 7–11 in Figure 14) [163,175,177,179], but is also found for bent core molecules 12 [165,180], mesogenic trimers [171,175] involving rod-like or mixtures of rod-like and bent core mesogens [181], higher oligomers [174,182] and main chain polymers [155,162], as well as for hydrogen bonded oligomerosogen aggregates [183]. Although symmetric and unsymmetric di- and oligomesogens with different linking groups are known to exhibit the $N_{TB}$ phase, the symmetrical compounds with methylene spacers are the most commonly encountered and most detailed investigated materials [184]. The $N_{TB}$ phase usually occurs with weakly first order phase transitions from ordinary $N$ phases, in few cases also direct Iso-$N_{TB}$ transitions have been observed [185,186]. Though the XRD patterns with diffuse small and wide angle scatterings are similar to the typical patterns of cybotactic nematic phases there is no observable Brownian motions and the viscosity of the $N_{TB}$ phases is much higher than for typical $N$ phases [187]; even free-standing films and fibres can be drawn [188,189]. Also the textures are very different from ordinary $N$ phases, often showing

Figure 15. (Colour online) Typical textures and XRD patterns of $N_{TB}$ phases. (a) Well-aligned rope texture between crossed polarisers and (b) with a $\lambda$ waveplate inserted, (c) the ‘blocky’ texture, and (d) parabolic defects. (e) Two dimensional X-ray scattering patterns in the nematic phase and (f) in the adjacent $N_{TB}$ phase [168]. (g,h) Dark and bright domains as observed with slightly uncrossed polarisers after application of a square field [191]; (a–f) used under CC BY 4.0 from ref. [168]; (g,h) reproduced with permission from ref. [191], copyright 2013, APS.

not only observed for nematic phases of transiently chiral bent molecules, but also for lyotropic chromonic and micellar nematic phases formed by relatively large fluid aggregates (Figure 13(c,d)). In the latter cases the transiently chiral helical packing of the $\pi$-systems [16] or the amphiphiles [13,14] is highly compatible with the helical twisted organisation induced by chiral director fields. This could also explain the occasional observation of chiral domains in the thermotropic nematic phases of simple achiral 4-$n$-alkyl-oxybenzoic and 4-alkylcyclohexanecarboxylic acids [108].
stripe and rope patterns and features more typical for smectic phases, like focal conics (see Figure 15(a–d)) and batonnets [184]. It was demonstrated by recent synthetic work focussed on detailed structural variations of $N_{TB}$ materials by Mandle and Goodby that there is an almost linear relationship between the transition temperatures $N$-Iso and $N$-$N_{TB}$ and that the optimal bending angle is around 120° (110–130°), irrespective of the polarity, polarisability and mode of substitution and even if dimesogens, oligomesogens or main-chain polymers are considered [190]. The current understanding of the $N_{TB}$ phase is that it has a local helical structure with a short pitch of about 10 nm [151], the molecules are slightly tilted with respect to the helix axis, but lack long range positional ordering. This provides mobility for translocation of the molecules and incommensurate packing along the helix, thus leading to an entropic advantage of this helical model of self-assembly (Figure 8(c)) [174,193].

Chirality is expressed by helical features of the textures [174] and by stripe patterns formed under an electric field (Figure 15(g,h)) [148,191]. The bent molecular structure leads to a negative bend elastic constant $K_{33}$, which gives rise to a geometrical frustration of the packing in a nematic phase and leads to the helical organisation. Theoretical models indicate that helical twist of the molecules is not required for $N_{TB}$ formation [192]. However, Se resonant X-ray scattering, suggest that in order to follow a helicoidal path the arms have to be significantly twisted about the spacer axis, providing a denser packing of highly chiral conformers [193]. Hence, $N_{TB}$ formation appears to be associated with entropy supported chirality synchronisation of helical conformers. It has been demonstrated by deuterium NMR that there is indeed a bias of the conformer distribution of the involved molecules, though this effect appears to be small in the investigated case [157].

Soft resonant X-ray scattering gave strong evidence for formation of double helices (at least for the investigated compounds), which provide a better space filling than single helices [156,194,195]. In some cases there are additional transitions to other LC phases. At this transition long range 2D periodic ordering of the double helices in the $a$-$b$ plane could lead to columnar phases [159,196,197]. If a transition to a commensurate helix packing takes place as the segregation of aromatic and aliphatic units increases, this leads to heliconical smectic phases (SmC$_{TB}$) [131]. Often a transition to SmC$_A$ or denser packed hexatic phases (SmL$_A$) with in-plane order and anticular tilt was observed [169].

XRD patterns of $N_{TB}$ phases are typical for nematic phases with significant cybotaxis as indicated by the relatively high intensity of the small angle scattering compared to the wide angle scattering [119]. In aligned samples the small angle scattering, approximately corresponding to half the total molecular length, has its maximum around the meridian, but shows a wider distribution than in the ordinary nematic phase above (Figure 15(e,f)). This indicates some loss of alignment or the onset of a slight tilt due to the heliconical organisation of the molecules. It appears that enhanced cooperativity by cybotaxis contributes to the emergence of $N_{TB}$ phases. It also appears that a weakly tilted or non-tilted organisation in the cybotactic clusters is favourable for formation of the helicoidal $N_{TB}$ phases. Larger tilt angles in SmC-type cybotactic clusters were found for the conglomerate forming nematic (N$^{s,t}$) phases (see previous Section 9).

In general, weak tilt appears to support the heliconical organisation in nematic ($N_{TB}$), as well as smectic phases, (SmC$_B$P$_T^{hel}$ and SmC$_{TB}$) (Figure 8(c,d)) and large tilt leads to conglomerate formation in nematic and smectic phases and supports layer distortion in smectic phases with formation of fluid DC phases or soft crystalline HNF phases. The bent molecular structure with alternating aromatic and aliphatic segments and relatively short end chains (or small end groups, especially CN) appears to contribute to the suppression of smectic phase formation by favouring the incommensurate (non-segregated) packing along the helix direction [193,198]. Therefore, the number of $N_{TB}$ phases formed by mesogenic dimers is large compared to bent-core mesogens (Figure 14) providing a stronger segregation of the larger uninterrupted aromatic cores and the flexible chains. Investigation of the $N_{TB}$ stability of molecules differing in the linking

![Figure 16](image_url) (Colour online) Schematic illustration of the alternative model of the $N_{TB}$ phase (N$x$), showing the twisting of the polar director $\mathbf{m}$ and the preferred configuration of the molecules, with the molecular polar axis $y$ tending to order along $\mathbf{m}$ [202]; reprinted with permission from ref. [202], copyright 2016, RSC.
units (–CH=CH– and >C=O) connecting spacers and rods, combined with DFT computational studies, supported the view that the molecules do not only have to be bend, but also twisted. The intramolecular torsion provides a helical molecular shape which obviously favours N\textsubscript{TB} formation \cite{199,200}. Typically the XRD patterns indicate a short range periodicity corresponding to half the molecular length. However, for some compounds with alkyl end chains the N\textsubscript{TB} phase is characterised by two maxima in the small angle region of the XRD patterns, the first corresponding to the full length becoming more pronounced with growing alkyl-chain-to-spacer-length ratio and the second, stronger one to only one mesogenic unit, i.e. to half the total molecular length \cite{189,198,199}.

Besides single component systems also mixtures of rod-like and bent dimesogens show N\textsubscript{TB} phases, often with expanded mesomorphic ranges \cite{193,201}. An alternative model of the N\textsubscript{TB} phase, assuming escape from macroscopic polar order as the main driving force for N\textsubscript{TB} formation, was suggested by Vanakaras et al. Accordingly, the twist arises from an onset of transverse polar ordering of the molecules, dictated by the packing of their intrinsic polarity due to the shape \cite{202}. This phase has local monoclinic symmetry, with a single director \(\mathbf{m}\) defining the direction of polar ordering (Figure 16). The combination of twist of the director \(\mathbf{m}\) with the monoclinic local symmetry produces a chiral heliconical configuration which is determined by the pitch of the twist of the director \(\mathbf{m}\), whilst the conical angle is not unique and varies with the molecular segment considered. This model is in line with recent NMR observations which cannot be explained with the previous model \cite{158} and would mean that the low temperature nematic phases, commonly designated as N\textsubscript{TB}, would not correspond to the initially proposed twist-bend model \cite{152-154}. The presence of polar ordering was supported by recent dielectric studies indicating a field-induced gradually unwinding of the helical structure formed by the bent-core molecule 12 (Figure 14) by increasing \(E\), leading to a transition from the twist–bend to a splay-bend structure \cite{132}. This would mean that the SmC\textsubscript{TB} phase is likely to involve polar order, too, and thus would be identical with the previously reported SmC\textsubscript{s}P\textsubscript{F}\textsubscript{hel} phase. But it is also possible that polar order in heliconical LC phases can be more easily discovered for the bent-core mesogens due to the enhanced polar order.

11. Heliconical organisation vs. helical twist

There are two distinct modes of helical organisation in the smectic and nematic phases, heliconical (SmC\textsubscript{s}P\textsubscript{F}\textsubscript{hel}, SmC\textsubscript{TB}, N\textsubscript{TB}, SmC\textsuperscript{*}) and helical (N\textsuperscript{*}, TGB, HNF) formed either by permanently (N\textsuperscript{*}, SmC\textsuperscript{*}, TGB) or transiently chiral molecules (SmC\textsubscript{s}P\textsubscript{F}\textsubscript{hel}, SmC\textsubscript{TB}, N\textsubscript{TB}, HNF, see Figure 8). In the heliconical phases, the helix develops parallel to the averaged molecular direction (longitudinal, Figure 8(c–e)), in the helical phases it is perpendicular to the molecular long axis (transversal, Figure 8(f–g)); the first does not interfere with layering, the latter is incompatible with layer formation and is suppressed if layering is strong and leads to layer frustration if layering is weak and chirality is strong \cite{203}. Permanently chiral and chirality synchronised transiently chiral molecules can be considered as short helicoids, for which the helical properties (helix pitch, ‘twisting power’\cite{2}, mode of intermolecular interactions, etc.) and even the handedness depend on

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure17.png}
\caption{Transversal helix coupling. (a,b) Steric interactions between two chiral molecules produce a net relative rotation of their long axes. In (a) a tight right-handed pitch leads to a right handed twist whereas (b) shows molecules with a weak right-handed pitch providing a left handed twist. This show that the same ‘handedness’ of individual molecules, depending on the curliness, can lead to opposite handedness of the resulting superstructure \cite{205}; reprinted with permission from ref. \cite{205}, copyright 1999, APS.}
\end{figure}
the direction of view either parallel or perpendicular to the long axis (Figure 8(a,b)) [204]. Also the curliness of the molecules, which affects the intermolecular twist as shown in Figure 17 [205], is direction dependent. Accordingly, the contribution of longitudinal and transversal interactions to the overall effect should be affected by molecular biaxiality and the degree of tilt of the molecules in the layers/domains.

Figure 18. (Colour online) Chirality synchronisation in the hexagonal columnar phase of a C\textsubscript{60} substituted star mesogen 13 (R = C\textsubscript{12}H\textsubscript{25}). (a) Molecular structure; (b,c) models of the organisation of the molecules; and (d,e) XRD pattern with helical features in (d) indicating a triple helical packing (inset shows simulated pattern); (e) shows the LC state of the columnar phase (diffuse wide angle scattering) [219]; reprinted with permission from ref. [219], copyright 2015, VCH-Wiley.

Figure 19. Mirror symmetry breaking in a plastic columnar phase. (a) Formula of the dibenzo[g,p]chrysene based transiently helical mesogen 14 with a twisted core (due to the steric interaction between the aromatic C-Hs); (b) UV-vis spectrum and (c) corresponding CD spectra of the domains [97]; reprinted with permission from ref. [97], copyright 2009, VCH-Wiley.
From the collated experimental data it appears that weak tilt favours heliconical organisation (longitudinal twist) whereas strong tilt favours the helical organisation (transversal twist) and thus provides significant layer distortion (Figure 8). It is already known from the LC phase of permanently chiral molecules, that strong transversal twisting power leads to chirality frustrated TGB phases, tetragonal, cubic and even isotropic mesophases \[203,206\]. The combined effects of strong longitudinal and transversal helix coupling in the highly tilted and polar smectic phases of chirality synchronised bent-core molecules might contribute to DC phase formation by layer deformation into a disordered sponge-like structure (see Section 3). Likewise, the introduction of permanent chirality into bent-core mesogens \[207,208\] and bent mesogenic dimers \[209\] leads to a series of chirality induced and chirality frustrated LC phases. In any case, local or long range lamellar organisation provides significant restrictions to helical self-assembly in LC phases. In contrast, helix formation is supported by columnar self-assembly (Figure 2).

12. Helical order in columns

Helical order in crystalline columnar aggregates is well known and extensively reviewed \[10,12,13,20\]. In the vast majority of the fluid LC columnar phases of disc-like molecules, C\(_3\) symmetric star molecules, polycatenars, etc., the organisation of the flat or rod-like aromatic cores is perpendicular or slightly tilted to the normal to the column long axis \[210\]. In this case the clashing of peripheral chains or groups intrinsically tends to give rise to a helical twist along the column long axis (Figure 2(a)). In contrast to lamellar phases where helix formation (parallel to the layers) is in competition with layering, the columns retain their fundamental shape during helix formation. Thus, columns can be considered as templates, supporting helical molecular organisation \[211–214\]. Though helix formation does not require helically twisted molecules \[215\], the helical organisation could provide an efficient chiral template for the synchronisation of molecular conformations \[8\]. However, in the fluid LC state the coherence length of uniform helix sense is only short as long as cooperativity acts exclusively along the columns.

This short range helical structure appears to be an inherent feature in all columnar LC phases formed by molecules with a rigid core unit and a flexible periphery. The helix can become long range at lower temperature when core packing becomes crystalline \[211–214\]. In the fluid LC state the coherence length of the helix is short and can be extended by introduction of permanent chirality into the molecules \[216–218\] or by chiral dopands which remove helix inversions and lead to uniform chirality (sergeant and soldier principle \[25\]) \[54\].

The coherence length of the uniform helix direction along the individual columns can be enhanced by a stronger clashing of the peripheral groups, enhancing the helix inversion barrier as demonstrated for example for C\(_{60}\) modified star-shaped molecules showing a coherence length of about 4–5 helical pitches (Figure 18) \[219\]. Long range synchronisation of the helical sense between
columns was observed in a plastic columnar phase of a disc-like molecule with a transiently chiral (helical) core and short lateral chains (Figure 19) [97]. The short chains provide cooperativity for chirality synchronisation by lateral coupling between the columns in this plastic mesophase, which breaks down in the fluid Col\textsubscript{hex} phase obtained upon chain elongation. Because exciton coupling is negligible for non-staggered face-to-face packed disc-like π-conjugated cores (Figure 10(c)) [124], optical activity is in this case mainly attributed to the chirality synchronisation of the intrinsically chiral twisted π-conjugated systems.

Helical buckling of the columns (see Figure 2(f)) is entropically favoured for soft columns [23] and can additionally contribute to chirality synchronisation between individual columns and could lead to double- and multi-helical bundles (Figure 2(f–h)). It should be noted that the chirality synchronisation between helical columns is not in all cases enantiophobic (leading to conglomerates), often it is enantiophilic, leading to achiral racemates [220,221].

13. Helical order in networks of bicontinuous cubic phases

A powerful way to synchronise the chirality of helical column segments is network formation (Figure 7). Network formation is responsible for the development of uniform macroscopic chirality between the crystalline helical fibres in gels [28]. Such networks are also known to be formed in LC phases at the transition from lamellar to columnar organisation, i.e. when the

Figure 21. (Colour online) Chiral and achiral cubic phases of poly-catena\-molecular mesogens. (a,b) textures of the la3d and Im3m\textsuperscript{[+]} cubic phases between polarisers with slightly less than 90° rotation indicating a) the optically inactive phase la3d crystallising from the Is\textsuperscript{[+]}/ phase and (b) the chiral Im3m\textsuperscript{[+]}/ phase. (c) The two networks (red and blue) of the la3d phase in (e) decorated with schematic mesogens (rod-like molecular cores, green) showing the molecular twist along the network segments (the gyroid minimum surface is also shown in yellow) and (d) the three networks of the Im3m\textsuperscript{[+]}/ phase (red, yellow, blue), in (f) the middle of the three networks (on the Schwarz P-minimum surface, shown in yellow) is decorated with molecules; (g,h) show the network junctions g) in the la3d phase (70° twist) and h) in the Im3m\textsuperscript{[+]}/ phase (180° twist) [99]; reprinted with permission from ref. [99], copyright 2014, VCH-Wiley.
layers become curved into infinite minimal surfaces and the columns become branched into continuous networks. In the bicontinuous cubic phases thus obtained, the structural features associated with mirror symmetry breaking in lamellar and columnar phases are inherently coupled (see Figure 20) [222].

It was recently found that some bicontinuous cubic phases are chiral and form conglomerates (Figure 21(b) and 22) [99]. The first example has been reported by Kishikawa et al., but at that time the phase structure and the origin of spontaneous chirality were not clear [98]. We have observed conglomerate formation in several cubic phases formed by rod-like and polycatenar molecules (Figure 23) [99]. Depending on the lattice symmetry the cubic phases of these rod-like and polycatenar molecules are either achiral $Ia3d$ or chiral $Im3m$ [8,99]. In the bicontinuous $Ia3d$ lattice there are two networks that are enantiomorphous and the helices forming these networks have opposite sense. Therefore, this phase represents a racemate which is intrinsically achiral. In the tricontinuous $Im3m$ lattice [223], there are three networks that cannot cancel each other and therefore this phase is always chiral if there is uniform helical organisation in the networks (Figure 21(d)). A slightly modified model of the phase was proposed by Kutsumizu et al., in which the two networks containing octahedra (Figure 21(d), red and blue nets) are disconnected and form individual octahedrally deformed shells in the centre and at the corners [224].

These chiral cubic $Im3m$ phases of achiral, but transiently chiral molecules form conglomerates with opposite handedness, being very similar in appearance to the DC phases of bent-core mesogens. The space group $Im3m$ assigned for achiral compounds before the discovery of the intrinsic chirality of these cubic phases has then been referred as $I432$, because of its
This is the chiral cubic lattice with the highest symmetry, but the question of the true space group is still open, and therefore $Im\bar{3}m$ is used here to indicate superstructural chirality.

In these cubic phases, the CD curves cross zero at the UV-vis absorption maximum of the chromophore (Cotton effect, Figure 22) \[97\], indicating that exciton coupling provides a major contribution to optical activity (Figure 10(a, b)), though a contribution of optical rotation due to the intrinsic helically twisted core structure cannot be excluded. In the bicontinuous cubic phases the organisation of the molecules is helical and the rod-orientation has to match ‘in phase’ (with all rods aligned almost parallel) at the nodes where the helix segments are interconnected. The different cubic phase structures ($Ia\bar{3}d$ and $Im\bar{3}m\{^*\}$) provide different distances and angles between the nodes and therefore require different degree of helical twist of the molecules between them to match at the nodes ‘in-phase’ (Figure 21(e–h)). The required twist is 70° or 250° ($\pi + 70^\circ$) for the $Ia\bar{3}d$ and 180° for the $Im\bar{3}m\{^*\}$ phases. This explains the phase sequence $Ia\bar{3}d$–$Im\bar{3}m\{^*\}$–$Ia\bar{3}d$ with re-entrance of the $Ia\bar{3}d$ phase upon chain elongation usually observed for the cubic phases of rod-like molecules with growing size of the terminally attached alkyl chains \[225\]. The proper twist can be engineered by molecular design (length and number of terminal alkyl chains) \[99,226\] or by mixing compounds with short and long chains \[8,99\]. In this way the chiral $Im\bar{3}m\{^*\}$ phase was induced by mixing two achiral $Ia\bar{3}d$ phases of molecules with short and long chains \[227\].

### 14. The SmQ phase, a LC network of homochiral helices

A third, in this case non-cubic, network phase formed by rod-like molecules is the SmQ\{^*\} phase. The SmQ phase has originally been discovered for permanently chiral rod-like molecules with two branched end-chains as a chirality induced liquid crystalline 3d phase \[228\] with $I4_122$ lattice (SmQ\{^*\}) \[229\]. In racemic mixtures it is replaced by the $Ia\bar{3}d$ cubic phase and it often occurs besides an anticlinic SmC\{A\} phase \[203,206,230,231\]. Recently, we have shown that this phase can also be formed by transiently chiral polycatenar molecules (e.g. compound 4), capable of assuming strongly chiral conformations (SmQ\{^*\}) and the structure was found to be formed by a pair of networks with 90° branchings at four way junctions (Figure 24(a)) \[232\].

Remarkably, this structure is formed by two identical non-chiral networks having a helical molecular design of double swallow tailed polycatenar compound 24 ($n = 8$) forming a symmetry broken reentrant isotropic liquid phase (Iso\{re\}$_{^*}$) as a result of the competition between long range orientational order and emerging chirality synchronisation \[236\].

\[
\text{Figure 24. (Colour online) SmQ\{^*\} phase. (a) Model showing the two uniformly twisted networks in the unit cell of the I4\_22 lattice; (b) DSC showing the phase transitions of compound 4 (m = 10, m = 1) on cooling and (c) triangular domains as observed during the growth of the Ia3d phase from the SmQ\{^*\} phase [232] reprinted with permission from ref. [232], copyright 2018, VCH-Wiley.}
\]

\[
\text{Figure 25. Double swallow tailed polycatenar compound 24 (n = 8) forming a symmetry broken reentrant isotropic liquid phase (Iso\{re\}$_{^*}$) as a result of the competition between long range orientational order and emerging chirality synchronisation [236].}
\]
organisation with identical helix sense in both networks. This birefringent SmQ* phase often replaces the optically isotropic \( Ia3d \) phase when formed by cooling from an \( Is0^* \) phase. On further cooling it is replaced by the achiral \( Ia3d \) phase, associated with a helix inversion of half of the involved molecules; this renders the SmQ* \( Ia3d \) transition slow. In the birefrigent SmQ* phase it is difficult to detect chirality by optical methods, as there is birefringence. In this case the growth of the achiral \( Ia3d \) phase with a triangular shape (instead of hexagonal) indicates that the surrounding SmQ* phase has to be chiral (Figure 24(c) [232]).

15. Spontaneous chirality synchronisation in isotropic liquid conglomerates

The SmQ* structure allows an improved understanding of the most mysterios of the spontaneous symmetry broken mesophases formed by liquid crystalline molecules, which is the \( Is0^* \) phase (see also Section 5) [8,89]. The \( Is0^* \) phase occurs on cooling the achiral isotropic liquid before the transition to one of the bicontinuous cubic phases (\( Ia3d, Im3m^* \)), to anisotropic 3D phases (SmQ* [232] or to other tetragonal phases [233]) or to a lamellar phase [234]. However, the lamellar phase has to be close to the transition to a cubic phase, so that increasing temperature easily leads to curvature. Concerning the chemical structures (Figure 23), the molecules (or supramolecular aggregates [235]) have to be transiently chiral with a sufficient helicity of the preferred conformers. Thus the benzoates of diphenylbithiophene (4, Figure 9 (a)) and 15 (Figure 23) have turned out to be the most efficient presently known, but also phenylbenzoates and benzoates of azobenzenes [233–235] are capable of forming the \( Is0^* \) phases. In contrast, molecules with shorter core structure or reduced helicity, as for example the compounds 20 and 21 (Figure 23) [225], though showing chirality in the \( Im3m^* \) phases are not capable of forming the \( Is0^* \) phases [8,99].

XRD investigation of the \( Is0^* \) phase indicate a diffuse small angle scattering as typical for a locally ordered cybotactic structure of these liquids [89], similar to the cybotaxis in nematic phases [119]. It is assumed that in the cybotactic clusters there is a short-range network structure, which can be considered as formed by short branched helical column segments with uniform chirality, similar to the long range structure in SmQ*. These uniform helices provide a template for cooperative chirality synchronisation of the transiently chiral molecules, which in a feed-back process stabilises the local helical superstructure. The cybotactic clusters interact with formation of dynamic networks. As soon as the connectivity of this network exceeds a certain critical value a phase transition from the macroscopically achiral to the macroscopic symmetry broken chiral conglomerate phase takes place (Figure 7). In the \( Is0^* \) phases, the network structure is provided by weak dynamic interaggregate interactions retaining the liquid state, whereas in the DC phases they are formed by random connections between the layer fragments, and in the \( Im3m^* \) and SmQ* phases by the evolving periodic networks. In this order, there is an increasing support of chirality synchronisation by the network formation, i.e. chirality synchronisation becomes more likely.

An \( Is0^* \) phase was also observed as re-entrant isotropic liquid in the phase sequence of the polycatenar molecule 24 below an achiral nematic phase and before the transition to a cubic phase (Figure 25) [236]. In this case the growing coherence length of chirality synchronisation with lowering temperature is in competition with the long range orientational order in the N phase. The nematic phase is removed and the denser segregated helical packing of the molecules in the chirality synchronised domains of the \( Is0^* \) phase obviously provides an energetic advantage for the packing at lower temperature. Similar effects can be expected for the N DC transitions observed for some bent-core mesogens [93].

According to computer simulations all chiral superstructures observed in LC phases of achiral molecules, ranging from the DC phases [237] via \( N_{TB} \) phases [192] to the columnar phases [215] can be formed without assuming any conformational chirality, i.e. totally rigid molecules should also be capable of forming these...
chiral phases. It is difficult to prove this hypothesis practically with totally rigid and achiral molecules, because they would immediately crystallise before forming a LC phase. However, the observation of spontaneous chiral conglomerate formation in isotropic liquids provides a strong experimental argument for the existence of a cooperative conformational chirality synchronisation process, which is very likely to support the formation of the helical superstructures in the LC phases of transiently chiral mesogens [8]. Moreover, the observation of the SmQ$^*$ phase for transiently chiral molecules, but not for racemic mixtures of permanently chiral molecules [203,206] indicates that at least the formation of the SmQ phase requires helical molecules with synchronised helix sense and it appears that also the Im3$m^{[*]}$ phase in thermotropic LCs of rod-like molecules represents a chirality synchronisation induced LC phase. In contrast, the Im3$m$ phase formed in lyotropic systems is achiral and has a simpler structure, formed by only two networks involving six-fold nodes, separated by a Schwarz P-surface [222].

16. Development of homogeneous chirality in fluids

Under achiral conditions spontaneous mirror symmetry breaking leads to conglomerates composed of equal amounts of the distinct enantiomorphic superstructures, i.e. symmetry breaking is only local (Figure 1(a,b)). However, chirality amplification (Figure 1(c)), leading to a non-equal distribution of the enantiomeric domains is a typical feature of all LC conglomerates [66,89]. For example, in the case of Iso$_1^{[*]}$ phases $10^{-8}$ mol% of a chiral dopand were found to be sufficient for a deviation from equal distribution of the chiral domains in the conglomerates and $10^{-3}$ mol% were sufficient for development of uniform chirality [89]. Likewise, chiral surface effects can easily lead to homogeneous chirality [36,39]. Complete deracemisation can also be achieved spontaneously as a consequence of the phase transition kinetics, if slow seed formation is combined with fast growth, as observed at the Iso$_1^{[*]}$ – Im3$m^{[*]}$ transition, shown in the video attached to ref. [99]. The first nucleus of Im3$m^{[*]}$ is formed arbitrary in one of the enantiomeric domains of the Iso$_1^{[*]}$ phase and grows fast within the domains with the same chirality and slower (due to the required helix inversion) in the domains with opposite chirality, while preserving the chirality sense once chosen. In this way, the boundaries of the chiral domains are crossed and uniform chirality develops throughout large areas or even across the whole Im3$m^{[*]}$ phase. This process is stochastic, i.e. depending on the initially formed nucleus, either sense of chirality is obtained with equal probability. Thus, chirality synchronisation of transiently chiral molecules in the liquid state provides a transition from local to global symmetry breaking, thus leading to route to homogeneous chirality, not achievable with racemic mixtures of permanently chiral molecules.
In principle chiral segregation, i.e. the spontaneous separation of permanently chiral enantiomers of racemic mixtures into a conglomerate is also possible (Figure 1(a)). This has been shown for field induced deracemisations in SmC phases of racemic rod-like or bent-core compounds [111–113]. However, it is diffusion controlled and therefore slow and, even more importantly, it cannot lead to uniform chirality in the absence of any accompanying racemisation process. This means that development of uniform chirality requires a sufficiently fast racemisation kinetics leading to a temporary loss of the chiral information (chiral amnesia) [238–240]. Thus, liquid or liquid crystalline states formed by transiently chiral molecules or supramolecular aggregates, capable of cooperative chirality synchronisation, provide the ideal medium for the development of homogeneous chirality.

**Summary and conclusions**

In summary, dynamic chirality synchronisation of transiently chiral molecules or supramolecular aggregates in liquids and liquid crystals is a new mode of mirror symmetry breaking under thermodynamic control, providing long term stable symmetry broken fluids, even at high temperatures. These fluids form conglomerates which are capable of strong chirality amplification eventually leading to homogeneous chirality. Especially the observation of spontaneous chiral segregation in isotropic liquids provided a strong boost for the conformational chirality hypothesis, which is also supported by recent simulation work [114–116]. However, chirality synchronisation in the fluid state requires cooperativity, i.e. a local cybotactic or long range ordered structure; therefore, it is often stabilised or supported by surface effects. On the other hand, chiral configurations induced by surface alignment or chiral director configurations (chiral surface effects) can be efficiently amplified in these liquids and thus can cause surface induced mirror symmetry breaking in nematic and SmC phases (Figure 26).

Diastereomeric coupling of transient molecular chirality with the aggregate chirality, which could be provided by a twisted or helical superstructure or by layer chirality, can additionally support chirality synchronisation. A still open question concerns the actual strength and importance of this coupling in the distinct liquid crystalline phases, i.e. is it the chirality synchronisation which determines the long range superstructural chirality [138], or, the other way around, does the chiral superstructure only provides some bias for a partial synchronisation of chiral conformations [157] or could it even disregard chirality at the lower level, as shown for some crystalline columnar assemblies [241]. According to the present state of knowledge it appears that only the organisation in ribbons or columns can act as template for the synchronisation of molecular conformers of properly designed molecules, whereas the lamellar organisation acts as an ‘anti-template’ disfavouring or suppressing conformational chirality synchronisation. In the non-distorted lamellar organisation (this also includes lamellar cybotactic clusters) only layer chirality and heliconical structures can develop and the latter are stabilised by the escape from macroscopic polar order. However, due to the strong coupling between these layers and between layers and surfaces any surface induced chiral director alignment can easily be amplified to give macroscopic chirality. Thus, heliconical structures can be very sensitive to surface effects.

Even the spontaneous chirality synchronisation in columnar aggregates can only become long range if there is strong homochiral lateral coupling between the columns or cooperativity develops in all three dimensions by network formation (Cub, Iso\(^{Ia3d}\), Figure 7). In the optically isotropic DC phases of bent-core molecules the layers are strongly distorted by steric and geometric frustration and the sponge-like structure provides cooperativity in all three dimensions (Figure 20). So there is at least the possibility that conformational chirality synchronisation contributes to conglomerate formation in the polar smectic phases of bent-core mesogens. In all mirror symmetry broken isotropic mesophases (Iso\(^{Ia3d}\), Cub\(^{Ia3d}\), DC) the local structure must be distinct from the achiral \(Ia3d\) structure and the preferred interaggregate coupling has to be homochiral. The SmQ phase structure provides a good model for a possible uniformly chiral local aggregate structure in the isotropic liquid phases occurring besides bicontinuous (cubic and non-cubic) mesophases. Chirality of these local aggregates is synchronised at a phase transition to Iso\(^{Ia3d}\) as the number of
interaggregate connections exceeds a critical size (Figure 7). The optical rotation in the chiral liquids and the LCs formed by permanently, as well as transiently chiral molecules can have different origins and depends on the phase structure, as shown in Figure 27.

The impact of this dynamic mode of mirror symmetry breaking in the liquid state goes far beyond the field of LCs. It leads to an alternative ‘non-chemical’ mode of chirality amplification, and provides a medium for chirality detection, as well as a templates for enantiomer separation and enantioselective synthesis. Moreover, it provides an alternative view on the emergence of uniform chirality at the transition from prebiotic to biotic systems. Accordingly, chirality could have developed first with transiently (conformational or configurational) chiral molecules which provided thermodynamically stable symmetry broken prebiotic fluids; in these fluids uniform chirality became permanent during formation of the (bio)polymers. This is supported by some preliminary experiments. For example, chirality synchronisation in Iso* phases of polycatenar compounds like compound 4 (Figure 9) can be retained in lyotropic systems with up to 50% of an achiral hydrocarbon solvent [89]. In addition, even simple polar substituted heterocycles, being in some respect related to the nucleobases, both combining hydrogen bonding flat \( N \)-heterocycles with hydrophilic units (see Figure 28), are capable of conglomerate formation in an isotropic mesophase [243]. This shows that this hypothesis might not only be illusive. Moreover, cubic phases, which appear adjacent to the symmetry broken liquids are common in aqueous lyotropic systems [222], so that also aqueous Iso* phases are feasible in the future. In any case, LC science has the capability to advance the development in the field of spontaneous mirror symmetry breaking in fluids with great impact for the understanding of the fundamental question of development of homogeneous biochirality [1].

**Note**

1. A similar chiral domain texture as observed for compound 6 (Figure 12) was also reported for a SmCP \( R \) like phase of a bent-core molecule derived from 4-chlororesorcinol, but in this case there is a much larger tilt and a DC phase is induced under an applied field, so that this phase appears to be somewhat different [63].

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