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INVITED ARTICLE

meta-Cybotaxis and nematic biaxiality

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In 1970, two seemingly unrelated reports about nematic liquid crystals appeared in the scientific literature: at Kent State University, Adrian de Vries reported local smectic order in a nematic that he termed *cybotactic*, and at IBM, Marvin Freiser showed the possibility of a lower symmetry nematic that he named *biaxial*. These two discoveries are connected through consideration of the origins of spontaneous symmetry breaking, in particular, how broken symmetry within transient clusters permeating a nominally uniaxial nematic may lead to a biaxial nematic.

Keywords: biaxial nematic; cybotactic; bent-core mesogen; nematic

1. Introduction

Alfred Saupe's 1968 paper '*Recent Results in the Field of Liquid Crystals*' [1] remains to this day a valuable review that masterfully documents the understanding at that time of the micro-, meso- and macroscopic subtleties underlying this curious state of matter. The section titled *Nematic Liquids* begins, 'Nematic liquids differ structurally from normal isotropic liquids only in the spontaneous orientation of the molecules with their long axes parallel (Figure 1).' In an accompanying schematic figure (similar to Figure 1 here) Saupe indicates an absence of translational order in the nematic but he does not say anything about the short-range structure in this simplest of all the liquid crystal phases. Short-range angular correlations between nearest neighbour mesogens are also omitted from the molecular field Maier–Saupe model of the isotropic to nematic (I–N) phase transition [2]. The experimental manifestation of short-range structure in liquid crystals (e.g. magnetic/electric birefringence, light scattering, etc.) is usually studied in the isotropic state above the I–N transition and referred to as pre-transition phenomena. Experimental data are adequately described by the mean field theory of Landau–de Gennes, a formalism which gives an explicit temperature dependence of the observables as the I–N transition is approached [3]. A component of that theory is the extent of local positional/orientational order: it persists over a characteristic distance $\xi(T)$ called the coherence or correlation length, and the theory predicts that $\xi(T) = \xi_o[T^*/(T - T^*)]^{1/2}$, where ξ_o is a molecular dimension, and at T^*, just below the I-N transition, the correlations extend over macroscopic dimensions, i.e. $\xi(T^*) \to \infty$ [3].

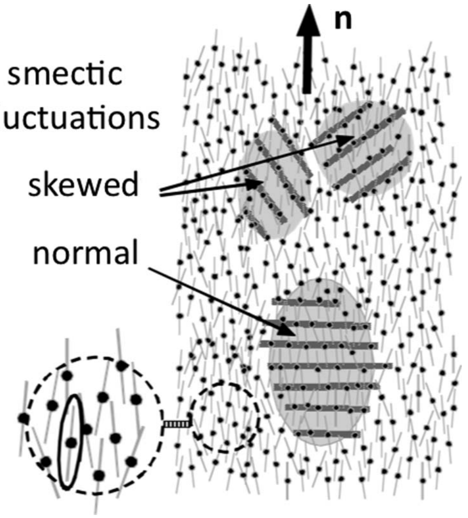

Figure 1. Idealised two-dimensional rendering of a nematic phase exhibiting skewed (top) and normal (bottom) smectic fluctuations; the inset depicts the excluded area of a calamitic mesogen represented by an ellipse.

In the nematic phase every configuration – every instantaneous conformation of each mesogen and its orientation – weighted by the conformer's internal energy and its multiple short-range intermolecular interactions in the nematic, contributes to the structure. However, because of the challenges associated with atomistic simulations, simplifying concepts have emerged such as the 'statistical mesogen' – an average mesogen shape defined by its van der Waals envelope that, in turn, may be envisioned by conceptualising an average over the mesogens' internal degrees of freedom. Such simplifications have facilitated the development of coarse-grain modelling via the formulation of idealised attractive potentials in conjunction with simple excluded volume considerations. Concomitantly,

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Saupe's descriptor, *long axes* (of liquid crystal molecules), appears to have evolved and acquired the status of a pseudo-symmetry axis of the statistical mesogen. Considering the work of de Vries and Freiser together gives us a new way of appreciating lower symmetry nematic phases discovered in the intervening years since Saupe's review (see Note 1).

1.1 Cybotactic nematic

One of the first direct observations of short-range structure in nematics was reported in 1970 when Adrian de Vries of Kent State University presented 'evidence for the existence of more than one type of nematic' [4]. His evidence took the form of four off-meridional X-ray scattering peaks along the direction of the globally aligned nematic director, **n**. The peaks were located at wavevector $Q \sim 2\pi/\langle L\rangle$, where $\langle L\rangle$ is the average length of the mesogen derived by weighting the length of each mesogen conformer by both the conformer's internal energy and its orientational energy in the nematic mean field. This four-spot scattering pattern coexists with the usual equatorial scattering (two arcs on the equator at $Q \sim 2\pi/\langle D\rangle$, where $\langle D\rangle$ is the average mesogen diameter). The equatorial scattering is associated with nearest-neighbour positional correlations among the quasi-parallel mesogens in the transverse direction (normal to **n**). The extra four-spot scattering observed by de Vries in some nematics was also independently discovered by Chystyakov and Chaikowsky [5], and eventually there was a consensus interpretation: it was ascribed to transient, local, positional order in the nematic in the form of smectic fluctuations – evanescent density waves [6] having the smectic layer either normal or tilted relative to **n**. The propensity for nematics to exhibit this extra scattering was attributed to a type of pre-transitional phenomenon because the off-meridional scattering was reported to intensify as the temperature was lowered in the nematic approaching an underlying N–smectic phase transition.

The X-ray evidence for smectic C-like fluctuations, skewed short-range translational correlations among mesogens in the nematic phase, was named a smectic C nematic by de Vries; in the more widely adopted nomenclature it is called a (skewed) *cybotactic nematic*. Similarly, a smectic A nematic refers to transient positional correlations among the mesogens resulting in evanescent density waves perpendicular to **n**, and nematic phases showing this additional scattering are sometimes called normal cybotactic nematics. These smectic fluctuations are illustrated in Figure 1 with a two-dimensional cartoon wherein a calamitic mesogen has its molecular long axis represented by a line, and a dot is placed at the idealised mesogen's centre of mass. Marginally more realistic illustrations of nematic phases use cartoons that incorporate a space-filling statistical shape to represent calamitic mesogens, e.g. ellipsoids of revolution, or parallelepipeds.

1.2 Biaxial nematic

Coincidentally, and concurrently with de Vries in 1970 but working in a corporate laboratory at IBM, Marvin Freiser predicted the viability of a new type of nematic having three directors, **n**, **m**, and **l** (and correspondingly, two optic axes), that he termed a *biaxial nematic* [7]. Freiser extended the Maier–Saupe mean field theory [2] developed for idealised, uniaxial, calamitic mesogens to biaxial, rectilinear, parallelepiped-shaped mesogens. He observed that on lowering the temperature, the isotropic phase transformed via a first-order phase transition into a typical uniaxial nematic phase (N_U). On lowering the temperature further, however, Freiser's system exhibited a second-order phase transition to a biaxial nematic phase (N_B). Since Freiser's statistical mesogens had D_{2h} symmetry (i.e. an orthorhombic, parallelepiped shape), it was reasonable to find that the biaxial nematic phase exhibited the same symmetry as that of the mesogen, an orthorhombic biaxial nematic denoted N_{Bo}. Both types of nematic phases, N_U with $D_{\infty h}$ symmetry, and the N_{Bo} phase with the same orthorhombic D_{2h} symmetry as its constituent statistical mesogens, are translationally disordered fluids and are schematically illustrated in Figure 2.

Considered together, and with the benefit of hindsight, the contemporaneous discoveries of de Vries and Freiser can deepen our understanding of the interplay between short-range structure and macroscopic attributes of the nematic phase. De Vries' adoption of the term cybotaxis was divorced from the context in which

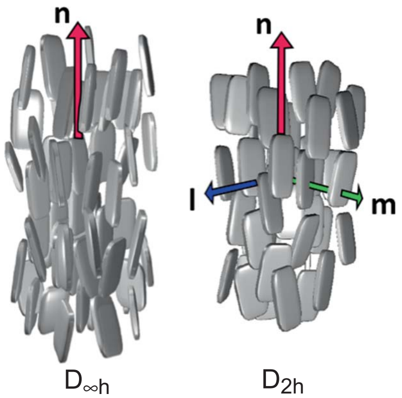


Figure 2. Schematic illustrations of volume elements of an apolar, uniaxial nematic phase (N_U) exhibiting $D_{\infty h}$ symmetry (left), and an apolar, orthorhombic biaxial nematic phase (N_{Bo}) with D_{2h} symmetry (right); each volume element is composed of rectilinear, parallelepiped statistical mesogens.

it was originally invoked, simple molecular liquids. And Freiser did not consider the possibility that mesogen shape might conform and couple to spontaneous symmetry breaking. However, the conjuction of de Vries' and Freiser's concepts can reconcile new experimental nuclear magnetic resonance (NMR) data indicating biaxiality in the nematic phase of bent core mesogens.

2. Results and discussion

2.1 Cybotaxis versus meta-cybotaxis

The term *cybotaxis* has been used so variously that it has almost lost its scientific usefulness. To differentiate the kind of local supramolecular positional correlations in some nematics from the cybotaxis that is present in all liquids, I suggest adopting the term *meta-cybotaxis*. One of the meanings of the prefix *meta-* is 'beyond, transcending, encompassing.' Another is 'higher, more developed.' By suggesting the term meta-cybotaxis I am trying to distinguish correlated positional correlations that are beginning to be recognised as an underlying dominant attribute of bent-core nematics [8–10], from the very short-range, non-specific, nearest-neighbour molecular packing that characterises all liquids. It is the latter that was originally termed cybotaxis; I refer to it as *classical cybotaxis*. In order to appreciate these distinctions and perhaps justify the need for more precise terminology, it may be helpful to review the origin of the term cybotaxis.

The nature of the structure observed in the liquid state was unresolved in the early part of the twentieth century, and at that time it was difficult to accept that a modest change in temperature or pressure could transform a crystalline solid into a fluid with molecules exercising completely random motion without any evidence of positional ordering. Shortly after the discovery that simple liquids exhibit a diffuse halo X-ray diffraction pattern (at scattering vector $Q \sim 2\ \pi/<D>$ where $<D>$ is the mean molecular diameter), scientists tried to rationalise the existence of a space array, that is a rigid array of molecules positioned on lattice sites, in simple liquids. The emerging picture of non-associated liquids as fluid phases with no semblance of a space array was hard to accept and the diffuse halo scattering observed in simple liquids reinforced that incredulity. It was in that context in 1927 that Stewart and Morrow, studying the X-ray diffraction from simple alcohols, introduced nomenclature to describe short-range translational order in liquids. The Greek noun *cybotaxis* (adjective, *cybotactic*), meaning space arrangement, was proposed to differentiate the short-range structure apparent in the scattering from simple liquids from the long-range structure in the crystalline state [11]. By analogy, de Vries proposed the term cybotactic nematic to differentiate the short-range smectic structure (fluctuations) in simple nematics from the long-range stratified structure of the smectic phase.

As characterisation techniques are refined, it may become necessary to differentiate the different kinds of positional correlations in liquid crystals. The very-short-range packing-mediated positional order in simple liquids (classical cybotaxis) is also present in nematic liquids, but diffraction evidence for such may be masked in unoriented phases by long-range orientational correlations. In order to emphasise the distinctions between short-range structure and supramolecular positional order it is useful to consider the evolution in a nematic liquid on cooling from its isotropic state, tens of degrees above T_c, where the orientational correlation length $\xi(T) = 0$, i.e. molecules move randomly under close-packed conditions influenced only by nearly independent, nearest-neighbour considerations (classical cybotaxis). As the temperature in the isotropic state is lowered and the I–N phase transition is approached, transient supramolecular organisation develops (cluster formation in which $\xi(T) > 0$). The embryonic, short-lived nematic clusters are characterised by long-range mesogen orientational order. The *i*th cluster has its own director $\mathbf{n}^i$, and the directions of the $\mathbf{n}^i$ in the absence of external fields are uncorrelated so that the overall symmetry of the liquid appears to be isotropic. The locally broken symmetry within each cluster subtly influences the short-range mesogen packing and it is anticipated that classical cybotaxis would exhibit some degree of anisotropy within a cluster, i.e. positional correlation lengths along $\mathbf{n}^i$ are expected to be different from the extent of correlations normal to $\mathbf{n}^i$. Such anisotropy would be apparent in large clusters oriented by a sufficiently strong field; it is readily apparent in the diffraction pattern from a macroscopically oriented, fully developed nematic phase.

As previously stated, simple uniaxial nematics are characterised by an absence of translational order, longitudinal or transverse positional correlations along or perpendicular to **n**, respectively. Does this imply that the correlation lengths derived from X-ray scattering of an oriented nematic, $\xi_{||}$ and $\xi_{|}$, are of the same magnitude as that observed in simple liquids, i.e. that structure in the nematic persists for at most a couple of molecular dimensions? Along **n** the relevant dimension is the statistical mesogen's average length $<L>$, and it is anticipated that $\xi_{||}\ /<L> \sim 2$ for classical cybotaxis. This appears to be experimentally confirmed [12]. However, the transverse positional correlations are larger by a factor of two or so ($\xi_{|}/<D> \sim 4$, where $<D>$ is the average mesogen diameter). Also, $\xi_{|}$ appears to be independent of temperature in conventional calamitic nematics, e.g. MBBA and EBBA [12]. Moreover, $\xi_{|}$ does not change significantly on passing into the isotropic phase just above T_c, confirming that intra-cluster structure in the pre-transitional region is similar to that in the fully developed nematic phase. This suggests that the observed anisotropy of ξ in nematics is simply a manifestation of classical cybotaxis in molecular liquids composed of close-packed anisometric molecules. The suggestion that classical cybotaxis advanced by Stewart and Morrow may depend on the aspect ratio of the molecules comprising the liquid, i.e. the possibility that $<L>/<D>$ might influence the extent of local packing preferences, does not appear to have been quantitatively and systematically investigated. Even if we assume that the anisotropy and attendant increase in transverse positional order in nematics and in nematic clusters above T_c constitutes classical cybotaxis, then it is necessary to view the extra supramolecular organisation – stratification – engendered by (pre-transitional) smectic fluctuations in the nematic as an additional form of short- to intermediate-range structure, meta-cybotaxis. That is, meta-cybotaxis refers to the more developed, albeit transient, clusters of several hundred mesogens ($\xi_{\|}/<L> \geq 2$, and $\xi_{|}/<D> \sim 10$) that exhibit normal or skewed density waves with mesogens confined to strata normal to, or at an angle to, **n** in the nematic.

When de Vries interpreted the extra X-ray diffraction exhibited by certain nematics, in effect he was attempting to characterise an explicit type of supramolecular organisation, something beyond mere (anisotropic) nearest-neighbour packing (classical cybotaxis). He was searching for nomenclature that would describe the extra meridional or off-meridional scattering that resulted from the mesogens' tendency to condense into two-dimensional strata normal to or aligned at an angle to **n**. Figure 3 coarsely depicts embryonic clusters of normal smectic A strata (left) and skewed smectic C strata (right) nucleating in a nematic host of parallelepiped-shaped molecules. Skewed density waves induce spontaneous local symmetry breaking of the uniaxial nematic locally transforming its $D_{\infty h}$ symmetry into short-lived biaxial domains of lower symmetry, e.g. D_{2h}, C_{2h} or C_2 symmetry. In the following section cooperative selection of statistical shapes of mesogens that are consonant with spontaneous symmetry breaking is examined for the case of bent-core mesogens.

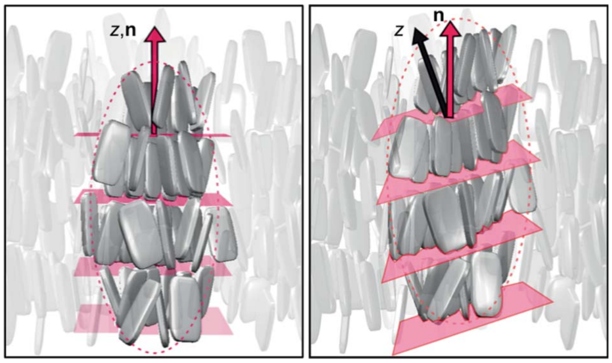


Figure 3. *Meta*-cybotatic clusters of rectilinear parallelepipeds in a host nematic medium. Left: Smectic A cluster formation with the *z*-axis (normal to the layers) parallel to **n**. Right: Smectic C cluster with the *z*-axis tilted with respect to **n**.

Note that the depiction of the smectic C cluster (Figure 3, right) is inaccurate: the cartoon fails to show that a molecular shape change is coupled with the (local) symmetry breaking of the phase. The lower cluster symmetry, D_{2v}, grows into the $D_{\infty h}$ symmetry of the N_U host medium, and that spontaneous symmetry breaking is accompanied by a change in the statistical shape (conformer population) of the mesogen. For example, the rectilinear orthorhombic parallelepiped statistical shape might transform into a skewed rhomboid statistical shape. And accommodating that shape in tilted strata would be accompanied by overt transverse orientational correlations, rotations about rhomboid long axes would be correlated, enabling the large surface faces of neighbouring rhomboids to be adjacent to one another, defining a second local director in the (biaxial) smectic C-like cluster.

2.2 Mesogen statistical shape

In an effort to ascertain the underlying physics in ordered fluid phases, the molecules comprising liquid crystals are frequently idealised as highly symmetric, rigid bodies, e.g. cylinders, discs, parallelepipeds and space-filling boomerangs (see Figure 4) for calamitic, discotic, orthorhombic/sanidic, and bent-core mesogens, respectively. In all of these representations the aliphatic tails are left out. However, such simplifications can be misleading and often are not consonant

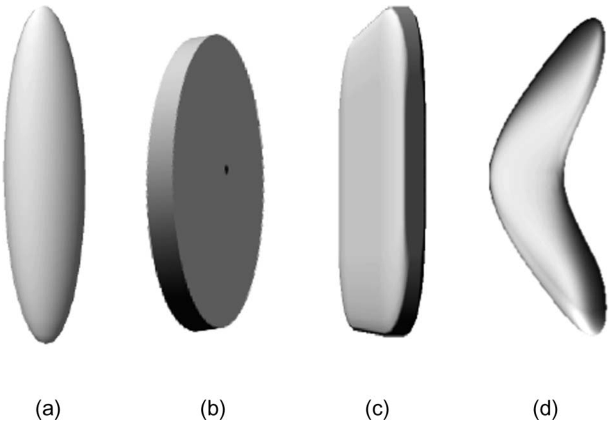
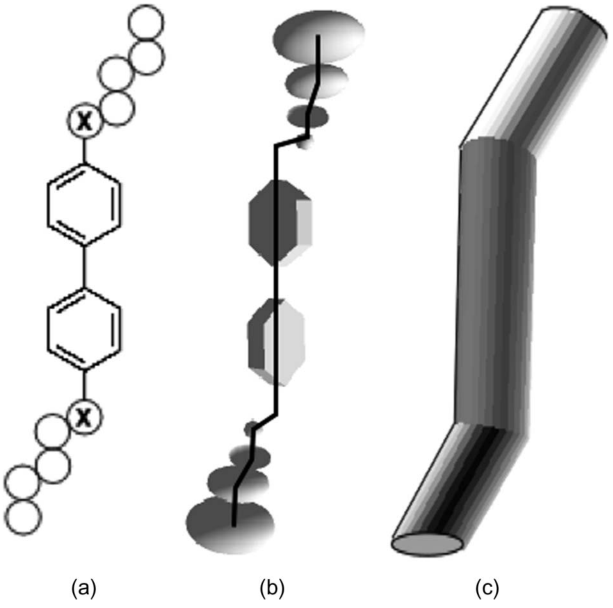


Figure 4. Coarse grain rigid bodies used to represent the idealised statistical shapes of (a) calamitic, (b) discotic, (c) orthorhombic/sanidic, and (d) bent-core mesogens. These global, statistical shapes are devoid of crucial molecular details, i.e. the excluded-volume envelope of the flexible tails.

with the symmetry of the mesophase (see e.g. Figure 3, right). While there are examples of real mesogens without flexible tails, e.g. *p*-quenquiphenyl [13], in general the tails play a pivotal role in stabilising the mesophase relative to the crystal, and often determine the phase type (nematic or smectic). In order to capture the interplay between mesogen symmetry and phase symmetry, especially the cooperative selection of mesogen statistical shapes and spontaneous symmetry breaking, more realistic models of mesogenic architectures are essential.

Figure 5(a) shows an atomistic primary structure of a prototypical calamitic mesogen that is based on a biphenyl core terminated with flexible aliphatic tails. The latter are shown as a contiguous chain of open circles that represent the united atom –CH_2- and terminal –CH_3 groups. In Figure 5(b) the nebulous envelope of the positional locations of the methylenes and terminal methyl groups are depicted as ellipsoids of probability density relative to the more defined core atoms. That approximate statistical shape is based on the findings of Emerson *et al.* [14]; they computed the probability of finding specific tail atoms relative to the core (using a core-fixed frame of reference). They noted changes in the statistical shape of the mesogen between the isotropic and nematic phases, subtle differences in the atom probability densities on passing from the isotropic state to the nematic state wherein each conformation is constrained by a potential of mean torque [14]. Similar shifts in conformer probabilities were noted in alkanes solubilised in nematic solvents [15], i.e. flexible solutes and flexible mesogens bias their conformer probabilities in order to accommodate the constraints of the nematic molecular field. Embedded in Emerson *et al.*'s depiction (see Figure 5(b)) are the geometrical consequences of how valence and dihedral angles in the linkage of the aliphatic tail to the aromatic ring-plane dictate the mean direction in which the tail propagates away from the mesogenic core. A coplanar tail trajectory is anticipated for **X** = -O-, whereas tail propagation in a plane normal to the adjacent ring-plane is favoured by dihedral angle energetics for **X** = -CH_2-. However, since ring-flips and ring-rotations about the *para* axis occur on a timescale comparable to molecular libration/rotation dynamics, the illustration in Figure 5(b) must be recognised as a statistical shape that readily conforms to the local packing influences of near-neighbour mesogens. The explicit positional probability densities of the tail atoms and core are abstracted further in Figure 5(c), a primitive statistical shape that captures the oblique, excluded-volume envelope associated with the mean direction of propagation of the tail segments relative to the core.



(a) (b) (c)

Figure 5. Calamitic mesogen statistical shapes. (a) A prototypical calamitic mesogen primary structure based on a biphenyl core and united atom flexible tails with linkage **X** (= ether or methylene); (b) approximate mesogen statistical shape according to Emerson *et al* [14]; (c) primitive mesogen statistical shape according to Vanakaras *et al.* [16].

Vanakaras *et al.* [16] extended our picture (Photinos and Samulski's) of spontaneous polarisation [17] with the first molecular model of smectics accounting for the spontaneous symmetry breaking associated with the tilt and adjacent layer clinicity. That model used the primitive statistical mesogen shape in Figure 5(c) and emphasised that the origin of tilt, polarity and spontaneous symmetry breaking depends explicitly on the inclusion of excluded-volume interactions stemming from the envelope of tail-atom configurations in the statistical mesogen [16]. In sum, Vanakaras *et al.* showed that their primitive mesogen shape captured the essential physics underlying the origin of spontaneous polarisation in tilted smectic liquid crystals, namely, that packing constraints drive a tilt-dependent correlation of the molecular shape (conformation) with molecular orientation in the smectic strata. Moreover, the same primitive shape proved to be sufficiently rich to link it directly with subtle effects such as sign inversions of the spontaneous polarisation [17] and the helical pitch in chiral smectics [18]. While their primary focus was on symmetry breaking in the smectic phases of calamitic mesogens, Vanakaras *et al.* [16] anticipated that similar considerations would apply to discotic and bent-core mesogens, and they illustrated schematic primitive statistical shapes for these types of mesogens as well (see Figure 3, in Vanakaras *et al.* [16].

Cognisant of those results, we can reconsider how a bent-core mesogen may be represented by a primitive shape that captures the essential directional-dependent excluded-volume envelopes of the flexible tails

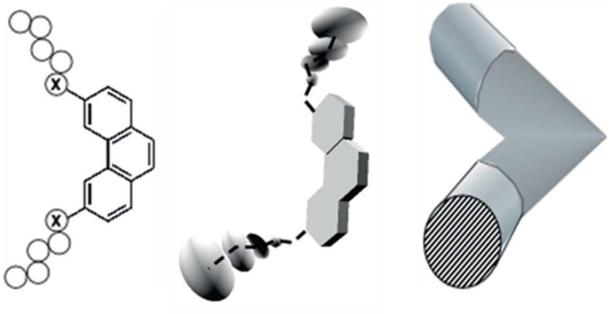

(a) (b) (c)

Figure 6. A prototypical bent-core mesogen primary structure based on (a) phenanthrene core and united atom flexible tails with linkage **X** (= ether or methylene); (b) approximate mesogen statistical shape after Emerson *et al.* [14]; (c) primitive mesogen statistical shape according to Vanakaras *et al.* [16].

relative to that of the core, and show how the symmetry of the bent-core shape is consonant with observed (polar) smectic and (biaxial) nematic phases. Statistical shapes of a bent-core mesogen are shown in Figure 6. In contrast with the idealised shape shown in Figure 4(d) having D_{2h} symmetry, the primitive shape representation (see Figure 6(c)) has considerably lower symmetry (C_2). This has implications for supramolecular organisation in banana phases.

In their seminal paper on chiral banana phases, Link *et al.* [19] did not explicitly include the envelope of the flexible tail configurations in their highly abstracted representation of bent-core mesogens. Rather, their focus was on chiral supramolecular arrangements displayed by achiral mesogens. Chirality was, in their representations, brought about by three symmetry-breaking considerations: (1) stratification of bow-shaped (bent-core) mesogens (with the layer normal denoted by z); (2) polar alignment (along $\boldsymbol{b}$, normal to z) of steric/electrostatic dipoles coincident with the C_2-axis of the bent-cores; (3) tilt of the aligned mesogens (along $\boldsymbol{c} = \boldsymbol{b} \times z$ by a rotation about $\boldsymbol{b}$, the mesogen C_2-axes). Such supramolecular chirality was divorced from any cooperative molecular transformation, and as a result, the $\mathbf{c}^{(+)}$ and $\mathbf{c}^{(-)}$ enantiomeric supramolecular packing arrangements (with opposite polarities, i.e. steric/electrostatic dipoles parallel and antiparallel to $\boldsymbol{b}$) were colour coded by Link *et al.* to differentiate the abstracted representations of the mesogens in arrangements having opposite chiralities (see Figure 1 of Link *et al.* [19]). In contrast, the Vanakaras representation can adopt inherently chiral shapes (see Figure 7). This will happen if specific conformations of the primitive shape are populated by cooperative lateral packing considerations when the bent-core mesogens stratify and tilt. Moreover, the primitive representation naturally conforms to the spontaneous symmetry breaking associated with the formation of homogeneously chiral supramolecular strata and racemic strata in mesophases as categorised by Link *et al.* [19]. The clinicity and (anti-)ferroelectricity of such phases also naturally result from optimally packing chiral primitive bent-core shapes.

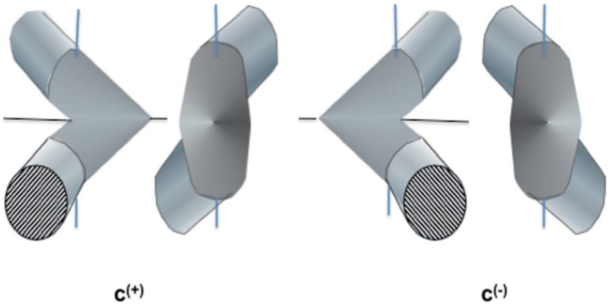


Figure 7. Primitive shapes of a prototypical bent-core mesogen (see Figure 6) showing side and end-on views of chiral enantiomers, non-superposable mirror images, $\mathbf{c}^{(+)}$ and $\mathbf{c}^{(-)}$; the single symmetry element, a C_2-axis (horizontal), is shown in the side views.

2.3 Spontaneous symmetry breaking

The canonical example of spontaneous symmetry breaking in liquid crystals is the smectic A to smectic C phase transition, where a tilt director **c** develops in a random direction in the plane of the smectic strata. Concomitantly, a configuration of the (primitive) mesogen that is best accommodated by the local tilted molecular field is selected. The direction of **c** is randomly chosen but may be correlated with that in neighbouring layers. Tilt may be the same from layer to layer (synclinic) or alternate opposing directions (anticlinic); tilt may also circumscribe a helix for chiral mesogens in smectic C* phases. A primitive mesogen shape with nominally C_{2h} symmetry is biased toward one having C_{2v} symmetry to enable the propagation of cooperative tilt, e.g. a primitive calamitic shape like that shown in Figure 5(c) is preferred in the tilted molecular field. The transformation of the statistical shape is driven by extra-molecular considerations, intermolecular spatial correlations that underlie spontaneous symmetry breaking in mesophases. Some degree of longitudinal translational order is a prerequisite for propagating mesogen shape correlations and mesogen tilt. Longitudinal translational order is present in the uniaxial smectic A phase, but the packing density in that phase is insufficient to nucleate domains with tilt-enabling conformer shapes [16]. That is, within a given stratum in the smectic A phase, domains having correlated conformation and tilt fail to exceed some critical embryonic size and are meta-stable. At the Smectic A–Smectic C transition, fluctuations exceed the critical size, the uniaxial symmetry of the smectic A is broken, and the lower C_{2v} symmetry of the smectic C phase is stabilised. It appears that related spontaneous symmetry breaking occurs in the biaxial nematic phase of the ODBC bent-core mesogens, i.e. the biaxiality is driven by cluster formation exhibiting stratification and tilt, skewed meta-cybotaxis.

2.4 *Deuterium NMR in a biaxial nematic phase*

The NMR technique obviates ambiguities such as surface-induced biaxiality as the sample volume is macroscopic. As a result, observed NMR phase biaxiality in a nematic is an unequivocal indicator of an N_B phase. In nematics with $\Delta\chi > 0$ (positive diamagnetic anisotropy with $|\chi_n| < |\chi_m| \leq |\chi_l|$), the primary director **n** is aligned along the magnetic field, **B**. In the fluid phase all of the second-rank, tensorial, nuclear magnetic interactions (e.g. chemical shift, σ, dipolar, **D**, and quadrupolar, **q**) are incompletely averaged by rapid, nearly random molecular diffusive motion. Hence these averaged interactions reflect the symmetry of the phase. However, in NMR those averages are projected onto the **B**-direction (coincident with the laboratory frame *Z*-axis), and for a static, aligned sample, NMR detects only the **n**-component of the averaged interactions ($q_{ZZ} = <q>_{nn}$). In order to determine η, the biaxiality of the phase via, for example, the biaxiality of $<\boldsymbol{q}>$, the transverse components $<q>_{ll}$ and $<q>_{mm}$, the averaged quadrupolar interaction along the minor directors **l** and **m**, must be determined. This is most readily accomplished by rotating the sample about an axis (X) normal to **B**. Rotating the sample about X will align the smallest value χ_l along X, and uniformly distribute the other two components of the averaged interactions (e.g. $<q>_{nn}$ and $<q>_{mm}$, the **n**- and **m**- components of $<\boldsymbol{q}>$) in a plane normal to X. The random distribution of the **n** and **m** directors in a plane normal to X and tangential to **B** results in a two-dimensional powder pattern which can be fitted to extract the magnitudes $<q>_{nn}$ and $<q>_{mm}$. Finally, if $|<q>_{mm}| \neq ½|<q>_{nn}|$, the nematic phase is biaxial.

Our (Madsen *et al.*'s) NMR evidence for phase biaxiality [20] was obtained in the high-temperature nematic phases of ODBP mesogens, bent-core mesogens based on the non-linear oxadiazole biphenol core [21]. While those findings were not without controversy [22, 23], careful analysis and comparisons with known uniaxial nematics confirmed the validity of the NMR biaxiality [24]. However, those NMR studies were indirect in the sense that Madsen *et al.* [20, 24] used mesophases doped with a deuterium-labelled probe molecule (hexamethylbenzene-d_{18}). In fact, the initial deuterium NMR measurements were carried out with deuterium-labelled ODBP mesogens [25]. In one case ODBP-Ph-d_4-O-C_{12} (outer rings labelled), the observed biaxiality was very small, and in the other case, ODBP-d_4-Ph-O-C_{12} (inner rings labelled; Figure 8, inset), the absence of a correspondence between the measured chemical shift anisotropy (CAS) in the static sample ($\sigma_{ZZ} = <\sigma>_{nn}$) and the CAS required to fit the two-dimensional powder pattern was puzzling. The large value of the CSA used to obtain the fit in Figure 8 implies that identifying σ_{ZZ} with the maximum value of the CSA is misleading. This association would be expected for a uniaxial phase with $\mathbf{n}\|Z$ or, in other words, an orthorhombic biaxial nematic with D_{2h} symmetry like the N_{Bo} phase depicted in Figure 2. Recently, Peroukidis *et al.* [26] pointed out that monoclinic symmetry was also an option for biaxial nematics. Karahaliou *et al.* [27] spell out the implications for NMR and other experimental techniques if a biaxial nematic has the lower monoclinic symmetry (C_{2h} or C_2). Specifically, they explain that in the monoclinic phase (N_{Bm}) the principal axis frames (PAFs) of the averaged tensorial interactions do not necessarily coincide. In particular, their analysis of lower symmetry biaxial nematics enable the rationalisation of the use of a CSA value that is larger than σ_{ZZ} to fit the spinning sample spectrum (see Figure 8), i.e. the PAF of $\boldsymbol{\sigma}$ and the PAF of **q** are not necessarily coincident (apart from

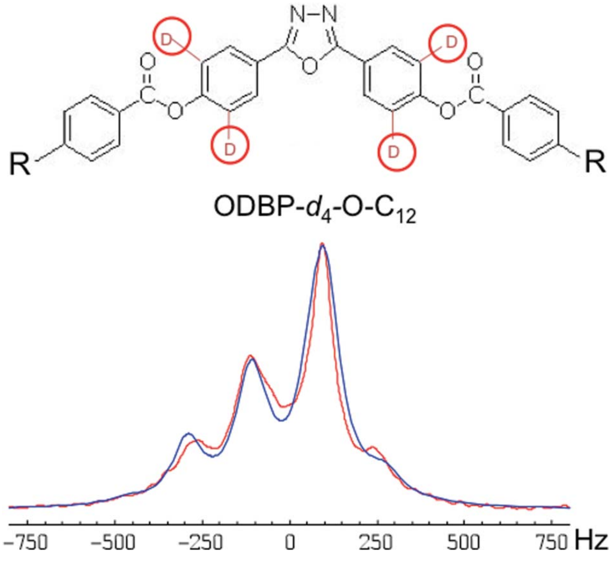


Figure 8. Experimental ^{2}H NMR spectrum (red) and simulation (blue) of a ODBPd_4-Ph-OC_{12} (R = -O-$C_{12}H_{25}$) nematic phase spinning about an axis normal to the magnetic field (T ~195°C; T_2 = 0.5 ms; spin rate 160 Hz); the best simulation (see details elsewhere [28]) gave $\eta = 0.3$ for the phase biaxiality, i.e. clear evidence for an N_B phase. However, the CSA required to fit the spectrum is a factor of two larger than the observed CSA in the static spectrum (colour version online).

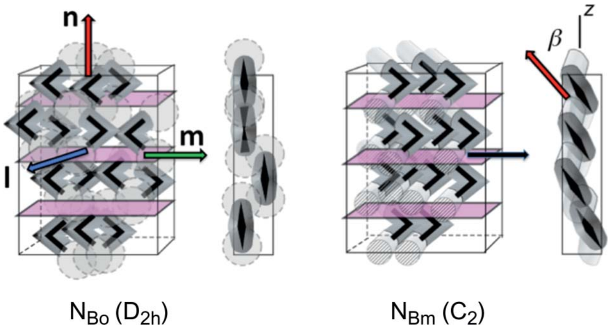
a common axis along the spinning direction). Nor is the PAF of $\boldsymbol{\sigma}$ coincident with the PAF of the magnetic susceptibility tensor. In summary, the fit to the data in Figure 8 implies that the N_B phase of the ODBP mesogens is a lower symmetry, monoclinic biaxial nematic phase [28].

2.5 **meta-*cybotactic biaxial nematics***

The deuterium NMR data and a new interpretation of the X-ray diffraction data from the nematic phase of ODBP bent-core mesogens [10] are compatible if the Vanakaras–Photinos cluster model of (biaxial) nematic phases [29] is adopted. Therein, the authors posit transient clusters of biaxially shaped mesogens with strong transverse orientational correlations between the molecules within each cluster. Strong transverse orientational correlations in the absence of any longitudinal translational order would imply the existence of an orthorhombic, molecular biaxial nematic within each cluster. Such a molecular N_{Bo} with D_{2h} symmetry having transverse directors **l** and **m**, and major director **n** (see Figure 2, right) was the type that Freiser modelled [7]. In the presence of an external magnetic field, **n** is uniformly aligned along **B** (for $\Delta\chi > 0$). However, according to the Vanakaras–Photinos, picture, there is no long-range ordering of the transverse directors from cluster to cluster (in the absence of a second transverse field). They refer to the array of aligned cluster directors $\mathbf{n}^i$ as an effectively uniaxial composite phase, N_U' in their notation. On lowering the temperature, the larger clusters grow at the expense of smaller ones (Ostwald ripening) yielding domains with well-defined $\mathbf{l}^i$ and $\mathbf{m}^i$ directors. A uniformly biaxial macroscopic sample characterised by three directors can be created by changing the magnitude of the Vanakaras–Photinos model interaction parameters (temperature), or alternatively, by applying a second field orthogonal to $\mathbf{n}\|\mathbf{B}$. Spinning the composite N_U' phase about an axis normal to the **B** field would also result in a uniform alignment of the $\mathbf{l}^i$ directors along the spinning axis; the $\mathbf{n}^i$ and $\mathbf{m}^i$ directors and the two remaining PAF axes of various interaction tensors would be randomly distributed in the plane normal to the spinning axis.

As intimated earlier, orientational correlations among biaxial-shaped (bent-core) mesogens would be more coherent and exhibit larger transverse correlation lengths ξ_l if there were longitudinal positional ordering of the centres of mass, i.e. if there was a tendency to form strata within clusters – *meta*-cybotaxis. Figure 9 illustrates examples of strata with normal and skewed arrangements of bent-core primitive shapes. If the density is low within the strata no preferential orientation of the steric/polar dipoles is selected, nor is there a preferred orientation of the envelope of tail atoms (see Figure 9, left). Increasing packing constraints in strata couples mesogen tilt and polarity with the population of a preferred tail conformation. A chiral, enantiomeric primitive shape (see Figure 7) is selected and a supramolecular structure similar to that depicted in Figure 9 (right) results. Both of these *meta*-cybotactic supramolecular arrangements are inherently biaxial, but only a tilted supramolecular arrangement can account for both the X-ray and NMR observations in the ODBP mesogens. The off-meridional, four-spot X-ray diffraction pattern results when the local **n** director (see Figure 9, right) in each cluster is aligned by surface anchoring or an external **B** field, and the alignment direction is perpendicular to the incident X-ray beam [10]. In such a bulk sample the normals to the layers (z-axes) are azimuthally distributed about $\mathbf{n}\|\mathbf{B}$ at the mesogen tilt angle β. If the z-axes from multiple clusters are translated to a common origin they circumscribe two coaxial cones with cone-angle 2β, one up (cone axis parallel to **B**) the other down (antiparallel to **B**). Spinning the magnetically aligned sample above a critical rate about an X-axis normal to **B** will select a planar cross-section through the cones; the smallest diamagnetic susceptibility value (the X_M component of $<\boldsymbol{\chi}>$ with its PAF defined by X_M, Y_M, Z_M) of each cluster aligns along the spinning axis and the Y_M and Z_M axes will be randomly distributed in the plane normal to $X \| X_M$. Moreover, for a N_{Bm} cluster supramolecular arrangement, the PAF of the CSA ($X_C Y_C Z_C$-frame) and that of the quadrupolar interaction ($X_i Y_i Z_i$-frame) merely share a single common axis (X-axis).

Hence the skewed *meta*-cybotaxis can account for the two-dimensional NMR powder pattern and its simulation (see Figure 8). In the static case, mesogen diffusion between the biaxial clusters (molecular exchange between clusters) does not influence the



N_{Bo} (D_{2h}) N_{Bm} (C_2)

Figure 9. Two views (edge and end-on) of slabs of bent-core mesogens in two different supramolecular arrangements within *meta*-cybotactic clusters. Left: An apolar biaxial arrangement with orthorhombic symmetry (normal meta-cybotaxis). Right: A tilted, synclinic, polar (ferroelectric) biaxial arrangement of chiral primitive shapes (skewed meta-cybotaxis); the C_2-axis is shown in the edge view together with the local primary director **n** and tilt angle β in the end-on view.

observed NMR interaction $q_{ZZ} = <q>_{\mathrm{nn}}$, a projection on **B**. Rotation of the sample about X brings all of the PAF X-axes into coincidence but the remaining components of the various PAFs need not necessarily be coincident. As a result, diffusive motion within this partially *aligned* rotating array of $\mathrm{N_{Bm}}$ supramolecular domains results in averaged tensors $<\boldsymbol{q}>$, $<\boldsymbol{\chi}>$ and $<\boldsymbol{\sigma}>$ having only the X-component of each tensor's PAF sharing a common direction, the rotation axis. If Z_M and Z_C are not coincident, the value of the CSA needed to simulate the spectrum (see Figure 8) may be larger than σ_{ZZ} observed in the static measurement.

3. Concluding remarks

Liquid state structure or classical cybotaxis is ubiquitous and is observed in fluid phases ranging from monatomic liquids and simple molecular liquids to colloidal suspensions. It results from molecular packing considerations in fluid phases. Intermolecular forces, the attractive electrostatic and dispersion interactions that cause molecules to cohere in condensed phases and the excluded volume repulsion that determines nearest-neighbour packing, determine classical cybotaxis. The dominant role of excluded volume in determining the nearest-neighbour packing is very well accounted for by the van der Waals' picture of liquids [30]. Excluded-volume interactions are dominant in the isotropic phase of nematogens well above the clearing temperature, and these interactions persist as T_c is approached and short-lived nematic clusters of mesogens condense in the surrounding isotropic host liquid. The clusters exhibit the attributes of nematic order, long-range orientational correlations of the molecular long axes of the anisometric mesogenic molecules. In addition to the local breaking of the isotropic symmetry, the orientational correlations impart anisotropy to the underlying classical cybotaxis, orientationally biased packing preferences that persist for a few molecular dimensions.

However, in some nematics there appears to be a qualitatively different level of positional organisation above and beyond (anisotropic) classical cybotaxis. Transient normal or skewed strata form in the nematic, smectic A or smectic C fluctuations appear below T_c. Usually this is observed above a smectic–nematic phase transition and observables exhibit pre-transition-like critical behaviour. This meta-cybotaxis is longer ranged, involving a greater number of molecules, and seems to be particularly prevalent in nematics formed by bent-core mesogens [9]. The formation of tilted *meta*-cybotactic clusters that locally select chiral, statistical bent-core shapes in the nematic (or in the pre-transitional region above T_c) may account for chiralty reported in the nematic phases (and in the isotropic phase) of bent-core mesogens [31, 32].

The persistence of *meta*-cybotatic clusters in the nematic phase below T_c has implications for the general topic of biaxial nematics. A skewed (tilted) supramolecular structure within the clusters is locally biaxial, but in the absence of external aligning fields/surfaces, the overall symmetry of the phase is effectively uniaxial, unless, of course, the clusters coalesce and grow to macroscopic sizes [29]. If the orientations of the local cluster directors $\mathbf{n}^i$ become correlated over macroscopic distances via external constraints, a new type of biaxial nematic may be formed, one that is distinct from the still-elusive *molecular biaxial nematic* presaged by Freiser (see Note 2). *Meta*-cybotactic clusters that persist throughout the entire nematic range [10] and which can be mutually aligned, appear to explain the observed NMR biaxiality in the ODBP mesogens [20].

The idea of a *meta*-cybotatic nematic is reminiscent of the swarm theory of liquid crystals that was advocated by Gray, Chistyakov and Chateain but dismissed by de Gennes; Saupe reviewed the swarm theory in his 1968 paper [1]. The idea of swarms (clusters) appeared to be acceptable in the isotropic pre-transition region according to de Gennes [33], but his primary objection to swarms within the nematic phase itself revolves around the consequences of an absence of orientational correlations between directors $\mathbf{n}^i$ in neighbouring swarms. This absence of orientational correlations predicts the wrong critical behaviour for pre-transitional phenomena. In the *meta*-cybotactic nematic this objection may be moot, as all of the major directors of all of the clusters (swarms) are mutually aligned and parallel to the primary director of the host nematic phase, i.e. $\mathbf{n}^i \| \mathbf{n}$.

It has been four decades since Adrian de Vries borrowed the term cybotaxis from early twentieth century scientists studying structure in the liquid state with X-ray diffraction. And, while some of the implications associated with the descriptor *cybotaxis* may not be appreciated by scientists considering short-range structure in nematics, I suspect that the term is too widely ingrained to be discontinued. *Meta*-cybotaxis is not a perfect designation. A more user-friendly term would be preferable for distinguishing classical cybotaxis from short-range, transient, smectic supramolecular structures in nematics. This review is not an attempt to introduce new terminology. Rather, it is intended to enable liquid crystal scientists to appreciate some of the subtleties of short-range positional order in certain nematics, positional order that maintains above and beyond that associated with classical cybotaxis. Also I wanted to illustrate how tilted supramolecular structure within clusters may give rise to apparent biaxial nematics, aligned cluster phases that were outside the scope of liquid crystal supramolecular structure considered by Marvin Frieser.

Throughout this paper I have stressed the dynamical aspects of clusters, e.g., the transient nature of the evanescent density fluctuations in the nematic phase. Of course the equilibrium correlation functions will not change with time, i.e., the X-ray diffraction pattern at a specific temperature does not reflect the dynamical nature of clusters. However, the time scale of the evolution of the clusters may be important for other techniques such as NMR where the dynamical aspects of clusters may have measurable implications — molecular diffusion within a powder of quasi-static ordered domains may be quite distinct from diffusion in a time-averaged assembly of rapidly interconverting clusters.

In summary, all nematics are cybotactic. Some exhibit additional structure with varying degrees of evanescent density fluctuations. When mesogens with a propensity to form transient strata cooperatively tilt in those strata, the clusters become inherently biaxial. An aligned (biaxial) nematic with clusters having C_{2h} or C_2 symmetry explains both the NMR and X-ray observations for the bent-core ODBP mesogens.

Acknowledgements

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Notes

1. Note that Saupe's 1968 review predates the experimental report of discotics and the rediscovery of bent-core liquid crystals and was, therefore, restricted to rod-shaped molecules, so-called calamitic mesogens. Apart from the sign of the birefringence, generally negative for disc-shaped molecules and positive for calamitics, both of those classes of nematics are characterised by long-range orientational order without translational order; the short axes are aligned along **n** in the case of discotic nematics.
2. Marvin Freiser understood the difficulty of realising the molecular biaxial nematic and concluded his 1970 publication [7] as follows: "Such a sequence of transitions [$N_U \rightarrow N_B$] is consistent with the symmetry of the molecules in real nematic liquids and should therefore occur. However, crystallization of the medium or the onset of a smectic phase may intervene."

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