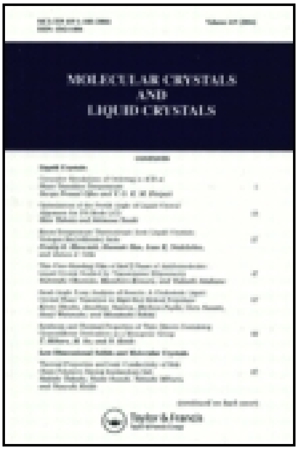

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POLAR MOLECULAR ORGANISATION IN LIQUID CRYSTALS

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Various possibilities of polar self-organisation in low molar mass nematic, smectic and columnar liquid crystals are discussed with particular focus on the underlying molecular symmetries and interactions. Distinction is made between vector and pseudovector polarities, their quantification in terms of molecular order parameters and their relation to spontaneous electric polarisation and to molecular chirality. The understanding of the molecular mechanisms that give rise to polar ordering in existing lamellar and columnar phases may be useful for the design of new polar variants of common a-polar liquid crystals.

Keywords: polar nematics; ferroelectric liquid crystals; polar ordering

INTRODUCTION

Phase anisotropy together with fluidity are the basic unifying features of all liquid crystals. Fluidity implies some disorder of the molecular positions in one or more spatial dimensions. Phase anisotropy reflects the directionality of the molecular organisation in these systems and can be of the a-polar type, if each direction in the bulk phase is physically indistinguishable from its opposite, or of the polar type, if such indistinguishability does not hold for all directions. In the latter case the underlying molecular organisation will exhibit polar orientational ordering. Accordingly, the bulk phase could in this case acquire spontaneous electric or magnetic polarisation if the molecules have permanent electric or magnetic dipoles. Aside from their purely scientific interest, the many actual and potential technological applications of liquid ferroelectric and ferromagnetic systems have stimulated intensive research on polar liquid crystals [1].

This paper is dedicated to the memory of Pier Luigi Nordio. Partial financial support for this work came from the EU ***TMR*** (contract FMRX-CT97-0121) and through the funding of the Polymer Science and Technology Graduate Studies Programme of the University of Patras.

In this paper we discuss various molecular mechanisms that have been proposed for the understanding of polar ordering in the most common liquid crystalline phases. We consider low molar mass nematic, smectic and columnar liquid crystal phases and we concentrate on (i) the molecular interactions that could promote or oppose polar organisation and (ii) the quantification of polar orientational ordering in terms of order parameters and of macroscopic physical properties. Our considerations are restricted to electric properties and interactions but all the theoretical arguments can be carried over to magnetic systems as well.

POLAR NEMATICS

A polar nematic would be a translationally uniform phase with long-range polar orientational order. The most symmetric such phase is a uniaxial polar nematic, i.e. a nematic with full rotational symmetry about a unique phase-fixed axis denoted by the unit vector **N**, the director, but with broken "up-down" symmetry so that the directions **N** and $-\mathbf{N}$ are not equivalent. The minimal molecular asymmetry requirements for the formation of such a phase correspond to uniaxially polar molecules, i.e. polar molecules with an axis **m** of full rotational symmetry, with the polarity rendering the molecule asymmetric with respect to the direction reversal $\mathbf{m} \to -\mathbf{m}$. Due to this asymmetry the ensemble average $\langle \mathbf{m} \rangle$ of the molecular unit vector **m** does not vanish. The single-molecule probability distribution is in this case a function of just one molecular variable, namely $\mathbf{m} \cdot \mathbf{N} = \cos\theta_{mN}$, where θ_{mN} is the angle of the molecular unit vector **m** relative to the director **N**. The moments of this distribution are conveniently represented by the ensemble averages (order parameters) $\langle P_l \rangle \equiv \langle P_l(\cos\theta_{mN}) \rangle$ of the Legendre polynomials of rank l. The quantification of polar ordering for such a system is given by the ensemble average $\langle \mathbf{m} \rangle = \langle P_1 \rangle \mathbf{N}$. The primary measure of the magnitude of polarity is thus the first rank order parameter $\langle P_1 \rangle$. The second rank order parameter $\langle P_2 \rangle$, which is the leading order parameter for common (a-polar) nematics, is related to the breadth of the polar distribution according to the relation

$$\left\langle \cos^2 \theta_{mN} \right\rangle - \langle \cos\theta_{mN} \rangle^2 = (2/3)\langle P_2 \rangle - \langle P_1 \rangle^2 + 1/3, \tag{1}$$

from which it becomes apparent that $\langle P_1 \rangle$ places the following lower bound on $\langle P_2 \rangle$,

$$\langle P_2 \rangle \geq (3/2)\langle P_1 \rangle^2 - 1/2. \tag{2}$$

If the molecules forming the uniaxial polar nematic phase carried permanent electric dipole moments $\boldsymbol{\mu}$ with a nonvanishing component $\mu_{\|} = \boldsymbol{\mu} \cdot \mathbf{m}$ along the direction of the molecular symmetry axis **m**, then the phase would exhibit spontaneous electric polarisation $\mathbf{P}_s^e = \mathcal{N}\langle\boldsymbol{\mu}\rangle$ where $\mathcal{N}$ denotes the molecular number density and $\langle\boldsymbol{\mu}\rangle = \mu_{\|}\langle\mathbf{m}\rangle$. Thus, the spontaneous polarisation vector would be in the direction of the phase symmetry axis **N** and proportional to the polar order parameter $\langle P_1\rangle$ according to the relation

$$\mathbf{P}_s^e = \mathcal{N}\mu_{\|}\langle P_1\rangle\mathbf{N}. \tag{3}$$

This equation relates, via a molecular property $\mu_{\|}$, a macroscopic electrostatic measure of polarity $\mathbf{P}_s^e$ to a microscopic measure of polarity represented by the "vector order parameter" $\langle\mathbf{m}\rangle = \langle P_1\rangle\mathbf{N}$.

There does not seem to be any thermodynamic or symmetry argument forbidding *a priory* the formation of a polar nematic phase, uniaxial or not. Yet, to date none of the existing low molar mass nematogens is known to exhibit such a phase [2]. It thus becomes theoretically challenging to rationalise, on the molecular level, the a-polarity of common nematics and from there to ask what sort of molecular interactions would be required to stabilise polar ordering in the nematic phase. For example, permanent electric dipole moments of a few Debyes are quite usual for molecules forming nematic phases and have measurable effects on their (a-polar) orientational order [3]. An obvious question is then whether electric dipole interactions could bring about phase polarity in nematics [4]. The answer is negative. A simplified explanation can be sketched as follows.

The interaction potential between two dipoles, $\boldsymbol{\mu}$ and $\boldsymbol{\mu}'$ is given by

$$u^{(d)} = [\boldsymbol{\mu}\cdot\boldsymbol{\mu}' - 3(\boldsymbol{\mu}\cdot\mathbf{r})(\boldsymbol{\mu}'\cdot\mathbf{r})]/r^3 \tag{4}$$

where $\mathbf{r}$ and r are the interdipole unit vector and distance respectively. Consider the condensed, positionally disordered, phase of dipolar spherical molecules (i.e. molecules whose interactions in excess the dipole-dipole interaction are isotropic). If short-range position-orientation correlations are completely ignored then the contribution of the electrostatic interaction to the free energy for the phase with polar orientational order (Fig. 1a) vanishes. This is a reflection of the particular dependence of $u^{(d)}$ on $\mathbf{r}$ for fixed dipole directions and interdipole distance. The most directly relevant feature of this dependence is illustrated in Figure 2a, which shows that the energy of "side-by-side" configurations of parallel dipoles is half the magnitude and of opposite sign relative to the energy of the "head-to-tail" configurations. Since in three dimensions there are two side-by-side configurations for each head-to-tail, the average dipole-dipole energy, in the absence of correlations, vanishes. The same null result is obtained when averaging the dipole-dipole contribution to the free energy in the orientationally disordered phase (Fig. 1b), which however has larger entropy and will therefore always be thermodynamically more stable than the polarly ordered state.

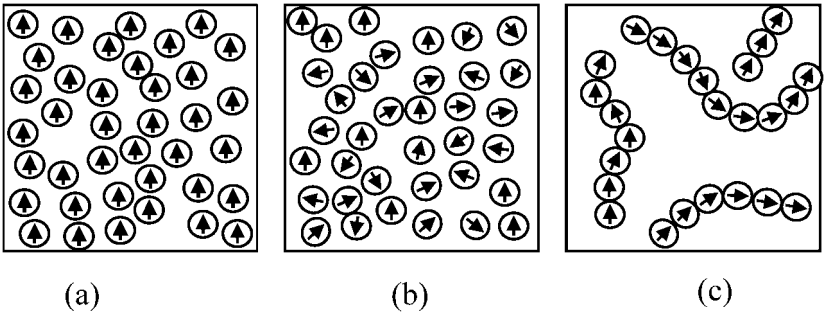

FIGURE 1 (a) Positionally disordered fluid of dipolar spheres in the perfectly oriented state and (b) in the orientationally disordered state. In both states the electrostatic contribution to the free energy of the system vanishes. (c) Molecular arrangements in the polar-string phase of the system at low densities.

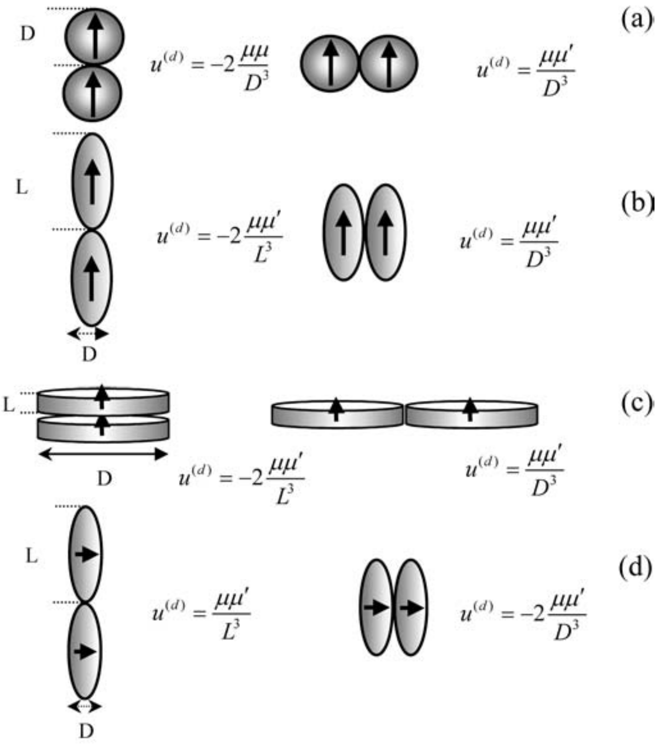

FIGURE 2 Dipole-dipole interaction energies for the parallel head-to-tail and side-by-side configurations of central dipoles carried by (a) spherical, (b) rod-like (longitudinally polar), (c) disc-like and (d) rod-like (transversely polar) molecules.

Essential to these arguments is the neglect of short-range correlations. The latter, however, are not always negligible. In fact, simulations of hard dipolar spheres have produced, for sufficiently strong dipoles and low densities, stable phases of polar strings, (linear aggregates of dipolar spheres in head to tail succession of the dipole moments, Figure 1c) [5,6]. The correlations in these strings are such that the head-to-tail configuration dominates at short distances whereas the side-by-side (parallel or antiparallel) configurations correspond to molecular pairs on different strings, which are therefore more distant. This leads to an electrostatic reduction of the free energy that could compensate for the entropy reduction associated with the formation of the polar strings and thus provide thermodynamic stability relative to the completely disordered phase. On increasing the density, the side-by-side configurations are forced to the same average proximity as the head-to-tail and the chains eventually decompose into a positionally disorder a-polar fluid.

If instead of dipolar spherical molecules one considers elongated molecules with longitudinal dipoles then the polarly ordered condensed phase is further destabilised with respect to the a-polar phase. This happens because now, due to larger separations of the dipoles, the magnitude of the head-to-tail energy is less than twice the magnitude of the side by side energy (Fig. 2b) and therefore the positionally uncorrelated averaging will yield a net increase of the free energy of the polar phase relative to the a-polar one. Thus the stronger the dipole the more it disfavours the polar nematic ordering of the elongated molecules and in fact turns out to favour the a-polar smectic A phase [7].

In the case of disc-like molecules with central dipoles along the disc symmetry axis, the electrostatic contribution favours the polar ordering. This is so because the head-to-tail energy, due to smaller interdipole separations, is now more than twice the magnitude of the side-by-side energy (see Fig. 2c). As shown in Monte Carlo (MC) simulations, however, the organisation of the polar discs does not correspond to a polar nematic but rather to a columnar phase with polar ordering within individual columns and antiferroelectric configurations of the columns [8].

It becomes apparent from these considerations that the formation of a polar nematic phase is not favoured by strong longitudinal electric dipoles. It rather requires interactions where the polar disposition of the molecules can be favoured but without forcing them to into any kind of positional register that would destroy the uniform distribution of their positions. Interactions of the amphiphilic type, for example, can favour the polar alignment of elongated molecules, as will be discussed below, but only as a result of (in the present context, at the expense of) phase micro-segregation [9]. Furthermore, steric repulsions originating from the polar shape-asymmetry of tapered molecules, wedge shaped, pear shaped, etc, disfavours polar ordering in the undisturbed bulk phase since such shapes pack more efficiently in antiparallel configurations. It thus seems that none of the basic interactions encountered in common liquid crystals, nor any simple combination thereof, favours nematic polar ordering. This explains, at least partly, why a low molar mass nematic phase has not been detected experimentally to date. Recently, Berardi, Ricci and Zannoni [10] where successful in tailoring a model potential that can produce, under certain parameterisation, a polar nematic phase in MC simulations. Their model interaction essentially behaves in the opposite way to the dipole-dipole interaction (Fig. 2b) in that it assigns the lowest energy to the side-by-side parallel arrangement of a molecular pair, high energy to the parallel head-to-tail and intermediate energy to the side-by-side antiparallel. Of course the identification of real molecules that would interact in the required way is the major step to be taken. In the present state of molecular design efforts, however, it appears that much more is known on what should be avoided than on what is to be pursued.

ORTHOGONAL SMECTICS WITH POLAR LAYERS

Polar ordering in orthogonal smectics is quite usual [11]. Known variants of the smectic A phase *(Sm-A)* with polar layers include the bilayer phases A_d, A_2 and $\tilde{A}$ (Fig. 3a,b,c). In these phases the polar asymmetry is exhibited in the direction of the layer normal, with adjacent layers having opposite polarities thus rendering the bulk phase macroscopically a-polar.

On the molecular scale, the structure of the phases A_2 and $\tilde{A}$ suggests that the molecular interactions giving rise to the polar ordering should be such as to favour the side-by-side parallel alignment of molecules within the same layer while favouring the head-to-head or tail-to-tail alignment of molecules in consecutive layers (Fig. 3a,c). Obviously neither the electric dipole forces nor the purely steric forces associated with wedge-type shape asymmetry favour such configurations; in fact they strongly disfavour them. In contrast, amphipile type forces favour both types of configurations and are therefore considered the primary interaction underlying the formation of these phases.

The bilayer structure of the A_d phase suggests molecular interdigitation among adjacent sublayers such that the favoured molecular arrangements produce side-by-side antiparallel configurations of the molecular tips (Fig. 3b). These configurations could be favoured by interactions from dipole moments situated near the ends of the elongated molecules and in fact theory and simulations show that model rod-like molecules with off centre axial dipole moments can produce the A_d phase structure [12].

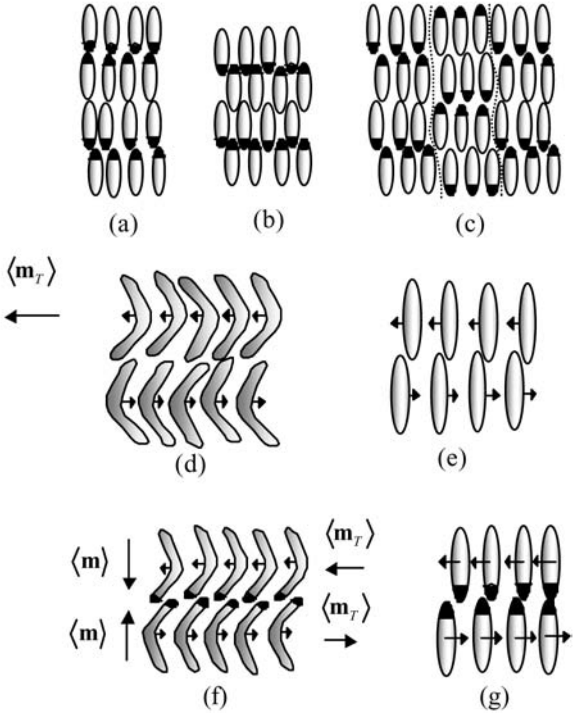

FIGURE 3 Schematic representation of molecular arrangements in some polar orthogonal smectics. (a) Bilayer *Sm-*A_2. (b) Semibilayer *Sm-*A_d. (c) Ribbon bilayer *Sm-*$\tilde{A}$. (d) Banana-type *Sm-*A_P, shown here in antiferroelectric succession of the layers. (e) Rod-like polar smectic A phase model, shown here in antiferroelectric succession of the layers. (f) Banana-type orthogonal smectic phase model with both, longitudinal (along the layer normal) and transverse polarity, shown here in antiferroelectric succession of the layers with respect to both polarities. (g) Rod-like orthogonal smectic phase model with both, longitudinal (along the layer normal) and transverse polarity, shown here in antiferroelectric succession of the layers with respect to both polarities. The arrows attached to the molecules in figures (d) to (g) indicate the molecular vectors $\mathbf{m}_T$.

However, the amphiphilic interactions also favour this type of configurations. Moreover, this arrangement makes the packing more effective in the presence of wedge like shape asymmetry, particularly in combination with amphipilicity. This is then an example of ordering where several types of interactions could separately or cooperatively produce the polarity. In fact, Photinos and Saupe [13] showed nearly three decades ago the theoretical possibility of longitudinally polar smectics based on a generic molecular field description of the polar interactions.

The type of polarity described above for orthogonal smectics is similar to that of nematics in that it consists of the local (within a sublayer) breaking of the up-down symmetry $\mathbf{N} \Leftrightarrow -\mathbf{N}$ along the director and entails the same minimal asymmetry of the molecular structure, i.e. uniaxial molecules with a polar axis $\mathbf{m}$ of full rotational symmetry. Consequently, the polarity in each sublayer is quantified by the vector order parameter $\langle \mathbf{m} \rangle$ as in uniaxial polar nematics. In the presence of longitudinal dipoles a spontaneous electric polarisation will be produced in each sublayer according to Eq. (3) and, due to the alternating polarity of the bilayer structure, the resulting "antiferroelectric" system will appear electrically a-polar on the bilayer scale. The term longitudinal will be reserved for the above type of polarity, namely the one that manifests itself as the breaking of the $\mathbf{N} \Leftrightarrow -\mathbf{N}$ symmetry along the director (coincident with the layer normal in the case of orthogonal smectics), in order to distinguish it from the transverse polarity that is manifested as the breaking of the twofold rotational symmetry about the director $\mathbf{N}$.

An orthogonal smectic phase with transverse polarity and positional disorder has been reported recently [14] for compounds with banana-type molecular shape asymmetry. The polarity of the layers in this case is thought to result from the stacking of the molecules so that the "steric dipoles" associated with their bent shape become aligned (see Figure 3d). This polar stacking can produce a spontaneous polarisation in the plane of the layers if the molecules possess electric dipole moments with non-vanishing component along the direction of the steric dipole. It should be noted that such electric dipole moments, if present, would contribute to the polar alignment because their configuration within each layer gives on average equal numbers of parallel side-by-side and head-to-tail pairs while the side-by-side pairs belonging to different layers are more distant and thus an overall reduction of the internal electrostatic energy relative to the a-polar system would result. In fact, unlike the case of longitudinal polarity, transverse polarity can in principle be generated by electric dipole interactions alone. Consider for example idealised smectic layers consisting of a planar arrangement of positionally disordered parallel rod-like molecules with central transverse electric dipoles (Fig. 3e). The internal electrostatic energy per molecule for the state with perfect alignment of the dipoles is lower than that of the state with randomly oriented dipoles by $\pi(\sigma/D)\mu^2$, where μ is the dipole strength, σ is the surface density of the molecules in the layers and D is the diameter of the rods (the distance of closest approach of the dipoles, Figure 2d). The entropy per molecule for the polar state is lower than that of the random state by $k_B T \ln 2\pi$ and therefore the polar state becomes the thermodynamically stable one for sufficiently large values of the quantity $(\sigma/D)\mu^2/k_B T$. At this level of approximation the intra-layer electrostatic interactions do not contribute to the internal energy of the system since the interaction energy between any dipole and all the dipoles belonging to a different layer averages to zero, both in the polar and the random states. This result suggests that, to a first approximation (i.e. ignoring orientational and positional fluctuations and correlations of inter- and intra-layer molecular motions), the inter-layer electrostatic interactions are indifferent to the mode of propagation of polarity across the layers (parallel or antiparallel disposition of adjacent layers). Monte Carlo simulations of rod like molecules with transverse dipoles give some indications of in-plane polar order [15]. Gil-Villegas, McGrother and Jackson [16] found that, even at fairly high densities, the dipoles in a layer self-organise to form ring domains that evolve, on lowering the temperature, into antiferroelectric elongated chain domains.

It is apparent from the examples of banana shaped molecules and of rods with transverse dipoles in Figure 3d,e that the minimal molecular asymmetry required for in-plane phase polarity corresponds to molecules with a plane of symmetry and a twofold symmetry axis $\mathbf{m}_T$ on that plane. The molecular "long axis" $\mathbf{m}$ is defined as the axis within the plane of symmetry and perpendicular to $\mathbf{m}_T$ and is no longer an axis of rotational symmetry. The molecular polarity consists in the lack of $\mathbf{m}_T \Leftrightarrow -\mathbf{m}_T$ symmetry. Accordingly, phase polarity can be quantified by the vector order parameter $\langle \mathbf{m}_T \rangle$. The direction of $\langle \mathbf{m}_T \rangle$ defines a second director $\mathbf{N}_T$ in the plane of the layer and thus perpendicular to the primary director $\mathbf{N}$. Consequently, transverse polarity makes the orthogonal smectic phase necessarily biaxial. The asymmetry associated with in-plane polarity consists in the breaking of the $\mathbf{N}_T \Leftrightarrow -\mathbf{N}_T$ symmetry while maintaining the $\mathbf{N} \Leftrightarrow -\mathbf{N}$ symmetry. When both symmetries are valid one has a biaxial (non-polar) orthogonal phase whereas the simultaneous breaking of both symmetries yields an orthogonal smectic with both in-plane and longitudinal polarity (see Figure 3f,g). The types of molecular interactions that can produce the combined polarity can in principle be furnished by the superposition of the interactions giving rise to the individual polarities, for example amphiphilic interactions for the longitudinal polarity and banana type steric dipole for the transverse polarity (Fig. 3f), since such interactions are not incompatible or counteracting. It thus can be seen that the consideration of the two types of polar ordering and of their combination broadens the variety of orthogonal smectics with positionally disordered layers. These possibilities of polarity are carried over and further enriched for orthogonal smectics with in-plane positional order, the discussion of which is beyond the present scope.

TILTED SMECTICS

The least ordered of the tilted smectic phases is the *Sm-C* phase. It consists of positionally disordered layers in which the orientational order of the molecules defines a director **N** forming an angle (the tilt angle) with the direction normal to the layers. The *Sm-C* layers have a plane of symmetry (the tilt plane, formed by the layer normal **Z** and the director **N**). They also have a twofold symmetry axis C_2 perpendicular to the plane of symmetry and a centre of inversion at the intersection of the twofold axis with the symmetry plane. The directions **N** and −**N** are equivalent (physically indistinguishable). However, the structure of the *Sm-C* phase is inherently polar since the tilt singles out a unique direction about the layer normal. This unique direction is often represented by the so-called **C**-director [17] whose direction is defined from the projection of the **N**-director onto the layer plane but with **C** and −**C** describing physically distinct states. A particularly useful alternative [18] representation is provided by the tilt pseudovector **t** defined in terms of the layer normal **Z** and the **N**-director according to the relation

$$\mathbf{t} = (\mathbf{Z} \times \mathbf{N})(\mathbf{Z} \cdot \mathbf{N}). \tag{5}$$

Obviously **t** is perpendicular to the tilt plane, it is invariant with respect to the replacement of **N** by −**N** and the states **t** and −**t** describe layers of opposite tilt and are therefore physically distinct.

The polarity of the *Sm-C* phase, being clearly a direct consequence of the tilted ordering, is referred to as indigenous polarity [19]. It is of fundamentally different nature from the polarity that could appear in orthogonal smectics or in nematics. First, when polar ordering appears in orthogonal smectics or in nematics, mirror symmetry perpendicular to the polar director (see Fig. 4a) is broken. This type of polar ordering is referred to as vector-type polarity, in accordance with the sign reversal of vectors under mirror reflection. In contrast, the indigenous polarity of the *Sm-C* phase is compatible with mirror symmetry in the plane normal to the direction of the polar asymmetry (the tilt plane) as illustrated in Figure 4b. By analogy to the invariance of the direction of pseudovectors under mirror reflection, the indigenous polarity of the *Sm-C* layers can then be termed as pseudovector-type.

In order to quantify the indigenous pseudovector polarity of the *Sm-C* layers and to illustrate its molecular origins we consider an idealised molecular model embodying the minimal asymmetry required for the appearance of tilted orientational ordering and positional disorder within the layers. For simplicity we consider a rigid molecule whose shape has the same symmetries as the *Sm-C* phase (equivalently, the minimal asymmetry compatible with the *Sm-C* phase). A convenient example is the oblique cylinder of Figure 5a. It has a plane of symmetry, a twofold axis and an inversion centre. Objects of this shape have been used as molecular models in a theory of the *Sm-C* phase by Somoza and Tarazona [20]. In the present

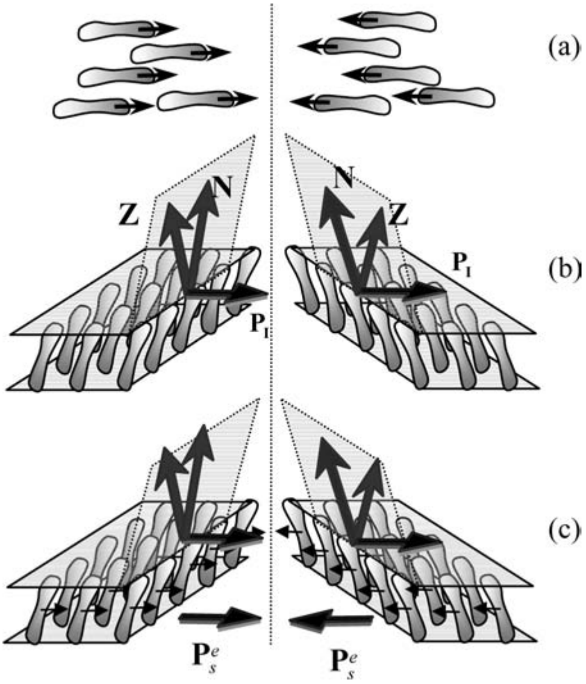

FIGURE 4 Molecular arrangements and their images in a mirror plane (dotted vertical line) perpendicular to the polar direction. (a) Polar nematic arrangement. Vector polarity breaks mirror symmetry; the two mirror images are distinct. (b) Tilted smectic layer, with the tilt plane containing the layer normal **Z** and the director **N**. Tilt-driven pseudovector polarity $\mathbf{P_I}$ is compatible with mirror symmetry of the layer; the two mirror images are identical. (c) Tilted smectic layer with chiral molecules carrying transverse electric dipole moments. The resulting spontaneous electric polarization $\mathbf{P}_s^e$ breaks mirror symmetry in the layer; the two mirror images are distinct.

context they are used merely in order to convey the molecular symmetry by means of simple images.

Let the vectors **s** and **s**′ be directed along the cylinder axis and normal to the oblique surfaces respectively. The two halves on either side of the symmetry plane of the molecule (the two "faces" of the molecule, for brevity) are distinct mirror images of each other. The pseudovector $\mathbf{a} = \mathbf{s} \times \mathbf{s}'$ can then be used for the distinction between the two faces. In the *Sm-A* phase there is clearly nothing to make any given orientation of **a** have a different probability from its opposite (Fig. 5b) whereas the tilted ordering of the *Sm-C* phase induces a preference of one of the two opposite orientations perpendicular to the tilt plane over the other (Fig. 5c).

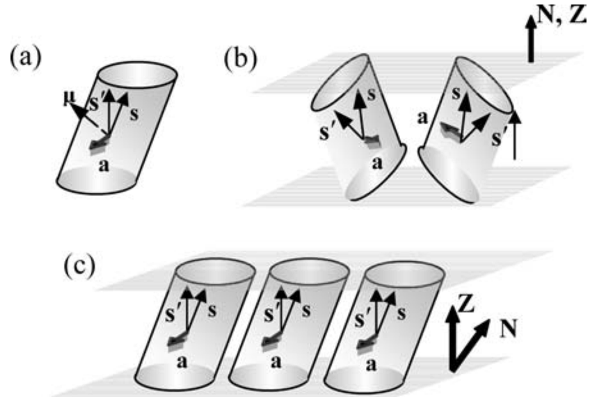

FIGURE 5 (a) Oblique cylinder idealization of a molecular structure bearing the minimal asymmetry (C_{2h}) required for the formation of the *Sm-C* phase. The vectors $\mathbf{s}, \mathbf{s}'$ are on the oblique-cylinder plane of symmetry, to which the pseudovector $\mathbf{a} = \mathbf{s} \times \mathbf{s}'$ is perpendicular. The possible presence of a dipole moment $\boldsymbol{\mu}$ directed out of the $\mathbf{s}, \mathbf{s}'$ plane would render the structure chiral. (b) Opposite orientations of **a** are equally probable in the *Sm-A* phase. (c) The tilted molecular arrangement in the *Sm-C* layer favours one of the two opposite orientations of **a** perpendicular to the tilt plane, thus generating psedovector indigenous polarity.

This preference gives rise to a nonvanishing value of the ensemble average $\langle \mathbf{a} \rangle$ and allows the definition of the (pseudovector) order parameter $\mathbf{P_I} = \langle \mathbf{a} \rangle / |\mathbf{a}|$ that quantifies the indigenous polarity. Clearly, the indigenous polarity is not related to chirality. This is depicted in Figure 4b where it is apparent that the presence of pseudovector $\mathbf{P_I}$ does not differentiate a layer from its mirror image. However, if the indigenously polar *Sm-C* phase is to exhibit spontaneous electric polarisation, it is necessity that the molecules possess an electric dipole moment with a nonvanishing component along **a**. In that case the indigenous polarity $\mathbf{P_I}$ will generate a spontaneous electric polarisation $\mathbf{P}_s^e$ normal to the tilt plane according to the relation

$$\mathbf{P}_s^e = \mathcal{N} \langle \boldsymbol{\mu} \rangle = \mathcal{N} \mu_\perp^* \mathbf{P_I}, \tag{6}$$

where $\mu_\perp^* = \boldsymbol{\mu} \cdot \mathbf{a} / |\mathbf{a}|$ is a pseudoscalar measure of the strength of what is often referred to as the "transverse dipole moment". It is obvious, however, that the attachment of a transverse dipole component to the molecules (see Fig. 5a) destroys the mirror plane symmetry of their structure, which thus becomes chiral. In this sense, the molecular parameter $\mu_\perp^*$ provides a measure of the electrostatic chirality of the molecular structure. The electrically polar layer is no longer identical to its mirror image (see Fig. 4c), i.e. the layers have become electrostatically chiral.

According to the above considerations, the relevance of vector and pseudovector polarity to spontaneous polarisation can be summarised by stating that vector polarity is not necessarily present and, when present, can give rise to spontaneous polarisation even if the molecules are not chiral whereas pseudovector polarity is necessarily present in all tilted smectics but can give rise to electric spontaneous polarisation only if the molecules are chiral. This difference is born by Eqs. (3) and (6), which are formally identical but the two different mechanisms by which $\mathbf{P}_s^e$ is generated are explicitly reflected on

(i) the different physical significance of the molecular quantities $\mu_{\parallel\square}$ (scalar measure of longitudinal dipole) and $\mu_{\perp}^{*}$ (pseudoscalar measure of chirality-related transverse dipole) and
(ii) the molecular order parameters $\langle \mathbf{m} \rangle$ and $\mathbf{P_I}$ quantifying respectively the direct (vector) polarity and the indigenous, tilt-generated, pseudovector polarity.

Having used an explicit molecular idealisation (Fig. 5) to illustrate the significance of the (pseudovector) indigenous polarity, its role in giving rise to spontaneous electric polarisation in tilted smectics, its differentiation from the latter polarisation and from the (vector) polarity appearing in orthogonal smectics and nematics, it is useful to give a generalised description of the above in terms of molecular and phase symmetry: The *Sm-C* layers have C_{2h} symmetry. The plane of symmetry is identified with the tilt plane and the twofold symmetry axis C_2 is perpendicular to that plane. As a result of the rotational symmetry about this axis, the projection of any vector or pseudovector order parameter onto the tilt plane necessarily vanishes. Furthermore, the plane of symmetry makes all vector order parameter components along the C_2 axis vanish but allows the appearance of pseudovector components along that axis. To exclude the possibility of such pseudovector components would require at least one symmetry axis in the tilt plane, but such symmetry axis is of course precluded by the monoclinic symmetry of the tilted layers. Hence, tilt generates pseudovector indigenous polarity $\mathbf{P_I}$ along the C_2 axis of the *Sm-C* layers. To identify the molecular origin of this polarity it is necessary to consider molecular symmetry. To this end, it is sufficient to consider molecules that are not less symmetric (in the statistical sense, when referring to rigid molecules) than the phase itself, i.e molecules with C_{2h} symmetry. Again, the existence of a plane of symmetry together with the lack of any symmetry axes on that plane makes it possible to define only molecular pseudovectors directed perpendicular to the plane of symmetry, i.e. along the molecular C_2 axis. The ensemble average of the projection of such a pseudovector of unit length along the C_2 axis of the layers defines the order parameter $\mathbf{P_I}$. The presence of the molecular C_2 axis is not essential to these considerations; only the molecular plane of symmetry is necessary in order to exclude molecular chirality. Now, if chirality is allowed for in the smectic layers then there will be no symmetry plane. The chiral analogue of the smectc-C phase, the *Sm-C**, has only one C_2 axis. This precludes the appearance of any vector or pseudovector order parameter components in the tilt plane (defined as the plane perpendicular to the C_2 axis, but no longer a symmetry plane). It allows, however, the appearance of both vector and pseudovector components in the C_2 direction. This leads to the possibility of simultaneous (pseudovector) indigenous polarity and (vector) spontaneous polarisation in chiral tilted smectics.

Combinations of pseudovector polarity with the vector polarity described in the previous section for orthogonal smectics are possible and generate several polar variants of the *Sm-C* phase. Thus, longitudinal vector polarity is present, in addition to indigenous pseudovector polarity, in the tilted analogues $Sm\text{-}C_2$, $Sm\text{-}C_d$ and $Sm\text{-}\tilde{C}$ (Fig. 6 a,b,c) of the orthogonal bilayer variants of the *Sm-A*. The tilted sublayers in these phases are polar along the director, i.e. have broken $\mathbf{N} \Leftrightarrow -\mathbf{N}$ symmetry, and are therefore lacking the twofold symmetry axis (normal to the tilt plane) of the common *Sm-C* layers. However, this symmetry is restored in the bilayers due to the opposite longitudinal polarity $\langle\mathbf{m}\rangle$ of their constituent sublayers. As in the case of orthogonal smectics, these sublayers could exhibit spontaneous electric polarisation $\mathbf{P}_s^e$ along the director (consequently in the tilt plane and tilted with respect to the layer normal). For chiral molecules with transverse dipole moments this component of $\mathbf{P}_s^e$ would be superposed to the component (perpendicular to the tilt plane) associated with the indigenous polarity and thus the total $\mathbf{P}_s^e$ in each sublayer would be in the plane containing the director $\mathbf{N}$ and the tilt pseudovector $\mathbf{t}$.

Transverse vector polarity can be combined with indigenous pseudovector polarity in many ways and results in the various banana-type tilted smectics. Thus, the vector order parameter $\langle\mathbf{m}_T\rangle$ can be in the tilt plane (therefore perpendicular to the direction of the indigenous polarity $\mathbf{P_I}$), resulting in the layer structure of the C_{B1} phase (Fig. 6d), or it can be perpendicular to the tilt plane (therefore parallel to $\mathbf{P_I}$), resulting in C_{B2} layers Figure 6e, or it could be in any intermediate direction (within the plane perpendicular to the director and to the tilt plane) resulting in C_G layers [21]. Finally, the possible polymorphism of polar tilted smectics could be further enriched by combining the indigenous pseudovector polarity $\mathbf{P_I}$, simultaneously with the transverse, $\langle\mathbf{m}_T\rangle$, and the longitudinal, $\langle\mathbf{m}\rangle$, vector-type polarities (Fig. 6f,g).

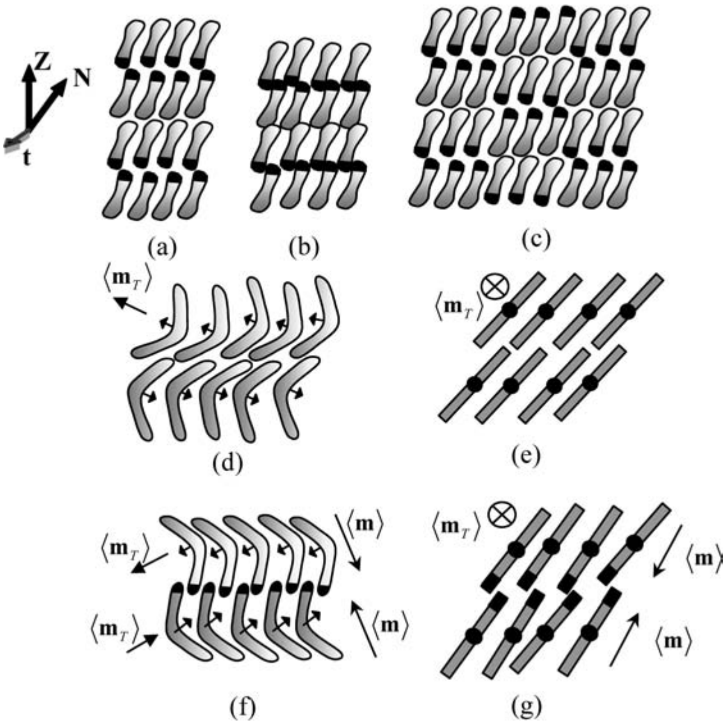

FIGURE 6 Tilted analogues of the polar smectics of figures (3a,b,c,d,f). In (e) and (g) the transverse vector polarity order parameter $\langle \mathbf{m}_T \rangle$ is directed normal to the tilt plane.

POLARITY IN COLUMNAR PHASES

Polar ordering, both of the vector and pseudovector type, is possible in columnar liquid crystals [22]. By analogy to smectic layers, the columns in orthogonal columnar phases can exhibit longitudinal vector polarity, with the order parameter $\langle \mathbf{m} \rangle$ directed along the column axis (Fig. 7a,b), or transverse vector polarity, with the vector order parameter $\langle \mathbf{m}_T \rangle$ directed perpendicular to the column axis (Fig. 7c). For flat plate-like molecules, the longitudinal polarity can be generated by polar intermolecular interactions along the plate axis (Fig. 7a), including electric dipole interactions [8]. The latter possibility obtains because, as shown in Figure 1c, the dipoles in head-to-tail configuration are separated by the "thin" dimension of the plate and thus the energy of that configuration becomes much lower than that of side-by-side. For bowl-shaped molecules (Fig. 7b), their polar ordering in each column is driven by their shape-dictated directional stacking.

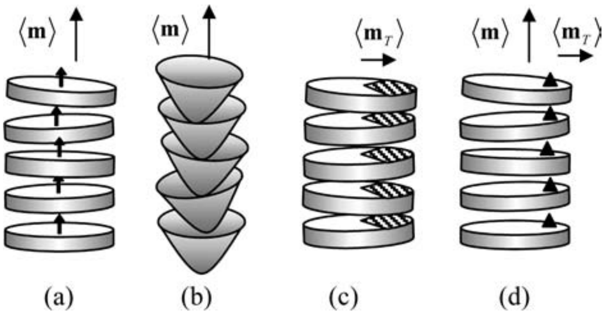

FIGURE 7 Schematic representation of molecular arrangements in polar columns of some orthogonal columnar phases. (a) Longitudinally polar discotic column. (b) Longitudinally polar bowl-column. (c) Transversely polar discotic column. (d) Discotic column with longitudinal and transverse polarity.

Transverse polarity can be generated in columns by amphiphilic interactions resulting from the partitioning of the plate into sectors of different philicity as shown in Figure 7c. In this case the up-down symmetry of the column is maintained but the rotational symmetry about the column axis is lost and the thus columns, by becoming transversely polar, become inevitably biaxial.

Columns exhibiting both longitudinal and transverse polarity have neither up-down symmetry nor rotational symmetry about the column axis and could be generated by combining the interactions corresponding to Figure 7a or 7b with those of Figure 7c, or, for example, by off-centre polar interactions directed across the plates, as shown in Figure 7d.

In tilted columnar phases [23] the director **N**, i.e. the direction of alignment of the molecular plate-normals, does not coincide with the direction **Z** of the axis of the column. These two distinct directions define the tilt plane of the column. The respective tilt pseudovector **t** is defined in terms of **N** and **Z** as in Eq. (6). The tilted ordering of the columns inflicts a pseudovector type polarity on the structure. The molecular origin of the indigenous pseudovector polarity for tilted columnar liquid crystals can be illustrated in close analogy with that of tilted smectics [24] by considering idealised molecules of oblique disc shape as in Figure 8a. The two molecular vectors **s** and **s**′ define a pseudovector $\mathbf{a} = \mathbf{s} \times \mathbf{s}'$ whose direction differentiates between the two mirror image halves, or "faces", of the oblique disc and whose ensemble average $\langle \mathbf{a} \rangle$ in the tilted column defines the indigenous polarity order parameter $\mathbf{P_I} = \langle \mathbf{a} \rangle / |\mathbf{a}|$ (Fig. 8c). The asymmetry is removed in an orthogonal column (Fig. 8b) making $\langle \mathbf{a} \rangle = 0$. The direction of $\mathbf{P_I}$ is along the tilt pseudovector **t**, i.e. perpendicular to the tilt plane of the column, and is therefore compatible with the two-fold rotational symmetry about **t**. Moreover, the pseudovector character of $\mathbf{P_I}$ makes it compatible with the mirror plane symmetry of the tilted columns. As in the case of tilted smectics, pseudovector polarity in tilted columnars can be combined with longitudinal vector polarity (along the director) or with transverse vector polarity, or with both, to provide polar columns in which either the mirror plane symmetry or the twofold rotation symmetry or both symmetries are broken.

CONCLUSIONS AND DISCUSSION

Strictly, none of the known low molar mass liquid crystals exhibit, in their thermodynamically equilibrated bulk state, spontaneous macroscopic polarisation, electric or magnetic. The repetitive building blocks (layers, columns, etc) of phases with partial positional order are often polar but arranged in polarity neutralising patterns (bilayer, antiferroelectric, helical, etc) to produce macroscopically a-polar phases. In this paper we have considered the different types of polar self-assembly of the building blocks, we have quantified the resulting polar ordering in terms of molecular order parameters and we have identified the underlying molecular symmetries and intermolecular interactions.

Vector-type and pseudovector-type polarity refer to two distinct asymmetries of molecular ordering. Vector type applies when there is no plane of symmetry and no symmetry axis perpendicular to the direction of polarity. Pseudovector-type applies when there is no symmetry axis perpendicular to the direction of polarity but there is a plane of symmetry. Vector polarity is theoretically possible for nematics but requires interactions of rather unusual position-orientation dependence. In contrast, amphiphilic, steric and electrostatic dipole interactions can, separately or cooperatively, give rise to vector polarity in the repetitive units of smectic and columnar phases. The polarity in these cases could appear along the primary direction of alignment (longitudinal) or in a direction perpendicular to it (transverse) or both. Pseudovector polarity is produced by the tilted molecular arrangement in all a-chiral tilted smectic and columnar phases. It is driven by the same interactions that give rise to the tilted ordering and reflects the asymmetry imposed on the molecular orientations by the packing constraints.

Introducing polarity, with its different types and combinations, to the common a-polar modes of molecular self-organisation enriches the polymorphism of mesophases with many polar variants. A good understanding of the molecular asymmetries and interactions that favour particular types of polar ordering is certainly essential to the design of such materials. However, in addition to these qualitative assessments, quantitative estimates could be crucial to the successful design. This is so because the thermodynamic stability of mesophases usually rests on a delicate balance between order-promoting interactions that are counteracted by entropy lowering. Therefore, the interactions need to be strong enough to produce the required molecular correlations but not so strong as to destabilise liquid crystallinity in favour of a solid phase. At present, theory and computer simulations could provide useful quantitative input but there are also many complications in obtaining realistic estimates. For example, almost all liquid crystal forming molecules are flexible. For qualitative considerations molecular symmetry is understood to refer to the "conformationally averaged" molecule and so are the intermolecular interactions. In a quantitative treatment, however, the individual molecular conformations (normally lacking any element of symmetry) have to be considered together with the detailed interactions of the various molecular segments. This usually introduces an enormous number of degrees of freedom. Assuming that the latter can be handled computationally, the predictive quality of the results rests on the detailed modelling of the intra- and inter-molecular interactions. A reasonably realistic modelling of interactions in liquid crystals is in general very difficult due to the subtlety of these interactions. For example, interactions associated with partial charge distributions are routinely modelled in terms of fixed electric dipole moments, quadrupole moments etc. This kind of crude modelling does not allow for the possibly significant deformations of the charge distribution caused by intermolecular interactions (polarisability). It also disregards the fact that the multipole expansion of a charge distribution is valid only at distances that are large compared to the spatial extent of the distribution. As a result the respective quantitative predictions would be at best indicative of the possible behaviour of the real system.

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