LIQUID-CRYSTAL STRUCTURE AND THEORY: THE CHIMERICAL MESOPHASE. TOWARDS A NEW PARADIGM BASED ON CHIRAL SYMMETRY BREAKING

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ABSTRACT: It is argued that the presumed mesophase theory of liquid crystals, which has evolved over the preceding century and is currently in vogue, is not only largely conjectural but also ignores fundamental theoretical principles and key experimental observations. Essentially, it is unsupported by hard experimental evidence, and the view that a large collection of molecules can remain both ordered and fluid over a wide temperature range can be challenged. Current theory overlooks the apparently unexceptional effects of liquid crystals on polarized light, which indicate the involvement of chirality (*cf.* the crossed-polarizers experiment). An alternative model proposed herein is based on the idea that chiral symmetry breaking is a fundamental property of matter (deriving from the thermodynamic advantage of the entropy of mixing of a racemate). Thus, even achiral molecules prefer to adopt chiral conformations when possible, which would open a kinetic channel to a non-equilibrium state that is chiral as a whole. This can happen if the racemic mixture of the metastable chiral conformers forms a 'pseudo-conglomerate', with 'like' enantiomers aggregating together. This can ultimately lead to a suspension of chiral nanoparticles in a fluid medium that is possibly also chiral, because of persistent proximity to the nanoparticles. This model of the liquid crystalline state can also explain its amazing electro-optical properties by invoking the development of surface charges on the nanoparticles in an electrical field; this would alter their aggregation behavior, and hence their optical properties. These phenomenal characteristics of matter are apparently manifested under suitable conditions leading to the liquid crystalline state.

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1. INTRODUCTION

Liquid crystal display devices are now practically ubiquitous, no modern home or work-place being without at least one of them. (This is indeed a guarded understatement as mobile phones and other portable devices would also need to be considered!) Liquid crystals, therefore, enable an apparently seamless interface between man and machine, a critical transfer of information that both creates and sustains the flux of modern life [1,2]. And apparently, quite apart from their phenomenal technological and practical impact, liquid crystals also play an intriguing, fascinating and even confounding role at the very frontiers of scientific knowledge!

The historical origins of liquid crystals (henceforth 'LCs') and their gradual evolution to current status as a key 'cog in the electronic-wheel' enabler of the modern information society, interestingly exemplify the (perhaps) stereotypical journey of a scientific discovery: An initial laboratory curiosity, its full potential barely recognized, which winds its way up in fits and starts to catch the attention of major industrial laboratories, these technological prime movers finally catapulting LCs to the status they currently enjoy. And a well-earned status indeed at the interface between materials science and digital electronics, a supreme contribution to the modern age of which chemists can be proud, along with pharmaceuticals, polymers, *et al*.

The first LCs were accidentally discovered during the late 1800s, a period when the structural theory of organic chemistry was rapidly maturing, and heading towards a meaningful partnership with physico-chemical ideas and concepts [2]. In hindsight, therefore, it seems fitting that the discovery of LCs was one among many events that presaged the birth of physical organic chemistry, an area of scientific endeavor that correlates material properties with molecular structure.

An early view of liquid crystals was that they represented an intermediate state of order between the crystalline solid and the isotropic liquid. Thus was born the idea of the 'mesophase' which was even touted as representing an entirely new state of matter. It is perhaps understandable that early workers were wont to jump to simplistic conclusions, but, remarkably, these models have

persisted through a period of conceptual upheavals in chemical science. Even more remarkably, they have steered LCs into a key technological niche in modern life.

There are, however, several problems with the mesophase view of LCs, which become apparent when it is examined critically, even at a qualitative level. The mesophase idea, apparently, also does not take into account all of the available evidence that indeed has accumulated over a century of dedicated effort by various workers who have been drawn from diverse backgrounds to these enigmatic chemical species. In fact, the evidence suggests that the current mesophase view may well need to be abandoned *in toto*, the truth about LCs apparently being more complex and fascinating than could have been imagined.

2. DISCUSSION

2.1 Current Models: the 'Mesophase'

As mentioned above, current models promote the mesophase view of LCs, based on an intermediate state of order between the crystalline solid and the isotropic liquid [2-19]. Although it was an obvious basis for an initial approach, hindsight now apparently indicates that the mesophase represents an overly simple solution to a complex problem.

2.1.1 A hierarchy of order: smectic, nematic, cholesteric

Current models view the liquid crystalline state as representing a measured and step-wise breakdown of the crystalline order, as a crystal melts and the resulting melt progresses towards the isotropic liquid phase. Thus, the incipient smectic phases maintain a semblance of two-dimensional order, the resulting sheet-like structures being able to tilt or slide past each other. The subsequent nematic phases possess an overall 'directional' order without the planar arrangements of the preceding smectic structures. The kindred cholesteric phase is believed to possess essentially nematic order supplemented by a helical pitch.
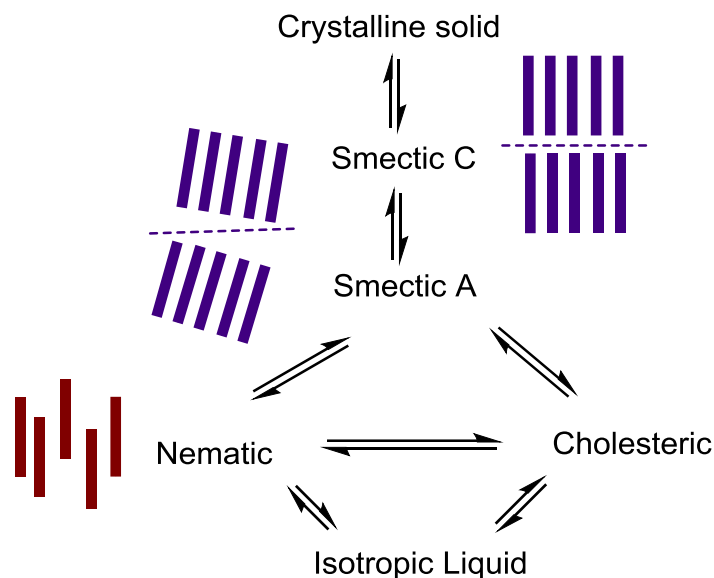
Figure 1. The hierarchical order envisaged in the mesophase model of liquid crystals

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Thus, the mesophase model traces the putative evolution of a hierarchical series of molecular orders that arise in the wake of the annihilation of the crystal lattice (Fig. 1). However, there are several problems with the mesophase model, as discussed sequentially below.

2.1.2 Problems with the mesophase paradigm

Firstly, the view that the collapse of the crystal lattice is followed by states of lower order and symmetry is unviable as these states cannot be sustained at energies higher than at the melting point (m.p.) of the crystal. This is simply because the forces maintaining the integrity of the crystalline lattice are much greater than the weak, long-range forces imputed to sustain the mesophase. Upon the melting of the crystal, the system is carried through a stage of increasing temperature until the free flowing liquid state is reached. It seems illogical to believe that the intermediate state ('mesophase') manages to sustain a level of long range order by virtue of relatively weak intermolecular forces at the higher temperatures (relative to the m.p.) employed.

Secondly, it must be borne in mind that the initial crystalline sample consists of an enormous number of small crystallites (and of the single crystals within each of them), and thus represents a state of relative disorder.

CRYSTALLITES

ISOTROPIC

LIQUID CRYSTAL

ANISOTROPIC!

Figure 2. The presumed coalescence of a partly melted set of crystallites to form LCs. A crystallite consists of a large number of single crystals as indicated by the random arrows

Thus, although each single crystal possesses an identically ordered lattice, these 'lattice vectors' (indicated by arrows in Fig. 2) are randomly ordered in the whole sample. However, current models imply that upon the partial melting of the collection of crystallites, the molecules realign themselves in parallel fashion in the putative mesophase (smectic, nematic, etc.).

Again, this seems highly unlikely in view of the weak dispersive forces that – putatively – not only sustain the mesophase but also replace the strong forces of the crystalline lattice. In fact, the mesophase would then enjoy a higher level of overall order than existed in the collection of crystallites! (The existence of microscopic domains of order in the melt, partly carried over from the crystallite lattice is, of course, possible. However, the domains are unlikely to be extensive and sustainable at higher energy inputs than at the melting point.) Overall, these arguments indicate that even a semblance of overall order is incompatible with loss of crystallinity.

Furthermore, the mesophase model is essentially unsupported by direct experimental evidence. Thus, LCs cannot normally be subjected to the vast array of spectral and related techniques that are routinely used to determine the molecular structural details of crystalline solids and isotropic liquids. Although this limitation does not *per se* invalidate the mesophase model, it represents a devastating sequel to the arguments presented above.

2.1.3 Crossed-polarizers and the twisted-nematics conundrum

In fact, a final piece of evidence that indicates a possible alternative paradigm, involves the well-known crossed-polarizers experiment. Thus, LCs possess the ability to rotate plane-polarized light, an intriguing property that is the basis of their most widespread application as electronic displays. Although this ability clearly indicates an inherent molecular chirality, the mesophase models invoke the twisted nematic effect (TNE) as an explanation [19].

The TNE itself has its origins in brilliant experimental work carried out in the early decades following the discovery of LCs. The TNE was based on the observation that imparting a twist to certain nematic LC samples enabled them to rotate plane-polarized light. This, in turn, was attributed to the nematic order acquiring helical chirality. However, this raises the question whether the macroscopic mechanical action of twisting can generate molecular level chirality! (The rotation of plane-polarized light, particularly in a controlled and consistent manner, implies chirality at the molecular level.)

However, the helical domains generated by mechanical twisting would be too large, hence the resulting chirality too minuscule to measure. Thus, molecular level helical distortions would be required to generate the TNE even in the context of the putative mesophase viewpoint. Similar considerations, in fact, invalidate the argument that the anisotropic nature of LCs can explain the TNE. (In fact, anisotropy is itself a consequence of chirality.)

It appears more likely that the TNE is a manifestation of a dormant molecular level chirality that is possibly amplified upon mechanical twisting. This is because the TNE is essentially unprecedented and certainly not demonstrated in a manifestly achiral sample (as far as is known)!

It is noteworthy that the observed optical activity of a compound depends not just on its intrinsic specific rotation, but also on concentration, solvent and path length (in particular). Therefore, the

mechanical twisting of a LC sample may well modulate its overall composition, thus enhancing the optical rotation to substantial and observable levels.

In fact, the tenuous nature of the TNE finds its most striking manifestation in the electro-optical effects of the crossed-polarizers experiment, the theoretical and practical implications of which will be discussed in some detail later (*cf.* section 2.3). At this juncture, however, it is noteworthy that the TNE − puzzling though it is − serves as a lead to a totally new view of LCs that is not only a departure from the mesophase model, but also defines a fundamentally novel approach centred on chirality.

2.1.4 The cholesteric choice – a remarkably fateful coincidence?

Intriguingly, in fact, the discovery of the TNE and the close relationship between LCs and chirality may well be the result of one of the most remarkable coincidences in the history of science. Thus, the first LC studied happened to be cholesteryl benzoate, a natural product and hence optically active. Furthermore, the workers who chanced upon the liquid crystalline behavior of these cholesteryl derivatives were apparently adept at using the polarizing microscope. Perhaps curiosity led them to extend these studies to other non-natural liquid-crystalline compounds!

Possibly, these early workers were unaware of the intricacies of optical activity and stereochemistry: a trained chemist would not have employed the polarizing microscope with other LCs that did not even possess a stereogenic centre! This would indeed have been tragic, as then the key discovery that was later to be the basis of the revolution in electronic gadgetry perhaps would never have occurred!

2.2 Hypothesis: Liquid Crystals as a Broken-Symmetry State

The above discussion indicates that the crossed-polarizers experiment inextricably links LCs with molecular chirality. This was previously unforeseen, essentially because the inevitable origins of the rotation of plane-polarized light in molecular level chirality were ignored,

apparently based on the presumed inviolability of the mesophase paradigm. Thus, the TNE was introduced to accommodate the crossed-polarizers observations within the mesophase model. The essential unviability of this now reveals the need for a new approach towards understanding the very existence of LCs and, of course, their enigmatic optical properties.

Thus, the above assessment leads to the inescapable conclusion that LCs represent an existential conundrum! The persistence of a manifestly metastable state of matter, which can be carried through a wide temperature range spanning its crystalline origins and the fluid liquid, poses a challenge to physico-chemical theory. An intriguing conceptual lead, however, becomes apparent based on an honest assessment – without preconceptions – of the overall evidence.

2.2.1 Spontaneous generation of optical activity and the liquid crystalline state

To reiterate, the crossed-polarizers experiment strongly indicates that LCs possess molecular level chirality. Also, this manifestly inescapable conclusion was – perhaps understandably – ignored by early workers, likely because certain stereochemical ideas and concepts were yet to become the commonplaces they are now [20]. Thus, the later discovery of biphenyl enantiomerism led to the realization that molecular chirality can exist in the absence of the traditional stereogenic centre, the resulting area of atropisomerism then experiencing explosive growth. Among other stereochemical ideas that were little known during the early evolution of LCs, the spontaneous generation of optical activity and its amplification are particularly relevant to this discussion.

It is now well recognized that achiral molecules can form chiral crystals (Fig. 3), and racemates of chiral molecules crystallize in a predominantly non-racemic form even in the absence of an external chiral influence. This latter phenomenon, usually termed 'second order asymmetric transformation', requires that the racemate crystals undergo 'spontaneous resolution' and exist as a conglomerate, with the formation of two enantiomorphous crystalline forms.
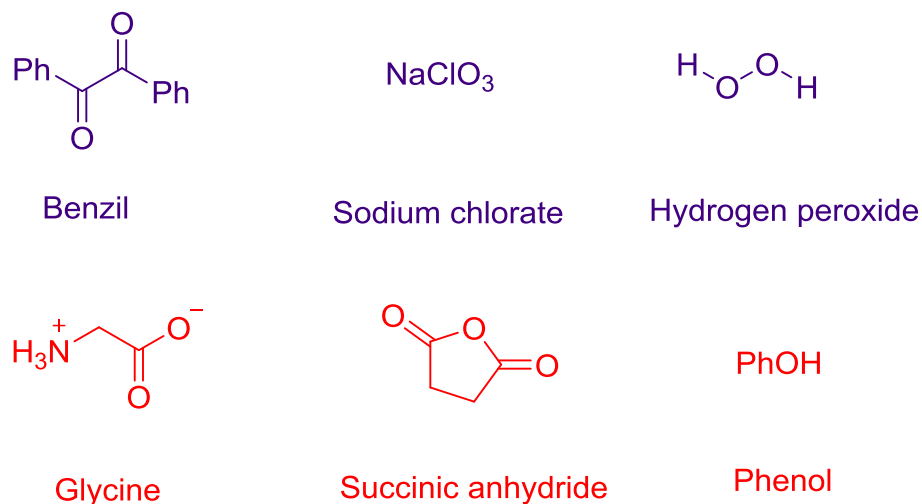
Figure 3. Examples of achiral molecules that form chiral crystals

Furthermore, if the enantiomers are inter-convertible in solution, the spontaneous crystallization (by accidental nucleation, say) of one enantiomer will shift this equilibrium and lead to enantiomeric enrichment in the crystalline state.

The solution state analogues of these phenomena, *i.e.* the spontaneous evolution of substantial levels of optical activity in the absence of crystallization, are practically unknown. However, the amplification of a pre-existing trace optical activity to considerable levels in solution is well documented, *e.g.* non-linear effects with chiral catalysts, autocatalysis, etc.

This necessarily brief discussion of relatively recent developments in stereochemistry [20], however, conveys the idea that the link between classical configurational chirality and observed optical activity can sometimes become tenuous. The case of atropisomerism, in particular, demonstrates that molecules can adopt stable chiral forms in three dimensions, even though they may lack a conventional stereogenic centre and thus appear achiral. More importantly, many of the above discussed concepts are germane to the apparent optical activity of LCs.

2.2.2 Racemates and the entropy of mixing – interconverting achiral and chiral forms

Atropisomerism is now indeed a well-documented phenomenon and represented by a very large number of examples. These, in most cases, lead to the existence of a single pair of enantiomers

that may or may not interconvert rapidly. In the archetypal case of biphenyl, for example, the enantiomers cannot be resolved, and are also unaccompanied by competing conformational changes. (Thus, there are a total of only two forms.)

An interesting variant that may be envisaged, however, involves an additional achiral form in equilibrium with two enantiomeric forms. This is possible in the case of relatively complex molecules with flailing moieties that possess several degrees of freedom. In such cases, expectedly, all the forms would have only a fleeting existence and hence would be non-isolable (and possibly non-observable, even spectroscopically). Such mixtures of conformers, however, are thermodynamically intriguing, as set out below.

It is known that a racemate possesses a relative thermodynamic stability by virtue of the presence of both the enantiomers, corresponding to the entropy of mixing [20]. This amounts to $Rln2$, relative to a single enantiomer. ('R' is the gas constant; in defining the entropy of mixing one mole of the racemate is being compared with one mole of either enantiomeric form.) However, this entropic advantage enjoyed by a racemate has intriguing consequences in the case of compounds that also possess an achiral form in equilibrium. Thus, in these cases, the achiral form and the two enantiomers would exist in nearly equal amounts in thermodynamic equilibrium, as seen from Eq. 1:

$$-RTlnK = \Delta G^o = \Delta H^o - T\Delta S^o = -RTln2 \qquad (1)$$

This relates the equilibrium constant (K) to the standard Gibbs free energy change (ΔG^o), and the corresponding enthalpy (ΔH^o) and entropy (ΔS^o) changes (T is the absolute temperature). Furthermore, if enthalpy changes are negligible in a particular case, ΔS^o corresponds to the above entropy of mixing of the enantiomers (worth $Rln2$). Hence, the equilibrium constant K = [racemate]/[achiral form] = 2, *i.e.* equal concentrations of the achiral and each of the enantiomeric forms.

Furthermore, an interesting consequence is noteworthy. Thus – whenever possible – an achiral form must perforce exist in equilibrium with alternative enantiomeric forms, as the latter enjoy a thermodynamic advantage *via* the entropy of mixing criterion! (The relative amounts would depend on the value of ΔH^o, assumed equal to zero above, but likely valid in many other cases too.)

2.2.3 The incipient melt scenario – the inexorable drive towards non-equilibrium

The above discussed conformational and attendant thermodynamic consequences could well follow the melting of a crystalline solid (assuming the presence of the requisite structural features). The resulting incipient melt would be subject to a number of thermodynamic and structural effects. In the case of a complex molecule that is capable of the above discussed conformational mobility, the molecule would be in a position to explore conformational space, once the restrictions of the crystalline lattice are lost. This would rapidly lead to the above discussed equilibrium mixture of achiral and enantiomeric forms. (Note that there may be several of them, none of which need have existed in the prior crystal.)

Furthermore, the chiral forms may be 'putative conglomerates'*, i.e.* capable of spontaneous resolution in the hypothetical crystalline form. This implies that in the incipient melt the same enantiomers possibly aggregate together, noting that these aggregates would persist until the melt attains full translational freedom. However, the evolution of the incipient melt in response to increasing temperature would depend on a number of factors. In an 'all-out equilibrium' scenario, in which heat flows rapidly and is absorbed by all species, the aggregates would rapidly break down leading to the fluid liquid state. Intriguingly, however, the following alternative scenario is also possible and noteworthy.

In this, heat flows are discontinuous and non-random, resulting in selective melting of the aggregates. It is also possible that disaggregation is autocatalytic, *i.e.* the accidental dismantling of an enantiomeric aggregate accelerates the destruction of the same aggregates elsewhere in the partial melt.
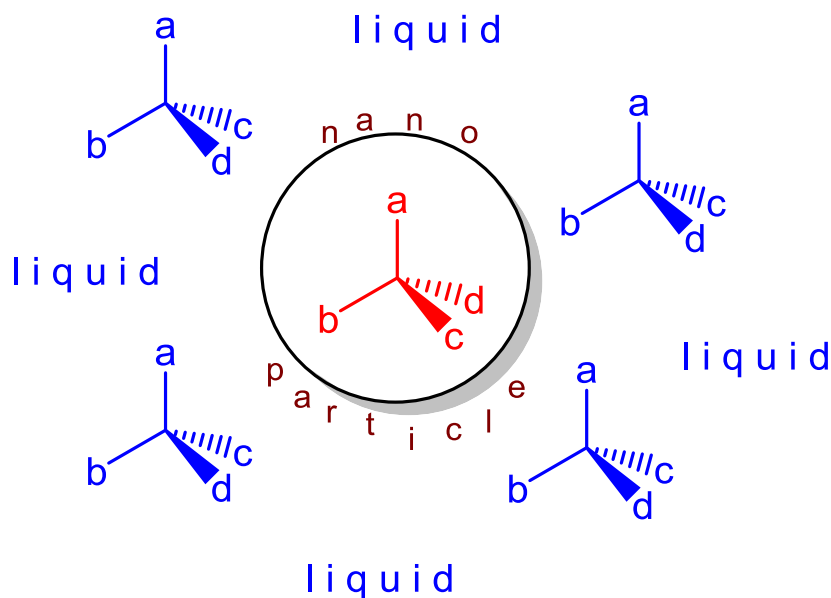
Figure 4. A LC as a chiral nanoparticle suspension in a liquid that is of opposite chirality (or achiral in the general case)

This would gradually lead to the formation of a mixture which is largely composed of only one type of enantiomeric aggregate. Thus, essentially, the system has spontaneously become homochiral (the other enantiomeric aggregates having melted away).

In fact, this state would represent a suspension of enantiomeric aggregates – possibly nanoparticles – embedded in an achiral liquid (Fig. 4): In essence, a 'liquid crystal'! The persistence of this state over a relatively wide temperature range would likely be due to 'thermal buffeting', itself resulting from the relatively high specific heat of the liquid phase. It is indeed well known that liquids generally possess higher specific heats than solids, as molecules in the liquid state possess greater degrees of freedom.

This would ensure that the above chiral nanoparticle suspension (aka LC) would undergo structural changes reluctantly as the temperature is raised. This would explain its persistence over a wide temperature range relative to the melting of the crystalline precursor. (This argument cannot be applied to the mesophase model, however, as in it the oriented molecules also

constitute the liquid phase, *i.e.* possess restricted freedom. In the present model, the random achiral liquid phase 'thermally protects' the suspended nanoparticle aggregates.)

In fact, the spontaneous generation of chirality and optical activity being proposed above are well served by precedent. As was discussed in section 2.2.1, the spontaneous generation of enantiomeric chirality is now very well established in a large number of cases, particularly in the crystalline state. The proposal herein draws upon this precedent as a key contributor to the overall phenomenon. It should also be noted that the overall chirality of the LC arises from the inherent chirality of the nanoparticles, and not from the manner in which they are arranged in the suspension. (This is a random arrangement, *i.e.,* there is no orientational order, and it would largely persist until the isotropic phase is reached.)

2.2.4 The broken-symmetry state: fundamental phenomenological significance

The above arguments – apart from providing a plausible alternative model of LCs – also raise an intriguing question of fundamental import. It was seen that the formation of a LC is accompanied by the spontaneous generation of both chirality and optical activity. Furthermore, the persistence of the liquid crystalline state – which proceeds towards the isotropic liquid in measured fashion – implies that the said state possesses a corresponding level of stability.

The spontaneous generation of chirality and optical activity in a LC are partly a consequence of the thermodynamic advantage gained from the entropy of mixing. This *per se* implies the existence of a thermodynamic drive towards the formation of chiral forms in the racemate condition; also inherent to this is a kinetic drive – *via* aggregation – towards the formation of a non-equilibrium state that is substantially homochiral. In this combine, a shallow thermodynamic sink and a kinetic *cul-de-sac* conspire to ensnare matter into a state of broken symmetry. To the extent that the evolution of the state appears inevitable under the above conditions, it represents a fundamental phenomenon involving a subtle and fascinating interplay of matter and energy.

The molecular structural features that enable this phenomenon can be discerned from the above discussion. Thus, considerable conformational degrees of freedom are clearly of key importance, in order to produce both achiral and chiral forms. The nature of the incipient melt, particularly its heat flow characteristics, is also critical in determining the rate of progression towards the isotropic liquid state (but *vide infra*).

It also bears mention that, in recent years, there has indeed been much interest in the spontaneous generation of chirality with subsequent amplification in several soft matter systems [21]. (These extend earlier studies essentially based in crystallization phenomena, particularly the second order asymmetric transformation of racemates.) It should be noted that these studies, although supported by compelling experimental evidence, pertain to select systems. However, what is being proposed herein is that spontaneous symmetry breaking is fundamental to the liquid crystalline state in general, being intricately involved in its formation and maintenance.

2.2.5 The crossed-polarizers experiment

The key application of LCs that revolutionized digital electronics lies in their ability to rotate plane-polarized light. LC based devices employ a set of polarizing filters aligned at right angles to each other, with an intervening film of the LC. Thus, the light polarized by the first filter is rotated by the LC film and is again transmitted by the second filter. As argued above, this intriguing phenomenon cannot be satisfactorily explained in the mesophase model.

In the current model, the proposed suspension of chiral aggregates would be chiral as a whole, by virtue of intimate contact between the achiral melt and the chiral aggregates. Thus, the rotation of plane-polarized light is an expected consequence and a natural property of the suspension. Also, the proposed spontaneous generation of optical activity implies that the involved chirality could be of either sense. Note, however, that the observed optical rotation would depend on the amount of twist imparted to the sample as also the orientation of the second polarizer in the crossed-polarizers set-up. These are apparently adjusted by trial and error until the TNE is measurably manifested (*cf.* section 2.1.3 above).

*2.2.6 Structural features of LCs – postulates and precedents*

The above discussion has focused on the thermodynamic and kinetic requirements for effecting the transition from the crystalline to the liquid crystalline state. However, LCs represent a select class of compounds that are able to evade a direct transition to the isotropic liquid state – the fate of the vast majority of crystalline compounds! This raises the obvious question about the molecular structural features that enable this incursion into the liquid crystalline state.

An important structural requirement that emerges from the above discussion is the presence of conformational freedoms, normally associated with long alkyl chains. Indeed, this feature has for long been known to lead to the formation of LCs, but was explained in the mesophase model in terms of enhanced long range attractive forces. In the present context, however, alkyl chains can fold themselves into chiral conformers leading them further into the chiral non-equilibrium state postulated above.

Although this would be an important requirement for molecules that are otherwise achiral, it is also possible to envisage molecules with pre-existing chirality in the racemate state. These do not need the complicated set of conformational changes outlined above to attain the liquid crystalline state. These molecules with prior chirality can indeed access a non-equilibrium homochiral state if the chiral conformers are rapidly inter-convertible. In such a case, selective enantiomer aggregation in the incipient melt can lead to the liquid crystalline state as postulated above. (Clearly, the presence of an achiral form is not a pre-requisite for the formation of a LC!)

The molecular structures of the currently known liquid crystalline compounds generally accord with the above conclusions (Fig. 5). Interestingly, a number of them are biphenyls and analogous compounds, recognized archetypes in the family of atropisomeric compounds. Also, the structural features generally recognized as desirable for the formation of LCs – rigidity, linearity, the presence of polar head and tail groups – are also conducive to the formation of the above (nanoparticle) aggregates. Many possess sterically-congested U-shaped moieties that would be forced into helical conformations, structural anisotropy ensuring that these are also chiral.
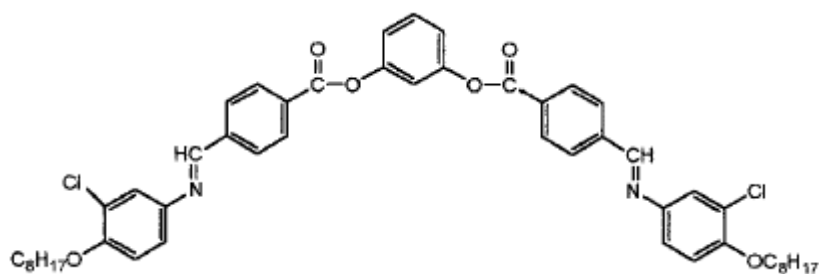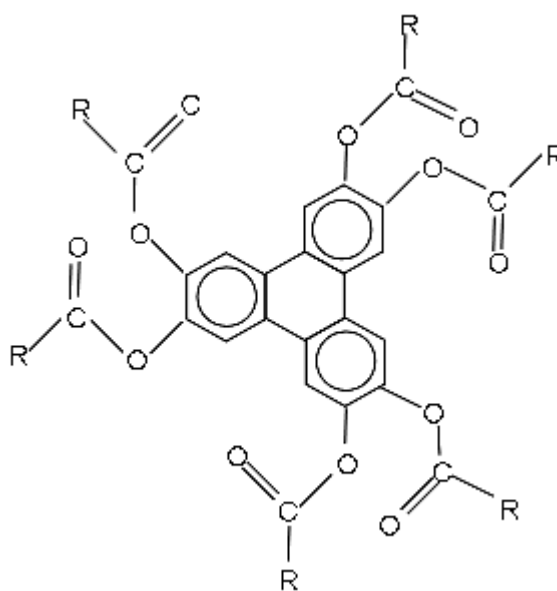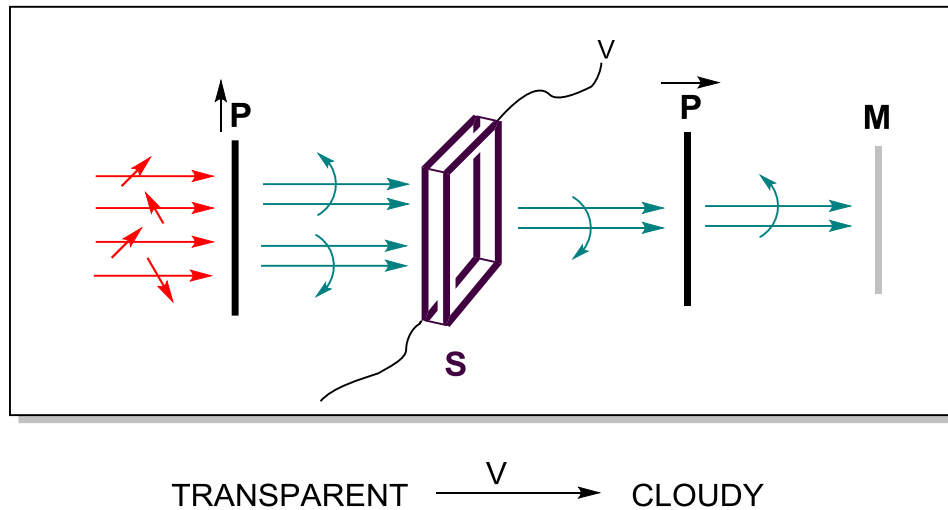
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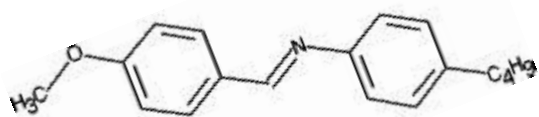
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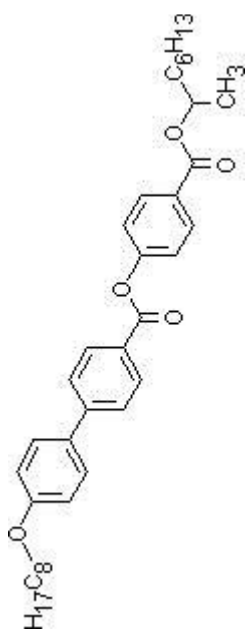
A DISCOTIC

Figure 5. Structures of a few compounds known to form liquid crystalline phases

TRANSPARENT $\xrightarrow{\text{V}}$ CLOUDY

Figure 6. A simplified depiction of the crossed-polarizers experiment; 'P' are vertical and horizontal polarizers (with corresponding arrows, set up orthogonally), 'S' is the LC film, 'V' is voltage, 'M' is a mirror; the randomly oriented incident light is plane polarized by the first 'P' (the resulting right and left circularly polarized light is shown by curved arrows); the rotation of this by 'S' and 'P' is represented by the presence of one type of circularly polarized light

A perceived focus of the mesophase model was that molecular structure determines the nature of the LC formed, *i.e.* nematic, discotic, etc. This structure-property relationship, however, can be accommodated in the model being proposed on the basis of the nature and type of the aggregates constituting the suspension. Thus, for example, linear molecules would form aggregates different from those formed by discotic molecules, in terms of shape, size, the number of molecules and the nature of their interaction, etc. The known classification of LCs can thus be related to molecular structure without recourse to the presumptions of the mesophase model (essentially based on molecular alignment and orientation).

2.2.7 Electro-optical properties: the TNE in an electrical field

Research on LCs has largely been driven by their application in electronic displays; the associated theory, however, has apparently served as a guiding principle rather than as *leitmotif.* The key characteristic that has enabled LCs to revolutionize electronic gadgetry lies in certain unique optical and electrical properties possessed by them. In effect, a sample of a LC that is normally transparent to polarized light becomes opaque when an electrical field is applied to it.

However, the effect is manifested only in an appropriately constructed device, generally referred to as a crossed-polarizer (Fig. 6). The mesophase model explains the effect in terms of a change in alignment of the oriented molecules in a nematic LC, which affects their ability to rotate plane-polarized light.

The above electro-optical effect is key to the revolutionary role played by LCs in modern electronic gadgetry, and one that has made the difference between a theoretical curiosity and an industrial-commercial triumph. In a supreme irony, however, and based on the preceding discussion of the TNE (*cf.* section 2.1.3), their currently accepted mode of action may need to be abandoned, as discussed further below.

2.2.8 The electro-optical TNE – theoretically implausible and practically unviable

In the mesophase model, the TNE brings the key assumptions together and links the theoretical with the practical (in its electro-optical manifestation). However, the pictorial representation of aligned molecules upon which the TNE is based is fundamentally dubious, as discussed further below.

In the TNE, 'nematically aligned' molecules are conferred, manually, with a helical twist [19]. Along with the imputed quasi-parallel alignment of the molecules in the ensemble, this perforce endows the system with chirality. The introduction of an electrical field is believed to untwist the very same molecules – an assumption introduced to explain the fact that polarized light is not transmitted in the untwisted state. Rather remarkably, however, turning off the electrical field, apparently, completely reverses all the observed effects. There are two problems with the current view of this stunning phenomenon.

Firstly, the untwisting experienced by the molecules in the presence of the electrical field would destroy the chirality inherent in the ensemble. <u>It is implausible, then, that they would recover their original helical form when the electrical field is switched off, as there is no chiral director present</u>. Secondly, the twisting and the untwisting of the ensemble should result in corresponding

mechanical motions of the entire LC sample, in the same manner as the original twisting performed manually. And, furthermore, these effects should persist over the life-time of the LC sample and be reproduced practically *ad infinitum*!

Clearly, the imputed spontaneous recovery of the chiral state by the LC upon the electrical field being switched off is theoretically forbidden. This is essentially because the twisting motion can occur in either direction (left or right handed) and there is no chiral director remaining. (Even a single act of twisting should thus destroy the chirality of the sample permanently!) The mechanical twisting-untwisting motions required of the LC sample in the mesophase model have also not been observed. (Note that the walls of the cell holding the sample cannot constrain the putative movement of the LC mass: in that case, the TNE would not be observed!) Overall, therefore, the mesophase model is manifestly unviable as an explanation for the observed effects.

2.2.9 Alternative explanation for the electro-optical effect: charged nanoparticles

The above discussion implies nothing less than the collapse of the paradigmatic mesophase model itself. Hence, it is now opportune to explore the electro-optical effects – stunningly remarkable *per se* as also for their immaculate reproducibility – *vis-à-vis* the new broken-symmetry model of LCs.

It is noteworthy, in fact, that the above onset of opacity in the LC sample can be due to two reasons. Firstly, it could indicate the loss of the ability to rotate plane-polarized light; this would not be detected as the second polarizer is itself set at right angles to the first one. This explanation, however, seems unlikely as it indicates a loss of the chiral state, although the effect is clearly reversible. Thus, the recovery of the chiral state in the absence of a chiral director is ruled out (*vide supra*).

Secondly, the opacity could indicate a general loss of transmission of light. In the broken-symmetry model, as argued above, LCs are viewed as a chiral-nanoparticle suspension. It is possible that the nature of the nanoparticles would be affected in the presence of an electrical

field, as they would likely acquire charges on their surface. Two effects then appear likely, both based on the fact that similar charges are mutually repulsive, as discussed below.

Firstly, the nanoparticles would tend to minimize the charge-to-surface ratio, hence larger particles would be favoured. Secondly, the level of aggregation of the nanoparticles would be lowered. Overall, therefore, larger and more dispersed particles would be favoured in an electrical field. It is plausible that this would essentially render the sample more turbid and thus opaque towards light. These effects would also be reversible, as the surface charges would be dissipated when the electrical field is switched off.

Furthermore, the mechanisms by which the proposed changes occur will not be the same as perhaps may be envisaged in the presence of a solvent. The LC is (generally) composed of a single chemical species, which, however, is present in many molecular forms. These include the chiral and achiral conformers, and the aggregated nanoparticles of the chiral forms, as discussed at length above. Also, the molecules in the achiral medium and their chiral isomers in the nanoparticles are rapidly inter-convertible. Thus, the proposed changes in particle size and aggregation level are not limited by diffusion, as the effects can be transmitted in 'relay' fashion.

In other words, the nanoparticles would be essentially embedded in a gel-like matrix with little freedom of motion, and hence incapable of diffusion in the normal sense. However, the proposed changes in their size and shape can still occur via a 'chain-relay' mechanism, involving molecules in the intervening space between the nanoparticles that constitutes the bulk of the sample. Thus, there would be a reversible transfer of molecules between the bulk and the nanoparticles, rather than the nanoparticles themselves diffusing towards each other. This is the most likely mode by which the LC undergoes changes at the molecular level in response to an electrical field, hence their seemingly instantaneous character.

2.3 Future Directions

The collapse of the mesophase theory, as discussed at length above, now raises intriguing questions about the status of LCs. Their technological utility and ubiquity in modern life notwithstanding, their theoretical status remains enigmatic and elusive. The hypothesis proposed above – although plausible and perhaps the most likely under the circumstances – remains experimentally unproven.

A particular problem with LCs is that they are not amenable to the physical techniques employed for the study of crystalline solids (on the one hand) and solutions (on the other). Therefore, considerable ingenuity is indicated in future attempts to pin down their exact nature. In the case of the present hypothesis, which is based on the possible formation of nanoparticle suspensions, it would be interesting to pursue the proposal by recourse to electron microscopic examination of the surfaces of LCs. An indication thereby of the presence of nanoparticles would go a long way in lifting the veil of mystery surrounding these fascinating and enigmatic species.

3. CONCLUSIONS

A careful consideration of the prevalent mesophase paradigm of the liquid-crystalline state indicates that it is fundamentally flawed. Essentially, it appears that the model of molecular order and alignment that are not only extensive but also maintained by weak long-range dispersive forces is *per se* unviable and also incompatible with the inherent fluidity of the medium. More pointedly, the breakdown of the crystalline order cannot be followed by a lower level of order – hence one maintained by weaker forces – that persists through a temperature range higher than the melting point of the crystal. (Thus, the weaker forces should be more easily obliterated at the higher temperature ranges!) The mesophase model also fails to satisfactorily explain the twisted nematic effect, in particular the crossed-polarizers experiment and its electrical-field variant.

An alternative model explored herein invokes the spontaneous generation of chirality and optical activity in the incipient melt as the key to the liquid crystalline state. Thus, conformational freedoms allow certain molecules to adopt chiral – albeit unstable – forms, the resulting

racemates being thermodynamically favoured over achiral isomers by virtue of the entropy of mixing. This is coupled with 'conglomerate-like' aggregation of the enantiomeric forms and followed by the selective and irreversible melting of one of the enantiomeric aggregates, leading to a suspension of chiral nanoparticles in an achiral melt. This partially-molten solid, apparently, represents the liquid crystalline state adequately.

The rotation of plane-polarized light – the crux of the twisted nematic effect – is a natural consequence of the overall chirality of the suspension, the electrical field effects then arising from the acquisition of surface charges on the nanoparticles that alter their aggregation behavior. These ideas not only satisfactorily explain all the known experimental observations but also lead to intriguing and novel theoretical insights into the liquid crystalline state. In essence, this state apparently represents the culmination of a remarkable series of molecular events that entrap matter in a metastable, non-equilibrium pit of sorts.

The future would possibly witness experimental tests of the above proposals. In particular, electron microscopic examination of the surfaces of LCs appears to be a possible approach, as it might lead to evidence for the existence of the proposed nanoparticles

Thus, the science and technology of liquid crystals – in enabling the rise and the ubiquitous dominance of modern electronic gadgetry – have carved for themselves an eternal niche in the saga of human progress. However, their essential nature, it appears, is only now beginning to unfold, to reveal an intricate web of matter and energy hitherto unfathomed.

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