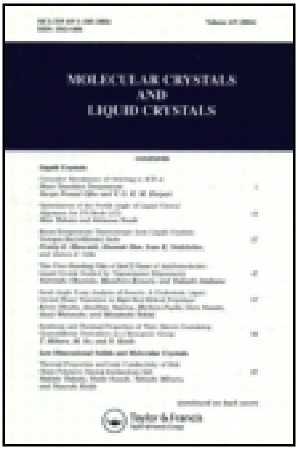

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A Pictorial Approach to Helical Macrostructures in Smectic Liquid Crystals

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A Pictorial Approach to Helical Macrostructures in Smectic Liquid Crystals

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Physical theories concerning the structures and properties of chiral smectic liquid crystals abound, however, very few are of practical use in the design and subsequent synthesis of materials. The development of macroscopic theories, although very useful in the explanation of physical phenomena, are not readily transferable to the microscopic state. Thus, the design of materials depends more on a qualitative approach supported by property-structure correlations than it does on quantitative deliberation. However, viewing the formation and stabilisation of mesophase structures from the microscopic molecular aspect can lead to some very interesting perspectives. In this article, crude or gross molecular shapes are used to investigate local packing arrangements of chiral molecules in layered mesophases. The formation of helical macrostructures is readily described using this form of modelling, and in turn the formation of antiferroelectric and twist grain boundary phases can be rationalised in terms of property-structure correlations.

Keywords: Chirality; helicity; ferroelectric and antiferroelectric liquid crystals

INTRODUCTION

After the explosion of interest in the nematic phase in the early 1970's and its successful implementation in display devices, attention naturally turned to the smectic state and its exploitation in solid state devices. Early in these investigations it was apparent that the smectic C phase had very interesting features and physical properties making it suitable for further study. Initial phenomenological theories linked the tilting of the molecules in the layers of the smectic C phase to molecular structure in terms of dipolar interactions [1] or through steric factors such as the favourable packing of zigzag shaped molecules [2]. Property-structure correlations soon showed that neither of these theories suitably explained experimental observations which

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correlated phase formation with molecular structure. For example, the formation of the smectic C phase was shown to be dependent on the number and length of the terminal aliphatic chains [3–5], rather than due to molecular polarity in terms of terminal outboard dipoles as proposed by McMillan [6]. Subsequently, other models appeared where induced-dipole-permanent-dipole interactions were introduced in order to unite the two theoretical approaches [7]. These investigations resulted in the development of a complex quadrupolar model to describe the physical features of the smectic C phase [8]. Sadly, however, as these complex theories were developed they became more abstract in terms of the structures of real molecules that had been synthesised and evaluated. However, structural studies by Bartolino, Doucet and Duran confirmed the important proposal that the molecules in the smectic C phase have zigzag gross structures similar to those proposed in the Wulf model [8]. They also proposed that the molecules are arranged in layers with their central rigid cores being more tilted than their overall molecular structures.

At a similar time to these developments, the seminal idea of the possibility of a ferroelectric smectic C structure was introduced by Meyer [9], and confirmed by Keller *et al.* [10]. The focus of interest in smectic C phases quickly switched to the analogous chiral state because of the clear potential for its use in display device applications [11]. However, apart from molecular tilting, new properties such as helical twist and spontaneous polarization had to be taken into account in the development new materials for device applications. The helical twist had to be suppressed, whereas the spontaneous polarization had to be optimised, consequently an understanding of both the magnitude and direction of these effects became important. Initially, empirical relationships between molecular architecture, helical twist and polarization vector were developed in order to create mixtures for the early forms of surface stabilised ferroelectric LCDs [12,13]. In addition, molecular models linked to the theories proposed by McMillan [1] and Wulf [2] for the achiral smectic C phase were resurrected in attempts to understand helicity and polarization. In particular, the zigzag packing arrangements of the molecules in the smectic C phase were used in part to rationalise the directional relationships of the helical structure and the spontaneous polarization [14,15]. More recently molecular simulations and recognition processes have been developed in order to provide a microscopic model of the chiral smectic C phase [16].

In a similar fashion to the physical phenomenological models, models based on molecular dynamics and recognition processes have become so complex that they are difficult to use in terms of designing and constructing new molecules. Spurred by recent publications by Yoshizawa [17–19], I have returned to the less complex approach of examining the packing requirements of simple molecular architectures. Yoshizawa has shown, by detailed NMR studies, that the molecules in the smectic C* phase have twisted structures, and the twist is propagated from one layer to the next through interlayer permeation, see Figure 1. In examining his model, it is clear that it is also applicable to antiferroelectric and twist grain boundary phases.

SMECTIC C* HELICAL MACROSTRUCTURES

The first materials that were found to exhibit twist grain boundary phases were derivatives of phenylpropiolates [20, 21], see Figure 2. Interestingly, as the homologous series of *R* or *S*-1-methylheptyl 4′-(4-n-alkoxyphenylpropioloyloxy)biphenyl-4-carboxylates is ascended, not only do twist grain

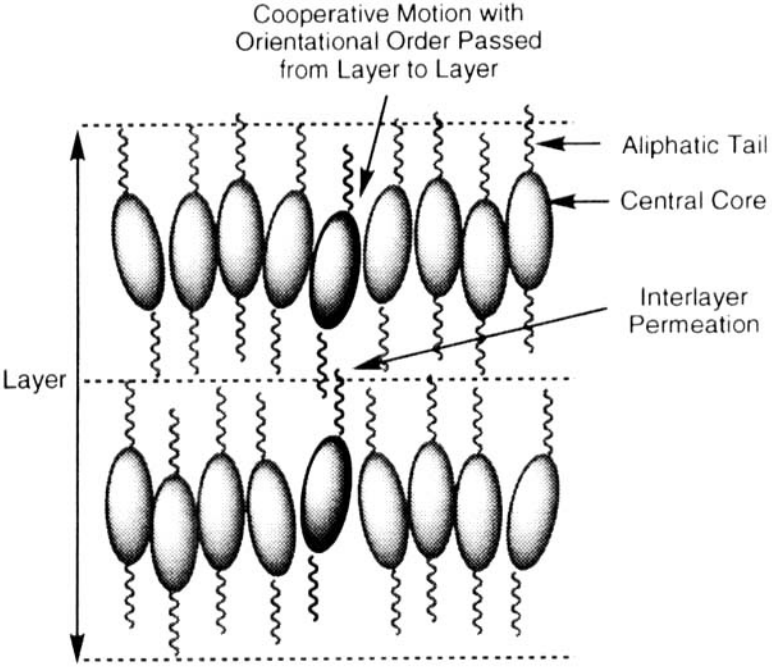


FIGURE 1 Interpenetration of the layers by molecules in adjacent layers in the smectic A phase.

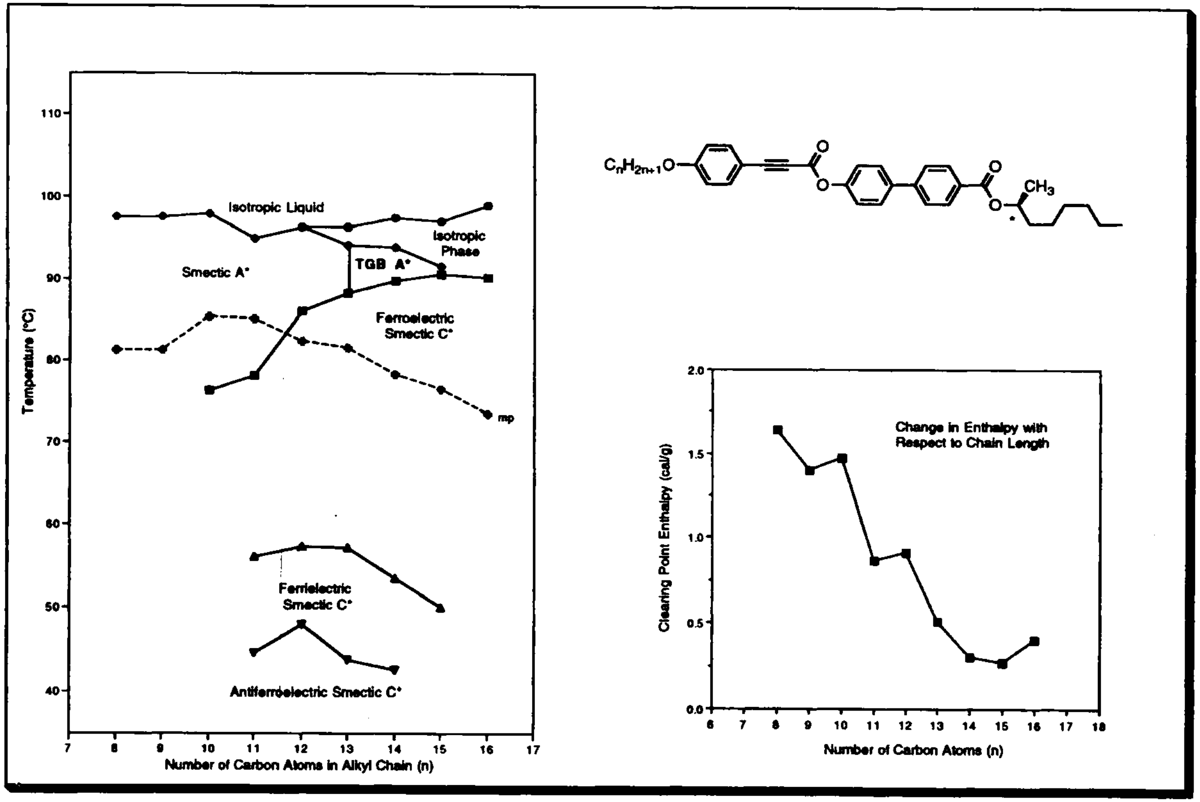


FIGURE 2 The transition temperatures (°C), phase sequences and enthalpic data (cal g^{-1}) for the *R* or *S*-1-methylheptyl 4′-(4-n-alkoxyphenylpropioloyloxy)biphenyl-4-carboxylates.

boundary phases appear, but also antiferroelectric and ferrielectric mesophases are found. The antiferroelectric and ferrielectric phases occur at slightly shorter alkoxy chain lengths than the TGB phases. This is common for many series examined subsequently where TGB phases occur. The fact that TGB and antiferroelectric phases occur together suggests they have some features that are in common with respect to their phase formation/stabilisation. For example, of the series of compounds shown in Figure 3, all exhibit TGB phases and many also exhibit antiferroelectric properties. In all of these compounds the chiral centre is adjacent to the central aromatic core of the molecular structure. In addition, for these phases to be observed the terminal aliphatic chains should be relatively long.

The first compound that was found to exhibit a TGB phase was *S*-1-methylheptyl 4′-(4-n-tetradecyloxyphenylpropioloyloxy)biphenyl-4-carboxylate (**14P1M7**). Its structure and transition temperatures are shown together in Figure 4. Also shown in the figure are the minimised energy structures of

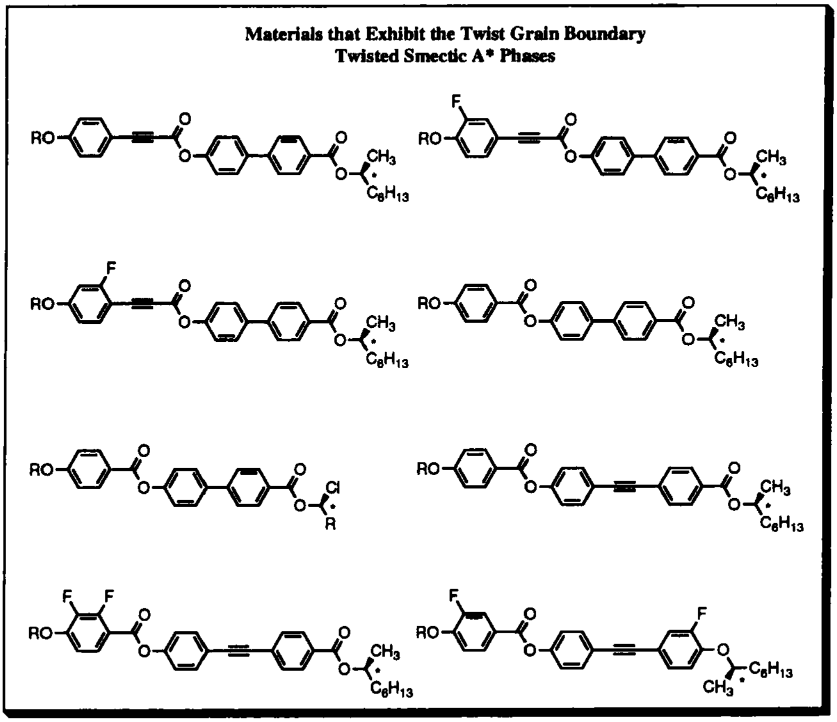


FIGURE 3 Materials that exhibit the Twist Grain Boundary phase.

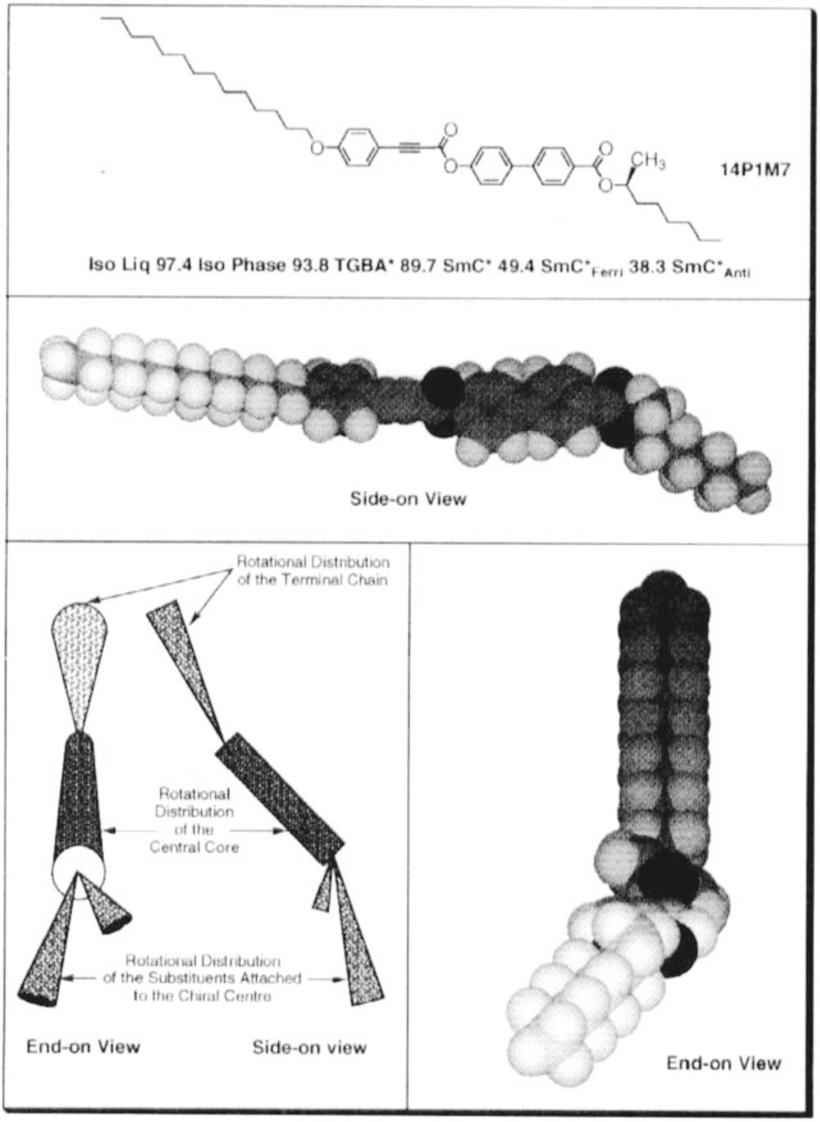


FIGURE 4 The modelled structures of *S*-1-methylheptyl 4'-(4-n-tetradecyloxyphenylpropioloyloxy)biphenyl-4-carboxylate.

the material (determined at 0 K in the gas phase using an Indigo XS24, 4000 Silicon Graphics Workstation with QUANTA and CHARMm software). The side-on and end-on orientations of the molecular structure are shown. The side-on orientation suggests a zigzag shaped gross structure, however, the end-on orientation demonstrates that the molecular structure is not rod-like, or zigzag shaped, or even banana-like (as utilised in many theories), but 'twisted' as depicted in the cartoon inset of the figure. The twist is essentially caused by the stereochemistry about the chiral centre. The degree of the internal 'molecular twist' will be proportional to (i) the molecular length, (ii) the angles that the chains make with the core, (iii) the rotational distribution functions of the terminal chains, the core, and the overall molecular structure, and (iv) the stereochemistry and location of the chiral centre relative to the core and the length of the terminal chain. If we assume that the molecules are fixed, ie, are not in dynamic motion, then a simple or crude way of describing the molecular twist is through the displacement of the end of the molecular structure relative to the racemate, as shown in Figure 5. The displacement will increase if the molecular length is increased or if the distribution functions for the various molecular rotations are sharp (ie, where the chiral centre is rotationally trapped). The displacement in some senses is therefore a measure of the degree of breaking of the mirror symmetry of the system.

Now consider how molecules with twisted structures pack together in the smectic C* phase. The molecules will be packed in a random head-to-tail arrangement within the layers, and there will be substantial interlayer mixing of the molecules at the interfaces between the layers. Thus the molecular twist will be passed from one layer to the next as described by Yoshizawa. As a result the tilt directors of the molecules will be rotated on passing from one layer to the next, thereby forming a helix. The pitch of the helix will be determined by the tilt angle θ, the molecular length l and the displacement α. The helical structure could, therefore, be envisaged as being a result of a three-dimensional molecular twist being superimposed upon the periodic two-dimensional interfaces of the layers. Figure 6 shows a cartoon of the proposed arrangement of the molecules in the helical smectic C* phase.

The helix direction will be determined by the molecular twist which itself is related to the stereochemistry about the chiral centre, the location of the chiral centre within the molecular structure, and the zigzag orientation of the molecule, ie, it will be related to the empirical property-structure correlations developed in earlier studies [15].

The twist direction and the pitch of the helix will be dependent to a large degree on the distribution of conformers present in the system. When the rotational freedom is reduced, the steric or shape (zigzag) factors become important. Figure 7 shows a schematic representation of the structure of a typical material that might exhibit a smectic C* phase. The property-structure correlations that relate various changes in the features of a molecular

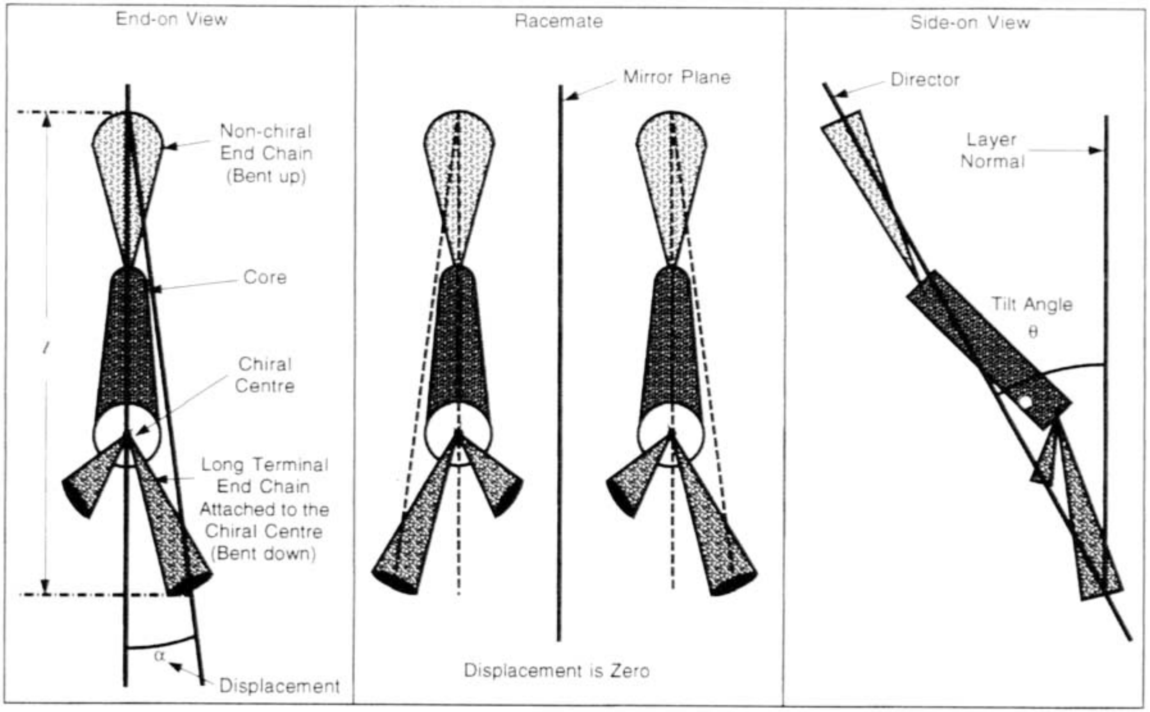


FIGURE 5 The zigzag and bent zigzag shapes that molecules in the smectic C or smectic C* phase can adopt.

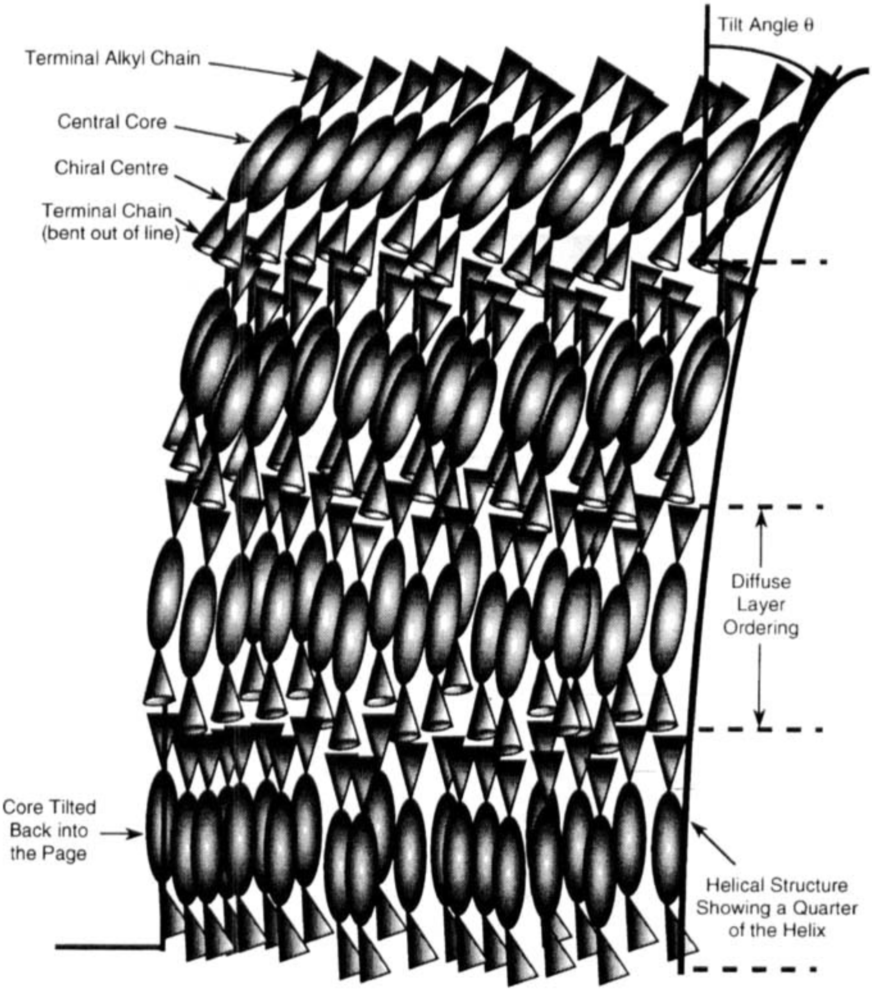


FIGURE 6 The helical structure of the smectic C* phase.

structure to physical properties are shown in this schematic. If we consider structural changes that can be made about the chiral centre, we see that as the chiral centre is brought nearer to the core the rotational freedom of the substituents will be less. Similarly as the length of the terminal aliphatic chain is increased, the chiral centre will have a reduced freedom of movement. Thus we might expect that as the following series of chiral centres shown in Figure 8 is ascended the pitch of the smectic C* phase will decrease.

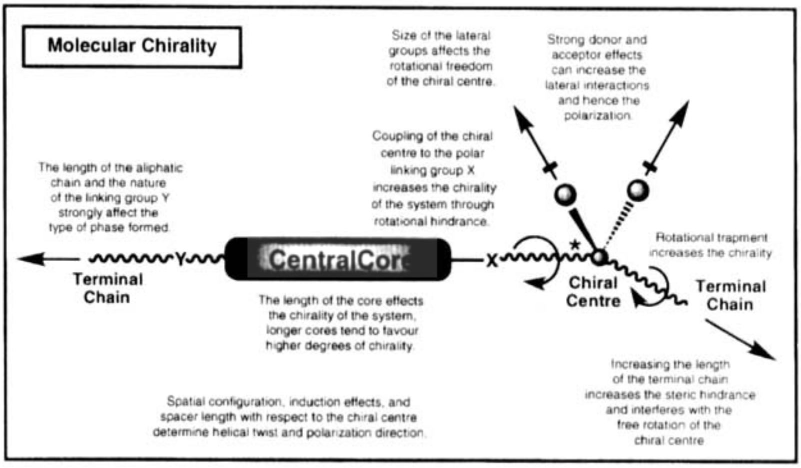


FIGURE 7 The general template structure for materials that exhibit ferroelectric smectic C* phases.

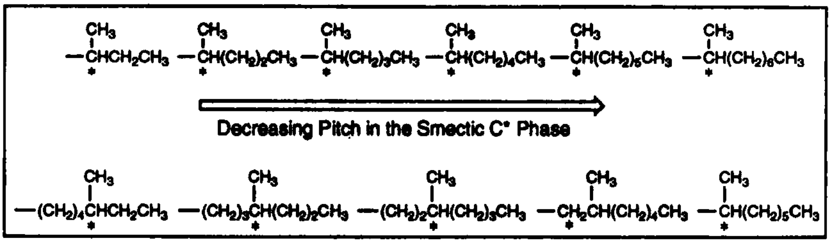


FIGURE 8 The effect of systematic changes at the chiral centre on helical pitch length.

By reducing the freedom of motion at the chiral centre the distribution of conformers is also reduced which has the effect of fixing the shapes of the molecules. One could almost imagine that when the motion about the chiral centre is relatively free the molecule will appear as a blur, but when it is reduced the molecule will come into sharper focus. As a consequence of the reduced rotational freedom the degree of broken symmetry and the molecular twist are enhanced. This means, for molecules that have better-defined shapes, the molecular twist will be transmitted between layers more efficiently. All of these observations are borne out from property-structure correlations.

ANTIFERROELECTRIC SMECTIC C* HELICAL MACROSTRUCUTRES

For materials with large values of l and α, and which exhibit tilted phases, the system will twist up tightly to give short pitch phases. However, there will come a point where the twist induced by the twisted molecular structure cannot be sustained because the ends of the terminal chains will meet the layer interfaces at a shallow angle, thereby causing the layers to rotate with respect to one another. Thus, for small molecular twists the ensuing helical arrangement of the molecules is a low energy escape mechanism, whereas for large molecular twists the resulting helical structure is high energy, and therefore in this situation a compromise becomes possible. The system would prefer to have a helical structure but with a longer pitch. This can be achieved by having alternating tilting of the molecules on passing from one layer to the next, as in the proposed structure of an antiferroelectric phase. Figure 9 shows this structure for zigzag bent molecules. Immediately it becomes apparent that by having back to back layer tilts the pitch

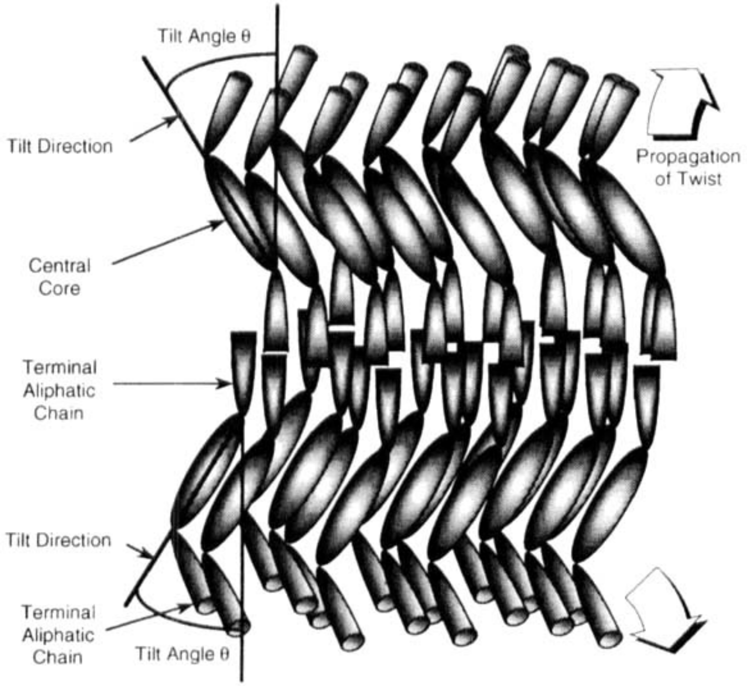
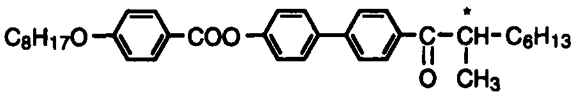


FIGURE 9 The alternating structure of the antiferroelectric smectic C* phase.

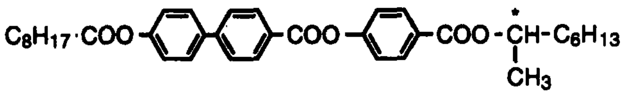
of helical structure is lengthened, and the pressure to form a twisted structure is greatly reduced. This structural transformation provides an escape from the system producing a high energy helical state. Thus a frustration is produced between the desire to twist and at the same time to maintain the layered ordering of the phase.

Not surprisingly, therefore, materials that exhibit antiferroelectric phases tend to have chiral centres that are adjacent to the central core region of the molecule, have long aliphatic chains attached to the chiral centre, and have long central core regions. Molecules with these structural attributes will have high populations of certain preferred conformations, have better defined zigzag bent shapes, high molecular twists, and as a result will be candidates for frustration to occur between helical twist and layer rotation. These effects of molecular structure are well demonstrated by materials shown in Table I. All of the compounds shown have relatively long core structures stretching over at least three aromatic rings, chiral centres adjac-

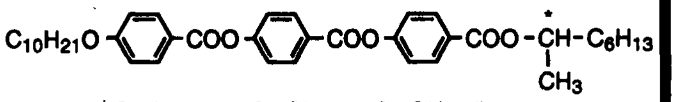
TABLE I Materials that exhibit Antiferroelectric Phases.



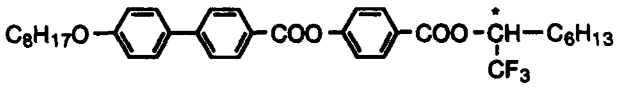
Iso 136 °C SmA* 108 SmC* 49 SmC*(anti)



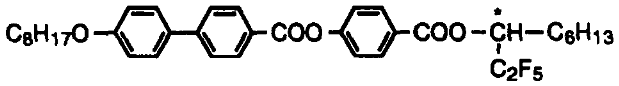
Iso 145.2 SmA* 115.0 SmC* 103 SmC*(anti)



Iso 137 SmA* 115 SmC* 96 SmC*(anti)



Iso 121.0°C SmA* 109.0 SmC*(anti) 60.1 Cr



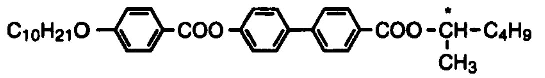
Iso 85.5°C SmA* 76.8 SmC*(anti) 38.8 Cr

ent to the core structures, and long terminal aliphatic chains. It is also interesting to note that these materials also have ester linking groups in the core section which, according to Yoshizawa, could aid the bending of the overall structures of the molecules and hence stabilise the formation of antiferroelectric phases.

The effect of molecular chirality and hence molecular twist can be tested through examining the variation of phase transition temperatures as a function of optical purity. Table II demonstrates this effect for some biphenyl benzoates. Here the antiferroelectric and ferrielectric phases disappear when the optical purity is below 0.8 ee. Thus, conversely these phases are only stabilised in environments where their is a high degree of chirality. As the enantiomeric purity is reduced so the effects of symmetry breaking are weakened.

The effect peripheral aliphatic chain length on the phase behaviour of materials that have molecules with twisted structures can be described in the following way. For short chains there will be little effective twist and weak interlayer permeations and so antiferroelectric phases will be unlikely to occur. For very long peripheral chains, the chain ends (maybe the last few carbon atoms in the chain) will have a high degree of mobility and freedom of rotation. therefore effective interlayer permeation will be reduced by the end chains bending, flexing and even doubling back on themselves. Therefore, antiferroelectric phases would not be expected to be found for such long chain lengths (i.e. C_{18+}). Consequently, antiferroelectric phases are most likely to occur at intermediary chain lengths where the aliphatic chains are long enough and inflexible enough to convey the molecular twist between layers. This effect is amply demonstrated in Table III, which shows that antiferroelectric phases occur in the window for chain lengths between 12 to 16 methylene units for the alkoxy end of the

TABLE II Effect of optical purity on the transition temperatures (°C) for 1-methylpentyl 4'(4-n-decyloxybenzoyloxy)biphenyl-4-carboxylate

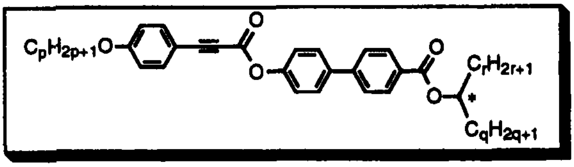


(R) Iso 135.5 °C SmA* 106.5 SmC* 86.6 SmC*(ferri) 74.2 SmC*(anti) 48.1 J*

(S) Iso 133.9 °C SmA* 106.7 SmC* 87.3 SmC*(ferri) 85.0 SmC*(anti) 48.5 J*

(R/S) Iso 132.4 °C SmA 105.4 SmC 46.1 J

TABLE III The transition temperatures (°C) for the *R* or *S*-1-methylalkyl 4′-(4-n-alkoxyphenylpropioloyloxy)biphenyl-4-carboxylates

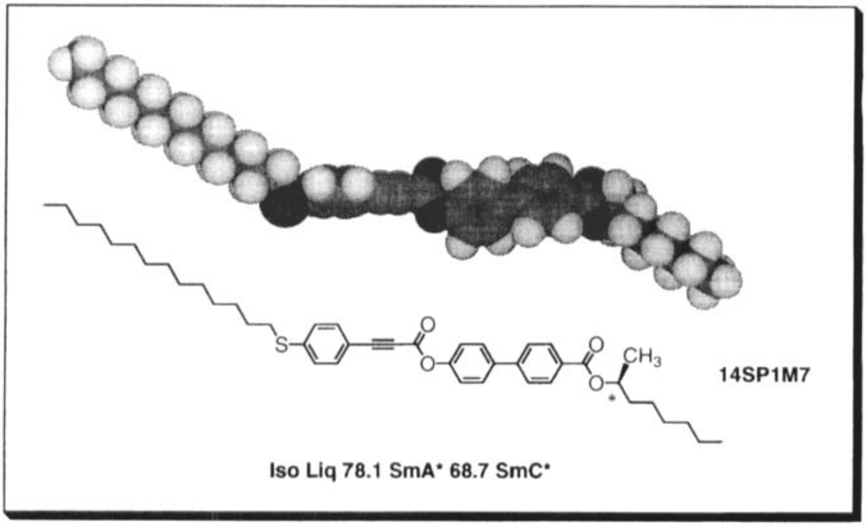


p	*q*	*r*	*Iso -TGBA**	*Iso or-TGBA* -SmA**	*Iso-SmC**	*TGBA* or SmA* -SMC**	*SmC* -ferri*	*SMC* -anti*	*config*
8	6	1		97.5					*S*
9	6	1		97.5					*S*
10	6	1		98.0		76.3			*S*
11	6	1		95.0		78.1			*S*
12	6	1		96.3		78.6			*S*
13	6	1	94.1			88.3	55.1	42.2	*S*
14	6	1	93.8			89.7	49.4	38.3	*S*
15	6	1	91.6			90.6			*S*
16	6	1			99.0				*S*
9	8	1		94.8		60.3			*S*
12	8	1		93.7		83.6			*S*
14	8	1	91.0	89.6		89.6	38.6		*R*
16	8	1				88.0			*S*
18	8	1				86.5			*S*
9	10	1		94.4		55.0			*S*
12	10	1		92.8		84.8			*S*
14	10	1	89.8			89.3			*S*
16	10	1				83.5			*S*
18	10	1				81.1			*S*
9	6	2		70.8		46.8		46.5	*S*
12	6	2		59.4		56.6		55.0	*S*
14	6	2							*R*
16	6	2							*S*
18	6	2							*S*
9	6	3		62.9				44.3	*R*
12	6	3							*R*

molecule, and 5 to 8 methylene units for the peripheral aliphatic chain attached to the chiral centre.

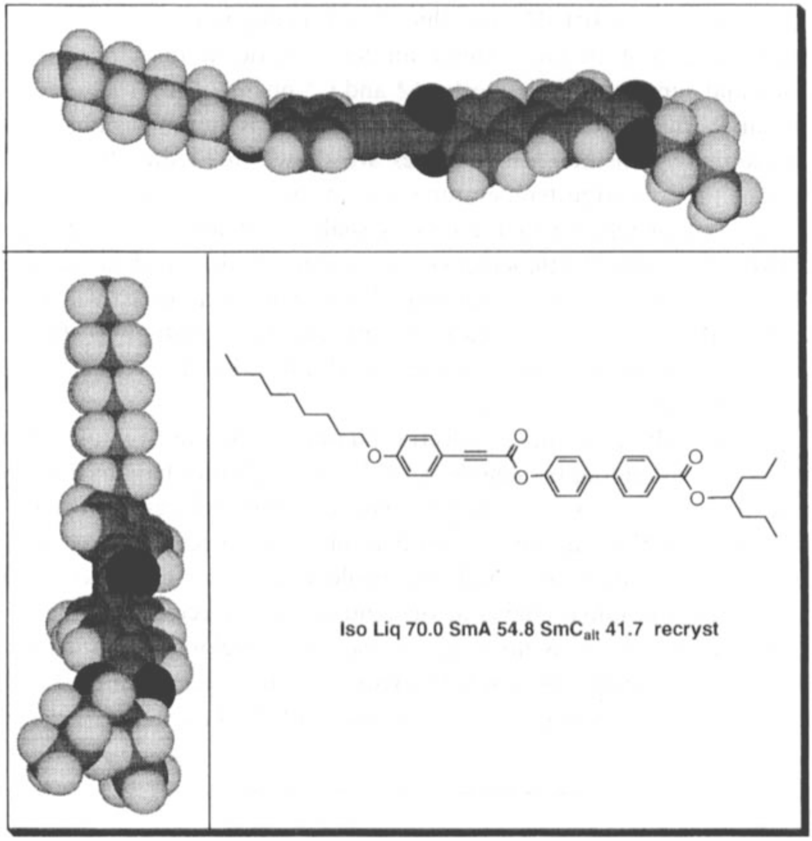
It is interesting to note that the molecular length is deemed as being important in this particular modelling, and therefore the length and angle of the terminal alkoxy chain, as well as that of the chain attached to the chiral centre, are also important in mesophase formation and properties [22]. For example, consider the mesophase properties of *S*-1-methylheptyl 4′-(4-n-tetradecylthiophenylpropioloyloxy)biphenyl-4-carboxylate [23] (**14SP1M7**) in comparison to **14P1M7**. The thiophenyl analogue of the first TGBA* material does not in fact exhibit antiferroelectric, ferrielectric or TGB phases, and simply exhibits smectic A* and C* phases. The structure of this material, its minimised energy conformation (at 0 K in the gas phase), and its mesophase transition temperatures are shown in Figure 10. It can be seen that the transition temperatures are much lower and the angle of the tetradecyl chain relative to the core is shallower than for the analogous **14P1M7**. Obviously the thioether connecting unit is also much larger in size and more flexible than the ether link. These structural factors will reduce the internal molecular twist and hence prevent the formation of TGB and antiferroelectric phases, even though the chiral units are identical in the ether and thioether compounds.

In the modelling of antiferroelectric phases it is interesting to compare the effects of extending the length of the lateral aliphatic chain at the chiral centre (methyl to ethyl to propyl). The experimental results shown in Table III show that the antiferroelectric phase becomes stabilised as the lateral chain length is increased. We could extend this chain to a point where the two terminal chains at one end of the molecule have the same length, and the system is no longer chiral and therefore does not form a helical macrostructure, as shown in Figure 11. The swallow-tailed material still shows an alternating tilted arrangement of the layers, but this is ex-



Iso Liq 78.1 SmA* 68.7 SmC*

FIGURE 10 The structure of a thioether which does not exhibit TGB or antiferroelectric properties.



Iso Liq 70.0 SmA 54.8 $\mathrm{SmC_{alt}}$ 41.7 recryst

FIGURE 11 Structure and transition temperatures of a swallow-tail compound that exhibits an alternating smectic C phase.

pected as now there are two equally matched interlayer permeations to consider for each of the terminal chains of the swallow end of the molecule. We have already indicated that interlayer interactions could lead to an alternating packing of the layers [24], and thus the mechanism for the formation of an alternating tilt smectic C phase in this instance would be the same as that for the formation of antiferroelectric phases in chiral systems.

TWIST GRAIN BOUNDARY HELICAL MACROSTRUCTURES

The helix in the twist grain boundary phase, unlike the helices in ferroelectric and antiferroelectric phases, is determined by lateral interactions of the molecules rather than by end to end displacements. Again the twisted zigzag structures of the molecules will determine the angle by which one molecule will be rotated relative to its nearest neighbour in the layered structure. A strong lateral twist is, however, required in order to overcome the layer ordering. Consequently TGB phases tend to be exhibited by materials that have long terminal chains because the ends of the chains will be substantially disordered, which in turn will produce weak interlayer interactions. Table III shows that TGB phases occur in four series of biphenyl propiolates where the alkoxy chain is 14 methylene units in length. It is also interesting to note that when the lateral aliphatic chain at the chiral centre is increased in size (ie methyl to ethyl) TGB phases are suppressed. This is because extending the lateral chain causes interference with the lateral interactions of the molecules, weakening them and reducing the lateral twist.

The competition between lateral twist and end to end or terminal twist can be demonstrated in systems where the chiral centre is inherently fixed in the molecular structure of the molecule, ie within the rigid part of the central core. In this location we can vary the terminal chain length and still have strong lateral interactions. Take for example the oxazoline derivative [24] shown in Figure 12, which only exhibits a smectic A* phase. This material has a chiral centre within the core structure, and hence its freedom of motion relative to the rest of the molecule is substantially reduced. When

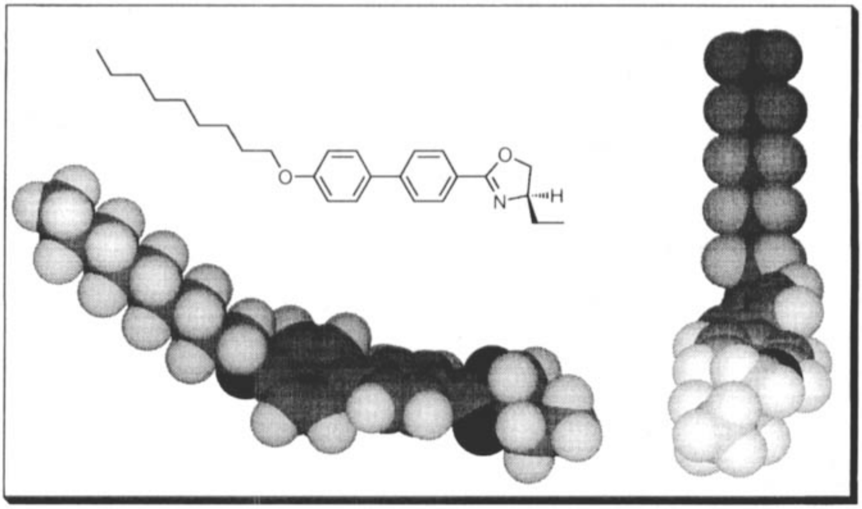


FIGURE 12 The structure of an oxazoline compound which exhibits TGB A* phases in mixtures with achiral compounds.

the material is incorporated into mixtures of achiral smectic C compounds the pitch of the helix induced in mixtures is relatively long. Extrapolation of the data shows that the pure chiral material would also have a long pitch in a smectic C* phase should it be able to exhibit such a phase. This result is to be expected as the chain attached to the chiral centre is relatively short, ie ethyl, and the interlayer permeations will be reduced. However, mixtures of the oxazoline with difluoroterphenyl smectic C host systems results in the appearance of the TGB phase. This phase is stabilised by the strong lateral twist caused by the chiral oxazoline ring structure. Normally we would expect TGB phases to be associated with tight pitch ferroelectric phases, but with the oxazoline this is not the case, and consequently this material serves as an example that the lateral twist associated with cholesteric, blue phases and TGB phases has not been fully explored yet as a function of molecular architecture. In addition, it is clear that the factors which determine terminal·helical formation are not necessarily related to those for lateral helix formation. Thus the helix direction in cholesteric and TGB phases need not be related to those in ensuing smectic C* phases.

CONCLUSIONS

A simple model using bent zigzag molecular shapes has been used to demonstrate how helical structures are formed in the smectic C*, antiferroelectric C* and TGB A* phases. This type of modelling does not provide a quantifiable method of determining helical pitch etc, however, it does provide a qualitative picture of how helical structures develop.

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