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A phenomenological approach to the inversion of the helical twist sense in the chiral nematic phase

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Optically active materials that show a temperature dependent inversion of the helical twist sense in the chiral smectic C* and chiral nematic phases have been known for many years. However, it has only recently been found that inversions can occur in compounds which have single chiral centres. It was found previously that the temperature range and the magnitude and sign of the helical twist in the chiral nematic phase are related to the concentration of the optically active material(s) dissolved in a nematic host. In a similar way, we propose to describe the inversion of the helical twist sense in the chiral nematic phase of pure materials containing a single chiral centre. Additionally, we seek to verify the possible validity of the latter model by means of molecular modelling on appropriate compounds, and by deriving a suitable mathematical expression to allow the direct use of experimental data.

Introduction

Addition of a chiral dopant to a nematogen will induce a helical distortion in the nematic structure. The same helical distortion is also found in pure chiral nematogens. Locally, a chiral nematic mesophase is very similar to its achiral equivalent, where there is no long-range positional ordering and the preferred molecular orientation is defined by a director $\hat{n}$. However, the preferred orientations of the molecules are such that the director $\hat{n}$ is not unidirectional in space but is helical with one of two possible helical twist directions, dextro (D) and laevo (L), as represented in Fig. 1. Other chiral mesophases, such as the smectic C* phase, exhibit helical distortions similar to the one described above.[1] Optically active compounds that show a temperature dependent inversion of the helical twist sense in the chiral smectic C* and chiral nematic phases have been discovered over a period of many years.[2–11] In particular, Slaney *et al.* showed that an inversion could occur for single chiral centre systems[6] and, more recently, a compound has been reported to exhibit a temperature dependent unwinding of the helix in both the chiral smectic C* and chiral nematic phases.[4]

It was hypothetically suggested[12] that the temperature range of the chiral nematic phase and, more importantly, the magnitude and sign of the helical twist are related to the concentration of the single optically active material dissolved in a nematic host. Within the dilute limit, the helical pitch length p is inversely proportional to the concentration.[13] Additionally, for concentrated solutions of cholesterol derivatives, it was empirically found that the total twist $\bar{q}$ of a mixture is approximately equal to the average of the component twists, q_i.[12] The various component twists may be positive or negative. Hence, a suitable mixture of two components with opposing twists can be nematic, when, $\bar{q}=0$, *i.e.* it was suggested that the helical twist, defined as the helical wavevector p^{-1}, is an additive property of the various components of a chiral nematic system. The observation of a temperature dependent pitch inversion in the chiral nematic phase of a pure material containing only one chiral centre[6] can also be seen to be due to a competition between component entities. In this case, the component species with opposing helical twists can be thought

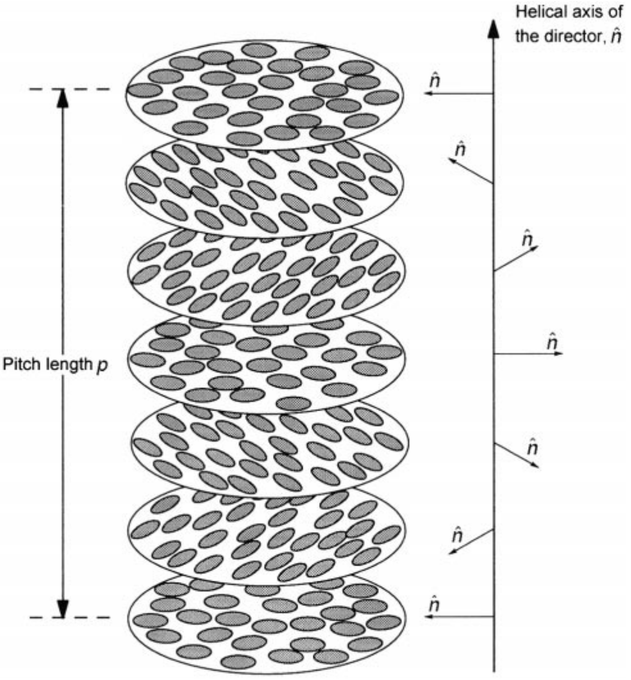

Fig. 1 Schematic representation of the arrangement of molecules in the chiral nematic mesophase. The successive planes have been drawn as a guide for the eye but do not have any specific physical meaning

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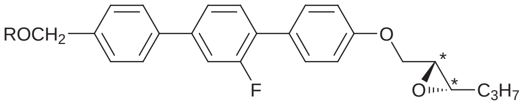
of as being molecular species, say conformational isomers, and that the relative concentration of the species varies with temperature. Thus, the additivity model can be extended to single molecular systems where the q_i's are the twists of the competing species of the system. Firstly, as for the dilute model, it is assumed that there is a linear dependence between reciprocal pitch and concentration, even at very large concentrations of component species, and secondly, it is assumed that the concentration of the component species will change with temperature. Hence, a pure system with opposite component twists may show a temperature dependence of the helical twist sense.

The purpose of this study is to provide a phenomenological model for the inversion of the helical twist sense in helical liquid-crystalline phases. Additionally, molecular modelling of materials which exhibit a helical twist inversion in the chiral nematic phase was performed and a microscopic origin to the phenomenon is proposed.

Experimental

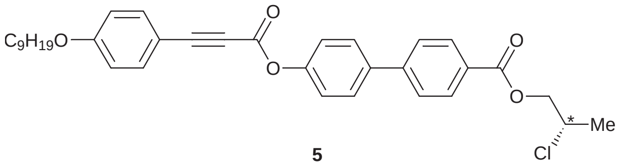
The compounds employed for the purpose of this study are given by structures **1**–**6** in Fig. 2, and were selected because some exhibit a progression in chemical structure (**1**–**4**) and the others, in relation, show a diversity in molecular structures (**5**, **6**). Materials **1**, **2** and **4** were prepared by Dr K. Takatoh, compound **3** was synthesised by J. D. Vuijk, and compounds **5** and **6** were synthesised by Drs A. J. Slaney and C. Loubser, respectively. The synthesis and optical purity of terphenyl epoxides **1**–**4**,[4,8] the phenyl propiolate **5**[6] and the difluorobiphenyl **6**[7] have been reported previously.

The latter two compounds clearly have single chiral centres. However, the first four have epoxide chiral ring structures that can, in principle, act as single chiral entities. Finally, for unequivocal comparison, all materials were selected on the criterion that they exhibit a helix inversion in the chiral nematic phase. The phase sequences, as determined by optical microscopy and DSC, are summarised in Table 1. In the first instance, compound **4** does not appear to exhibit a twist inversion. On the other hand, there is a N^*–N_∞^* transition which leads us to believe that the temperature range of the lower temperature chiral nematic phase is very short and was not detected.



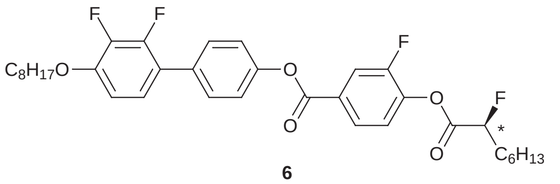
1 R = CH_3
2 R = C_2H_5
3 R = C_3H_7
4 R = C_4H_9

4''-*n*-alkoxymethyl-2'-fluoro-4-[(2*S*, 3*S*)-3-*n*-propyloxiran-2-ylmethoxy][1,1':4',1'']terphenyl



5

(*S*)-2-chloropropyl 4'-(4-*n*-nonyloxyphenylpropioloyloxy)-biphenyl-4-carboxylate



6

4-*n*-octyloxy-2,3-difluorobiphenyl-4'-yl 3-fluoro-4-[(*S*)-2-fluorooctanoyloxy]benzoate

Fig. 2 Compounds **1**–**6**

The pitch length was determined as a function of temperature for all compounds represented. For compounds **1**–**6**, the pitch was determined as a function of temperature by measuring the distance between the dechiralisation lines in the fingerprint texture of the phase using a calibrated Filar eyepiece attached as the ocular of a Zeiss polarizing light microscope. The pitch of compound **3** was determined as a function of temperature using the Grandjean wedge method (also known as the Cano wedge method).[4] The wedge cells were obtained from EHC (Japan) and calibrated by interferometry. The experimental errors for all pitch measurements were estimated to be *ca.* 10% of the experimental pitch.

Molecular modelling studies were performed on a Silicon Graphics workstation (Indigo XS24, 4000) using QUANTA and CHARMm. Within CHARMm, the Adopted Basis Newton-Raphson (ABNR) algorithm was used to locate the molecular conformation with the lowest potential energy. The minimisation calculations were performed until the root mean square (RMS) force reached $4.184\,\mathrm{kJ\,mol^{-1}\,Å^{-1}}$, which is close to the resolution limit. The RMS force is a direct measure of the tolerance applied to the energy gradient (*i.e.* the rate of change of potential energy with step number) during each cycle of minimisation. If the average energy gradient was less than the specified value, the calculation was terminated.

The results of the molecular mechanics calculations were generated using the programs QUANTA ver. 4.0 and CHARMm ver. 22.2. The programs were developed by Molecular Simulations Inc. The modelling packages assume the molecules to be a collection of hard particles held together by elastic forces, in the gas phase, at absolute zero, in an ideal motionless state, and the force fields used are those described in CHARMm ver. 22.2.

Results

Model

The additivity model described earlier expresses the total twist $\bar{q}$ as a function of the average of the component twists q_i of a mixture. As suggested, it is proposed to extend this model to pure systems where the competing entities are molecular species which could be, for example, conformational isomers or rotomers, and the q_i's are the molar twists of the system's contributing species.

Firstly, in a similar way to the model describing a single component in dilute solution,[13] it is assumed that there is a linear dependence between reciprocal pitch and concentration, even at very large concentrations of the single component. Secondly, it is assumed that the helical twist, defined as the inverse pitch or helical wavevector p^{-1}, is an additive property of the various components of a chiral nematic system.

For simplicity, it is proposed that the inversion of the helical screw sense in the chiral nematic phase is brought about by the action of two competing species within the phase, set *a* with a positive twist giving rise to a right-handed (D) helix and set *b* with an opposite twist favouring a left-handed (L) helix. These two groups are presumed to be two molecular species weighted around two energy minima corresponding to two static species. In fact, these are presumed to be in dynamic flux and are constantly interconverting from one species to another. The model therefore only describes an average picture of the structure of the mesophase.

In essence, these assumptions lead to the expression in

Table 1 Transition temperatures (°C) for materials **1**–**6** as determined by polarized light optical microscopy and differential scanning calorimetry

material	K		SmC*		SmA*		N*		N_{∞}*		N*		BPI		BPII		I
1[a]	·		—		—	86.3	·	90.7	·	90.7	·		—		—	176.3	·
2[a]	·	52.9	·		—	100.6	·	106.4	·	109.6	·	159.5	·	159.5	·	159.5	·
3[b]	·	<46.2	·		—	103.3	·	106.3	·	112.1	·	158.8	·	162.9	·	164.4	·
4[a]	·	32.6	·	112.4	·		—	114.1	·	116.1	·	138.8	·	138.8	·	139.5	·
5[c]	·		—	62.0	·	137.0	·	~141	·	~142	·		—		—	166.0	·
6[d]	·	89.7	·		—	139.3	·	~140	·	~140	·		—		—	149.6	·

[a]Ref. 8. [b]Ref. 4. [c]Ref. 6. [d]Ref. 7.

eqn. (1),

$$\frac{1}{p}=\frac{[a]}{p_a}+\frac{[b]}{p_b} \tag{1}$$

where p is the total pitch of the system, $[a]$ and $[b]$ are the concentrations, and p_a and p_b are the pitch coefficients, of the rival species, respectively. Thus, the reciprocal of p_a and p_b are a direct measure of the twisting power of the species considered.

Let the energy difference between the two species be ΔE. Their relative concentration will therefore be temperature dependent and will follow a Boltzmann distribution [eqn. (2)],

$$\frac{[a]}{[b]}=e^{\frac{-\Delta E}{RT}} \tag{2}$$

where R is the fundamental constant 8.314 J mol^{-1} K^{-1} and T is the absolute temperature. For simplicity, let $[a]+[b]=1$, which yields eqns. (3) and (4).

$$[a]=\frac{1}{(1+e^{\Delta E/RT})} \tag{3}$$

$$[b]=\frac{e^{\Delta E/RT}}{(1+e^{\Delta E/RT})} \tag{4}$$

Therefore, the total inverse helical pitch is given by eqn. (5).

$$\frac{1}{p}=\frac{1}{(1+e^{\Delta E/RT})}\left(\frac{1}{p_a}+\frac{e^{\Delta E/RT}}{p_b}\right) \tag{5}$$

Taking compound **5** as an example, the pitch length determined experimentally as a function of temperature is shown in Fig. 3. Examination of Fig. 3 shows that at the inversion temperature T_{∞} the pitch is infinite. This corresponds to the formation of a nematic phase which exhibits *schlieren* and homeotropic defect textures when observed optically under crossed polars. Thus, at T_{∞}, the reciprocal of the pitch is equal to zero. Furthermore, there appears to be a linear relationship between temperature and reciprocal pitch,[6] as shown in Fig. 4.

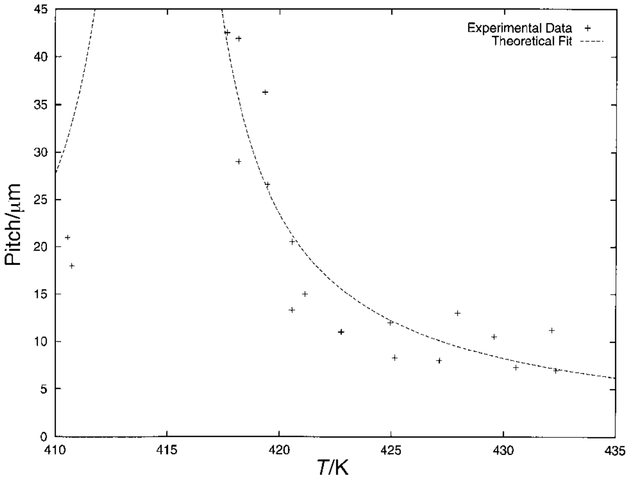


Fig. 3 Temperature dependence of the experimental and theoretical helical pitch of material **5**

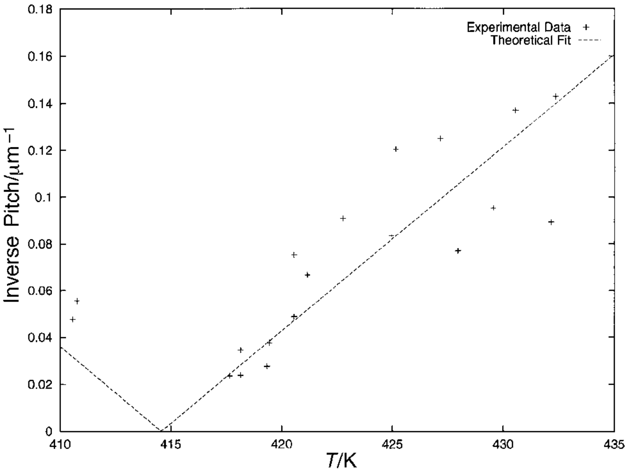


Fig. 4 Temperature dependence of the reciprocal experimental and theoretical helical pitch of compound **5**

Though such an apparent relationship has also been observed in other systems,[9] eqn. (5) clearly expresses inverse pitch as a non-linear function of temperature. However, in the temperature range under study, the relationship may appear to be linear.

Theoretical curves were fitted to the helical pitch and reciprocal helical pitch of compound **5** according to the model described by eqn. (5). These are shown concurrently with the experimental data in Fig. 3 and 4, respectively.

For all materials studied, the unknown parameters T_{∞}, p_a, p_b and ΔE were ascertained using a least-squares method and are summarised in Table 2.

It has to be noted that the theory will give good fits only if data points *ca.* 5 °C below the clearing temperature T_{Cl} are taken. Experimental pitch data between T_{Cl} and $T_{\mathrm{Cl}}-5$ °C tend to be distorted, possibly due to the effects of molecular fluctuations and the unpinning of defects at the surfaces of the cell. For materials **1**–**6**, all pitch length data points were taken below $T_{\mathrm{Cl}}-5$ °C.

Molecular modelling

Molecular modelling studies are described using compound **5** as an example. A conformational search around the O—C(1)—C(2)*—Cl dihedral angle, shown in Fig. 5, was performed on the geometrically optimised structure. The search was performed using a 360° grid scan. A 5° step size was

Table 2 Values for T_{∞}, ΔE, p_a and p_b derived from eqn. (1)

material	T_{∞}/K	ΔE/kJ mol^{-1}	p_a/µm	p_b/µm
1	361.6	6.480	−0.0297	0.2564
2	381.2	8.329	0.0257	−0.3559
3	389.7	6.757	0.031	−0.2495
4	377.3	7.065	−0.0389	0.37
5	414.6	8.261	0.0612	−0.6724
6	408.1	5.408	−0.0118	0.0581

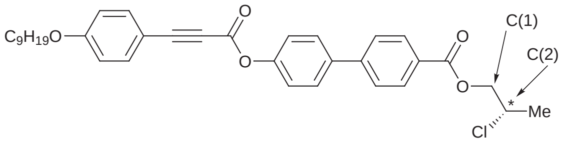


Fig. 5 Description of the O—C(1)—C(2)*—Cl dihedral angle in **5**

selected because, in this model, we are considering sets of conformers about energy wells. At each step, the grid torsion was artificially fixed to prevent the structure from returning to the initial geometrically optimised structure and the resulting conformation was minimised using a Steepest Descents algorithm; 200 iterations were sufficient because complete geometrical optimisation had already been performed. The search gives the variation of the relative torsional energy as a function of torsion angle θ for rotations around the C(1)—C(2)* bond, as shown in Fig. 6. Three energy minima corresponding to the three minimum energy conformers of compound **5** were observed. The computer generated models of these conformations are shown in Fig. 7.

The same study was conducted on the other materials where the bond containing the chiral centre was allowed to rotate in a stepwise manner with respect to the molecular core, and the resulting conformations were minimised at each step in the rotation. Table 3 lists the energy difference ΔE_c between the two lowest minimum energy conformers thus generated for materials **1**–**6**, and from Fig. 6, it can be seen that ΔE_c for **5** is 8.7 kJ mol^{-1}. The energy differences between the two lowest energy conformers of compounds **1**–**4** were found to be very similar at *ca.* 2 kJ mol^{-1}. This might have been expected since all the modifications in this molecular progression occur at the alkoxymethylene group and the group containing the chiral centre remains unchanged throughout the chemical progression.

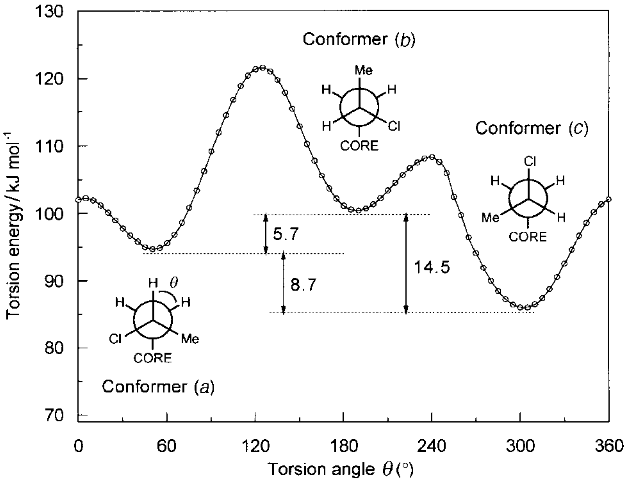


Fig. 6 Representation of the torsion energies of **5** for the O—C(1)—C(2)*—Cl dihedral angle plotted as a function of the torsion angle θ along with the Newman projections of the three energetically preferred conformers (*a*), (*b*) and (*c*)

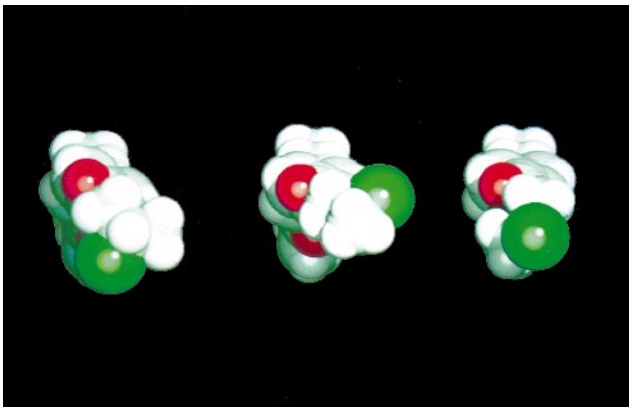


Fig. 7 Computer generated models of the three minimum energy conformers of **5**; left to right: conformers (*a*), (*b*) and (*c*)

Table 3 Comparison of the energy difference between the two lowest minimum energy static conformers ΔE_c, estimated by computer modelling, and the energy difference between two competing species, ΔE, evaluated from eqn. (5)

material	computer modelling ΔE_c/kJ mol^{-1}	theoretical model ΔE/kJ mol^{-1}
1	2.3	6.480
2	2.0	8.329
3	2.0	6.757
4	1.7	7.065
5	8.7	8.261
6	8.1	5.408

Discussion

Eqn. (5) was used to qualify and phenomenologically quantify changes in the helix of chiral nematic phases of thermotropic liquid crystals. However, pitch inversion in other mesophases can be modelled in the same way. These phases might include chiral smectic C*, chiral lyotropic phases or even mixtures of chiral materials.

It can be seen from Fig. 3 that eqn. (5) gives good theoretical fits to the experimental data with correlation coefficients of the order of 0.99 for all materials studied. Furthermore, it can be seen from Table 2 that the theory predicts realistic values for T_∞ and ΔE. In the first instance, the estimated temperatures at which inversions occur ($1/p=0$) agree with those determined by optical microscopy.

In the molecular modelling studies, the rotation around the bond containing the chiral centre was not selected arbitrarily. Indeed, the emergence of spontaneous polarization in chiral smectic C* phases is a chiral property, and it was found that its magnitude depends very strongly on the dipole at the chiral centre and the amount of freedom that the chiral centre has to rotate.[14] Likewise, helicity in liquid-crystalline phases is a chiral attribute and it is therefore reasonable to assume that the helical nature of a phase depends primarily on the chemical and geometrical environment around the chiral centre. This is confirmed by Kuball and co-workers, who showed that the contribution of a ‘chiral area’, induced around an asymmetric centre, to the helical twisting power (HTP)[15] depends on its orientation with respect to the director.[16,17] Ultimately, each conformer contributes differently to the HTP of a compound where a variation of the orientation of the “chiral region” could cause a change of sign of the HTP. In the preceding molecular simulations, the orientation of the ‘chiral region’ with respect to the director may be described as a function of the torsional angle for the rotation around the bond containing the chiral centre, *i.e.* the C(1)—C(2)* bond shown in Fig. 5 for compound **5**.

As pictured in Fig. 6, the energy difference ΔE_c between the lowest energy conformer (*c*) and the next conformational minimum, that of conformer (*a*) (8.7 kJ mol^{-1}), is of the same order of magnitude as the energy difference between the two hypothetical species described eqn. (5) (8.3 kJ mol^{-1}). This suggests that the competing molecular species in the pure component system are likely to be conformational isomers related to the structure about the chiral moiety, and that changing the temperature will alter their relative concentrations. Thus, the higher energy conformations, although in lower concentration, dictate the twist sense in the high temperature region of the chiral nematic phase. On the other hand, as the temperature is lowered below the inversion point, the increased concentration of the lower energy conformations is such that the said conformations now dominate and dictate the helical twist sense of the phase. As indicated in the description of the model, the two conformational groups are not static conformers but rather two groups weighted around two potential energy minima and are undergoing dynamic interconversion.

In this idealised case, conformations around the two lowest energy minima for rotations around the C(1)—C(2)* bond were selected on the criterion that they are most likely to be the more densely populated conformational groups and therefore are most likely to have the greatest effect on the mesophase structure. However, in a liquid-crystalline system at elevated temperatures, species weighted around higher energy conformational minima may also have to be considered because the conformers weighted around the lowest energy minima may not necessarily have opposing twists and will therefore not generate a temperature dependent twist inversion. This, in turn, may lead to different values for the energy difference between the minimum energy conformers of interest (see Fig. 6). This could be one of the many reasons why there seems to be a larger discrepancy in the energy differences for materials **1**–**4**, where the energy difference between the two lowest minimum energy conformations is *ca.* 3–4 times smaller than the energy difference between the two competing hypothetical species, as calculated from eqn. (5).

Obviously, the fact that ΔE_c and ΔE are of the same order of magnitude does not disprove the perception that the competing species could be entities other than conformational isomers, such as rotomers or molecular pairs. However, it does affirm that conformational interconversion is a reasonable mechanism by which twist inversion in helical phases can be brought about.

Special cases in the model

For all materials studied, the parameters p_a and p_b are shown to have opposite signs. This is wholly expected as it is one of the assumptions for the inversion model. On the other hand, p_a and p_b are approximately an order of magnitude different in their absolute values. One may infer that for a helical twist to occur at reasonably low temperatures in a pure system where the contributing species follow a Boltzmann distribution, the latter must have opposite HTP's of different magnitude. Indeed, consider a system composed of two species with opposite HTP, where $p_a = -p_b$. If the species are not degenerate ($\Delta E > 0$), then an inversion point will only be reached at infinite temperature. This is apparent from the notion that with a Boltzmann distribution, the two species will be equally populated only at infinite temperature. At this temperature, hypothetically, one would observe a nematic phase. This is confirmed by looking at eqn. (5) where, under these conditions, inversion occurs if $\Delta E/RT = 0$ or T is infinite. At all other temperatures, a chiral nematic phase is observed.

Let us now consider the case where competing species have degenerate energy levels, where $\Delta E = 0$. In this case, it is quite clear that a chiral nematic phase would result for $p_a \neq -p_b$, with the inverse pitch expressed in eqn. (6).

$$\frac{1}{p} = \frac{1}{2}\left(\frac{1}{p_a} + \frac{1}{p_b}\right) \tag{6}$$

The implication from eqn. (6) is that a system where all competing species have degenerate energy levels will have a pitch in the cholesteric phase which is independent of temperature. Practically, this means that the smaller the energy difference between the species, the smaller the changes in pitch. This oversimplified view does not take into account such things as fluctuations near transitions and relies on the assumption that the phase will exist at all temperatures. Also, one is forced to assume that p_a and p_b are independent of temperature. On the other hand, it would be interesting to search for materials where the conformations around the chiral atom have similar energies in view of providing, perhaps, constant pitch chiral nematic phases.

The third special case is where the species have degenerate energy levels and $p_a = -p_b$. Here, throughout the temperature range of the chiral nematic phase, and though the system may be entirely composed of chiral molecules, the macroscopic structure would be that of an achiral nematogen. This case is highly unlikely, however it does stress that the chiral character of a mesophase is not necessarily linked to the strength of chirality of a molecule. More so, it may depend on the constructive *vs.* destructive effects of opposing chiral species, whatever their nature.

An interesting point to note is that, according to the model and with parameters outside the boundary conditions given in the special cases above, there will always be an inversion in single chiral centre systems where the constituent species have opposite helical twists. Experimentally, however, it would often not be possible to observe an inversion point since it is likely to occur outside the thermal range of the chiral nematic phase as a hypothetical inversion point. Indeed, the model describes an infinite temperature range available for inversion to occur, whereas experimentally, we are confined to small temperature ranges, at best of the order of 100 °C.

Number of species involved in the inversion phenomenon

Competition between species with opposing helical twists is not limited to bi-component systems and experimental evidence indicates that many species compete, but it may happen that only a small number, and often only one, dominates. In fact, Vill *et al.* recently reported unusual changes in the chiral nematic helical pitch.[18] A liquid-crystalline trioxadecalin derivative shows a temperature dependent inversion of the chiral nematic helix at lower temperatures. At higher temperatures, the pitch reaches a minimum then increases, tending to a second inversion point just above the clearing point. This infers that at least three species contribute to the overall twist, albeit in varying degrees. Using the same assumptions as for eqn. (5), it is very easy to extend the model to take into account a number N of species [eqn. (7)],

$$\frac{1}{p} = \frac{\sum_{n=1}^{N}\left[\frac{e^{E_n/RT}}{P_n}\right]}{\sum_{n=1}^{N} e^{E_n/RT}} \tag{7}$$

where E_n is the energy level of the *n*th species. As an example of the flexibility of the model, a qualitative plot of a double pitch inversion as a function of temperature is represented in Fig. 8. Three contributing species *a*, *b* and *c* were chosen with appropriate values for the parameters $\Delta E_{ab} = 5$ and $\Delta E_{ac} = 10$ kJ mol^{-1}, and $p_a = 0.1$, $p_b = -0.2489$ and $p_c = 2.507$ μm. The two inversion temperatures will therefore be $T_{\infty 1} = 350$ and $T_{\infty 2} = 400$ K. Hence Vill's observations can be explained using eqn. (7).

Limitations of the model

The assumptions described by eqn. (5), even though viable within the phases under study, are nevertheless limited. They do not take account of phase transitions, *i.e.* it is assumed that the phase under study will exist at any temperature. To compensate for this, and therefore estimate the pitch divergence near phase transitions, other terms are required, however this is outside the scope of this study. Also, the model described is phenomenological and gives no insight into the microscopic origin of the phenomenon of twist inversion. Furthermore, it is seen from Table 1 that the inversion of the helical twist sense

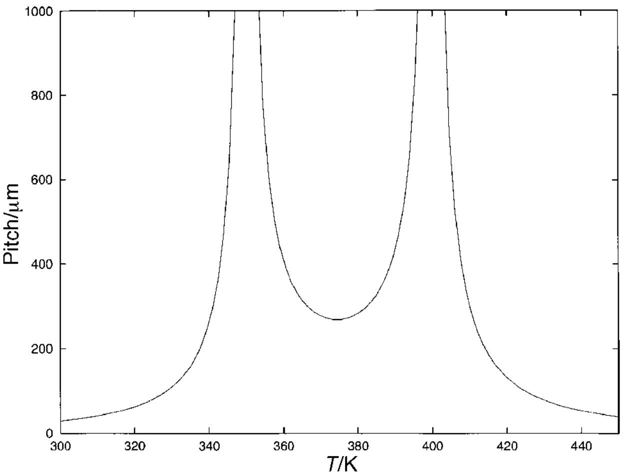


Fig. 8 Representation of the temperature dependence of pitch in a system where three species affect the sense of the helix of the chiral nematic phase in such a way that a double inversion of the helical twist sense occurs ($\Delta E_{ab}=5$ and $\Delta E_{ac}=10$ kJ mol^{-1}, $p_a=0.1$, $p_b=-0.2489$ and $p_c=2.507$ µm. Hence $T_{\infty 1}=350$ and $T_{\infty 2}=400$ K)

in the chiral nematic phase of material **4** is close to the SmA phase. Therefore, we might expect strong smectic fluctuations to adversely affect the quality of the fit between the phenomenological model and the experimental pitch data. However, this was not found to be the case, implying that the model allows for good fits even when there are presumed substantial deviations from an ideal system. This may therefore yield erroneous values for the parameters p_a, p_b and ΔE.

Even though values for ΔE can be estimated to a certain degree *via* computer simulations, unfortunately, it is difficult to use the model in a predictive fashion because the quantities p_a and p_b cannot be estimated *a priori*. However, a range of values for the quantities p_a and p_b can be approximated from the results reported in Table 2, *e.g.* $p_a \approx 0.06$ and $p_b \approx -0.6$ µm. This might then assist in determining whether inversion is likely to occur within the temperature range of a chiral helical phase. However, one ought to emphasise that, at the present stage of computational or even experimental evaluation, the predictive nature of the model is rather limited.

Inversion phenomena in related systems

Describing the behaviour of a system by summing up its components' properties is not a new concept. Component property averaging was used to describe the inversion of the spontaneous polarization in chiral smectic C* phases[3,5,10–11] of single chiral centre systems. The model assumed that the relative magnitude and direction of the dipole for all molecular species present and their rotational distribution about the director have to be taken into account in the generation of the polarization. It was proposed that the species would fall into two groups, one where the average dipole lies in a direction $f(+\vec{v})$ relative to the *c*-director and another where the average dipole lies in an opposing direction, $f(-\vec{v})$. In this way, the two species are in competition. Thus, for two such species a heuristic approach was used in order to describe the temperature dependence of the polarization.[3,5,10] If the polarization directions of species *a* and *b* are opposite, then the polarization can fall to a zero value with decreasing temperature[5,10] when $\chi_a P_a = \chi_b P_b$, where χ_a and χ_b are the temperature dependent concentrations of species *a* and *b*. Additionally, the energy difference between the two rival species, which can be determined from fitting polarization data, was found to be similar in magnitude to the torsional energy for the rotation around a C—C bond. This observation led the authors to suggest that the competing species were likely to be conformational isomers.

Additionally, Saito *et al.* described inversions in spontaneous polarization in the chiral smectic C* phase as being driven by the competition between the dipolar and quadrupolar coupling of molecules,[19] *i.e.* it was proposed that dipolar and quadrupolar coupling produce polarizations with opposite signs and that, at a critical temperature, the two can be exactly compensated and give rise to an inversion in the direction of the polarization. Therefore, it is not unreasonable to envisage that twist inversion in helical mesophases could also be explained by the competition between dipolar and quadrupolar ordering, though molecular correlations are much weaker in the chiral nematic phase than they are in the smectic phase where there is some positional order. This notion does not contradict the phenomenological model which is macroscopic and, moreover, changes in dipolar and quadrupolar coupling may be driven by changes in conformational distribution.

Conclusions

There is much open debate as to the nature of inversion of helical structures in liquid crystal systems. Unfortunately, the debate is clouded by the fact that many systems studied are multi-component ones comprising a variety of materials or single component systems with multiple chiral centres. The study of single component, single chiral centre systems negates this problem and we are now allowed to examine what happens on the molecular scale more critically. Clearly, the mechanisms involved in this process are different from inversions in multi-component systems. The understanding of single component, single chiral centre systems should however shed light on multi-component systems. At this present moment, no simple experimental techniques will allow us to measure the concentrations of conformers. Hence, the only way of rationalising this phenomenon is through predictive modelling.

Although this study gives no real insight into the mechanisms of pitch inversion, the experimental results observed in a variety of materials have been explained using a phenomenological model where twisting power is an additive property. Moreover, through molecular modelling, it is hoped that information has been added to the debate in such a way that conformational interconversion is a viable mechanism by which helical inversion can be effected.

It is also hoped that the present article may spur researchers in the field to hunt for new materials with the view of providing, perhaps, chiral nematic phases whose pitch is largely independent of temperature.

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