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The observation of a novel twist inversion in a chiral nematic phase and an induced TGB A* phase in a binary liquid-crystalline mixture of a chiral propanonitrile and a chiral 1-alkoxypropane†

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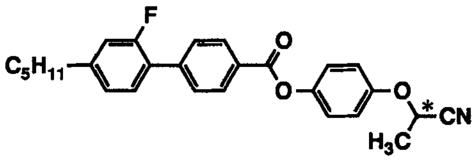
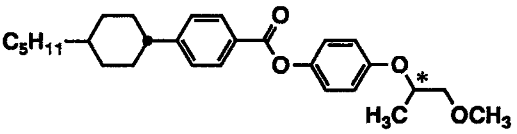
Binary mixture studies involving the chiral nematogens (*R*)-2-[4-(2′-fluoro-4′-pentylbiphenyl-4-carbonyloxy)phenoxy]propanonitrile and (*R*)-2-{4-[4-(*trans*-4-pentylcyclohexyl)benzoyloxy]phenoxy}-1-methoxypropane revealed that these compounds show opposite helical twist senses, reinforcing existing selection rules relating twist sense to chemical structure. Certain mixture compositions displayed a N^*_{RH}–N^*_{∞}–N^*_{LH} twist inversion sequence, while other compositions showed an induced TGB A* phase mediating the N^*_{LH}–S^*_A phase transition. This paper presents a complete phase diagram for the binary mixture as determined by polarizing light microscopy and differential scanning calorimetry and gives pitch measurements and determinations of helical twist senses above and below the inversion point.

1. Introduction

Earlier work revealed that both (*R*)-2-[4-(2′-fluoro-4′-pentylbiphenyl-4-carbonyloxy)phenoxy]propanonitrile (**1**) and (*R*)-2-{4-[4-(*trans*-4-pentylcyclohexyl)-benzoyloxy]phenoxy}-1-methoxypropane (**2**) show liquid-crystalline behaviour, notably chiral nematic phases [1, 2]. The structures of compounds **1** and **2** and their mesomorphic behaviour are given below in figure 1. According to Gray and



1, I–N* = 122·8, N*–S_A^* = 82·7°C.



2, I–N* = 123·9, N*–S_A^* = 107·1, S_A^*–B = 85·3°C.

Figure 1. Compounds **1** and **2**; structures and phase behaviour.

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† All phase assignments denoted with an asterisk (*) indicate a reduced space symmetry as a consequence of the constituent chiral molecules.

Table 1. Rules relating helical twist sense, parity, spatial configuration and bond polarization at a chiral centre.

Absolute configuration†	Parity‡	Inductive effect	Rotation of plane polarized light	Helical twist sense
S	e	+I	d	LH
S	o	+I	l	RH
R	e	+I	l	RH
R	o	+I	d	LH
S	e	−I	l	RH
S	o	−I	d	LH
R	e	−I	d	LH
R	o	−I	l	RH

† As defined by Cahn, Ingold and Prelog [4].

‡ Denotes parity displacement of chiral centre from the rigid aromatic core (o = odd and e = even).

McDonnell's rules [3], it is possible to relate helical twist sense to absolute configuration [4], parity, i.e. the separation of the point of asymmetry from the mesogenic core) and the direction of rotation of plane polarized light through the mesophase for non-sterol based mesogens. However, these rules apply only directly to materials with positively inductive (+I) substituents at the chiral centre. It has since been demonstrated in some cases that the sequence for the rules becomes reversed if the chiral centre possesses a negatively inductive moiety (−I) [5,6]; the rules are summarized in table 1. It was therefore of some interest to relate the behaviour of the helical twist sense in suitable mixtures of compounds **1** and **2** to these selection rules, since both compounds have the same absolute configuration and parity, but different bond polarizations relative to their chiral centres (i.e. compound **1** is −I (CN) whereas compound **2** is +I (CH_2OCH_3, relative to CN)). Additionally, compounds **1** and **2** have similar clearing points which allow for easy mixing and manipulation, and avoids problems in selecting a viable standard for twist sense determinations.

2. Experimental

The purity of compounds **1** and **2** employed in this work was established by using TLC, ^{1}H NMR and HPLC, and the spectral data (^{1}H NMR, IR and MS) were in accordance with the required structures [1, 2]. The mixtures were prepared by carefully weighing portions of compounds **1** and **2** into clean glass vials; the contents were then heated into the isotropic phase and thoroughly mixed to ensure homogeneity. The initial phase assignments and transition temperatures were determined on cooling (3°C min^{-1}) by thermal optical microscopy using a Zeiss Universal polarizing microscope equipped with a Mettler FP 82 microfurnace and FP 80 control unit. Pitch measurements for the chiral nematic phase were made using clean microscope coverslips and slides, and a Lasico eyepiece with digital readout calibrated previously with a 1 mm microscope stage graticule. Differential scanning calorimetry was carried out at a heating and cooling rate of 5 and 10°C min^{-1} on 5–10 mg samples using a Perkin–Elmer DSC 7 calorimeter and data station. The instrument was calibrated using an indium standard (measured $\Delta H = 28{\cdot}32\,\mathrm{J\,g^{-1}}$, literature value, $28{\cdot}45\,\mathrm{J\,g^{-1}}$).

3. Results

3.1. *Thermal optical microscopy*

It is apparent from the phase diagram shown in figure 2, that unusual phase behaviour was observed for mixtures of **1** and **2**. Cooling most mixtures from the isotropic phase revealed a N* phase, identified by its characteristic *Grandjean* (planar) texture; little variation was observed for this transition for all compositions of compounds **1** and **2** across the phase diagram. However, peculiar textures were observed at high percentages of compound **2** [>88 per cent (wt/wt)]; some compositions gave nematic *schlieren* or chiral nematic 'fingerprint' textures with clearly definable dechiralization lines. Closer examination of a number of these mixtures revealed that cooling through the chiral nematic phase was apparently mediated by a N*–N^*_{∞}—N* sequence, corresponding to the unwinding of a helix, and possibly indicative of a twist inversion. Closer examination of the 97 per cent (wt/wt) of

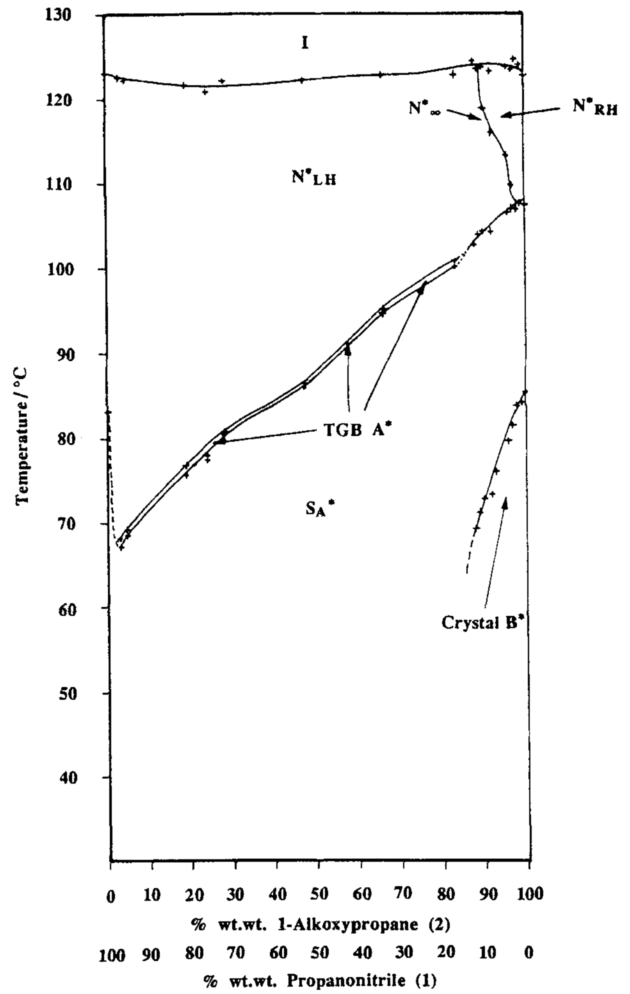


Figure 2. The phase diagram for binary mixtures of (*R*)-2-[4-(2′-fluoro-4′-pentylbiphenyl-4-carbonyloxy)phenoxy]propanonitrile and (*R*)-2-{4-[4-(*trans*-4-pentylcyclohexyl)-benzoyloxy]phenoxy}-1-methoxypropane.

Figure 3. The texture of the 97 per cent (wt/wt) of compound 2 mixture at the inversion point.

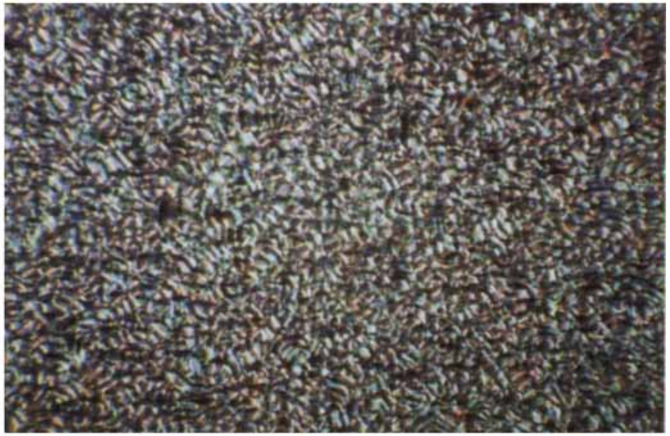


Figure 4. The platelet texture of the TGB A* phase.

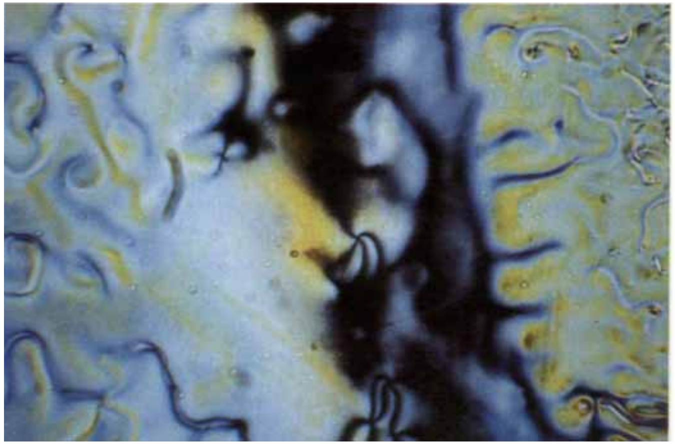


Figure 6. A contact preparation of 97 per cent (wt/wt) of compound 2 and **9O2Cl3MT** showing the compensated region between the chiral nematic phases at 123°C.

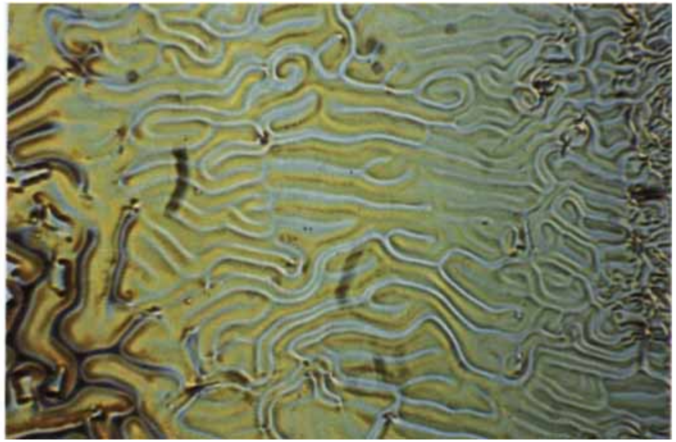


Figure 7. A contact preparation of 97 per cent (wt/wt) of compound 2 and **9O2Cl3MT** showing the continuous chiral nematic phase at 108°C.

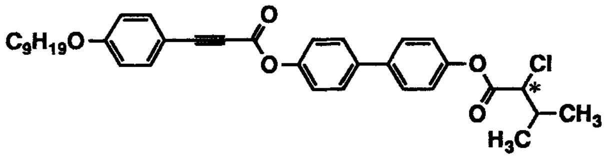
compound **2** mixture revealed that as the pitch became longer (clearly seen from the changes in the separation of the dechiralization lines), the planar texture broke down to give a series of chiral nematic finger-like structures against a black *pseudo*-homeotropic nematic background (see figure 3), the homogenous texture reformed on further cooling. The texture shown in figure 3 corresponds to an unwound chiral nematic state denoted here as N^*_∞ (∞ = infinite pitch) and the observations made represent another example of a twist inversion [7].

Similar behaviour was also noted for the mixtures of composition 96, 92 and 90 per cent (wt/wt) of compound **2**. Pure compound **2** gave no twist inversion, as the more thermodynamically stable smectic A* mesophase predominated on cooling; the same was also found to be true for 99 and 98 per cent (wt/wt) of compound **2** compositions. Similarly, no twist inversion was observed in compositions of less than 90 per cent (wt/wt) of compound **2**, and all these mixtures showed normal homogeneous textures with dechiralization lines. It is important to note that the nematic phase is still composed of chiral molecules, but the phase has lost all form chirality as a consequence of the unwinding of the helix, and so it is referred to as N^*_∞. In the phase diagram (figure 2) the centre of this nematic region is denoted by the line labelled N^*_∞. On further cooling, these mixtures with a high percentage of compound **2** result in the formation of the classical broken focal-conic texture of the smectic A* phase. The smectic A* phase eventually gives way to a crystal B* mesophase as characterized by the appearance of transition bars on the focal-conic fans, which is indicative of a change from short to long range order [8].

For compositions of less than ~85 per cent (wt/wt) of compound **2**, cooling from the N* phase to the smectic A* phase was mediated by the appearance of a short range TGB A* phase (~1–2°C). This was easily identified by its platelet (see figure 4) or *vermis* texture [9, 10]; on further cooling the TGB A* filaments/platelets quickly coalesced into a matrix of broken focal-conic fans interspersed with black regions of homeotropic smectic A*. The presence of this induced TGB A* phase is of considerable note because neither pure **1** nor **2** displays such a phase at the N* to smectic A* transition, and this presumably indicates an increase in the chirality of the system in the mixtures. In contrast, on the other side of the phase diagram, no smectic A* to crystal B* transitions were observed on further cooling, although this is not too surprising because compound **1** shows no B character.

3.2. *Determination of the helical twist sense above and below the inversion point*

This was carried out by performing a contact preparation with the aid of a sample of material of known helical twist sense [11]; (*S*)-4′-(4-nonyloxyphenylpropioloyloxy)biphenyl-4-yl 2-chloro-3-methylbutanoate (**9O2Cl3MT**, figure 5) which has a left hand twist sense and a suitable chiral nematic phase range [12]. The contact experiment was carried out using a small quantity of the 97 per cent (wt/wt) of



m.p. = 79·2; I–N* = 155·9, N*–S_C^* = 80·6°C.

Figure 5. The structure and phase transition temperatures of **9O2C13MT**.

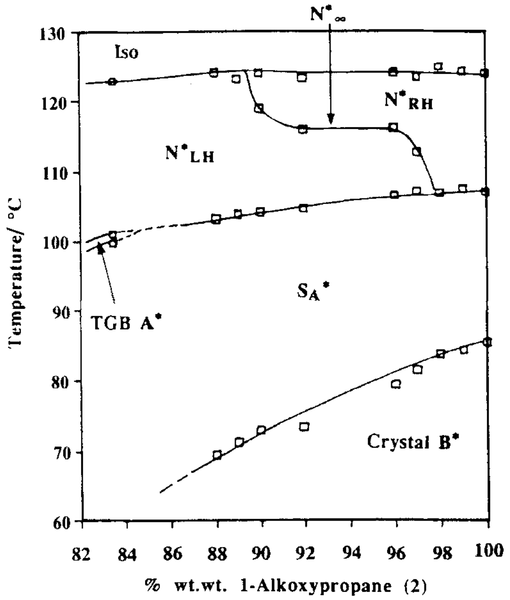


Figure 8. Detail for the binary mixture phase diagram at and around the twist inversion point.

compound **2** mixture; at a temperature of 123°C the contact boundary appeared as a nematic *schlieren* texture with 4-brush singularities or a *pseudo*-homeotropic nematic texture bordered by two regions of *Grandjean* texture indicating that above the inversion point the helical twist must oppose (or compensate) the helical structure of the standard, i.e. be right-handed (see figure 6). On cooling the contact preparation to a temperature of 108°C, what was previously the nematic *schlieren* interface becomes transformed into a continuous *Grandjean* texture. Therefore, below the inversion point the twist sense is identical to the standard, i.e. it is left-handed (see figure 7). This information now allows us to redraw the region of the phase diagram corresponding to 80 to 100 per cent (wt/wt) of compound **2** and to define the exact points of twist inversion (N^*_∞) and the twist sense above and below the inversion point (see figure 8).

One consequence of this observation is that in contact preparations of a compound with a standard twist sense and a compound of unknown twist sense, the N^*_∞ boundary may move with temperature through a range of compositions.

3.3. *Pitch length studies*

The pitch lengths associated with the chiral nematic phase were measured for the 97 per cent (wt/wt) of compound **2** mixture and for pure compound **2**; the results closely support the optical microscopy conclusions, and plots of pitch length (microns) versus temperature for both samples are shown in figure 9. For the 97 per cent (wt/wt) of compound **2** mixture (denoted by open circles in figure 9) the pitch length increases to infinity (N^*_∞), then decreases as the twist becomes inverted before reaching the underlying smectic A* phase. Measured pitch lengths varied between approximately 30 and 90 μm. Similar measurements on pure **2** (denoted by filled circles in figure 9) show that the pitch length steadily increases from approximately 10 to 100 μm before becoming infinite in the pretransitional region leading to the smectic A* phase.

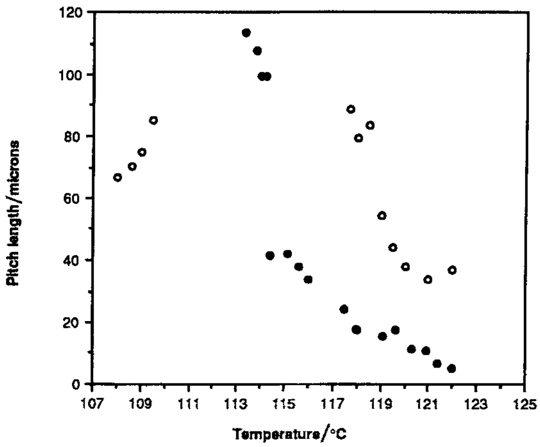


Figure 9. Pitch lengths measured as a function of temperature for the chiral nematic phase, ●, pitch for pure compound **2**; ○, pitch for 97 per cent (wt/wt) compound **2**.

Table 2. Thermodynamic data for two different mixtures of compounds **1** and **2**.

Per cent (wt/wt)**2**	Transition temperatures °C†					
	I–N*	N*–TGB A*	N*–S_A^*	TGB A*–S_A^*	S_A^*–B*	S_A^*/B*–C
24	121·2 [0·19]§	78·0 [0·13]	—	—‡	—	23·9 [5·78]
96	123·2 [0·26]	—	105·7 [0·63]	—	78·4 [1·12]	18·1 [6·12]

† Denotes DSC cooling runs performed at 5°C min^{-1}.

‡ Only observed as a small shoulder on N*–TGB A* transition; no enthalpy measurements were possible.

§ Denotes enthalpy of transition (cal g^{-1}).

3.4. *Differential scanning calorimetry studies*

Two compositions were selected for examination, one to reveal the nature of the N*–TGB A*–S_A^* transition sequence (i.e. a 24 per cent (wt/wt) mixture of compound **2**) and one to ascertain whether the twist inversion process occurs with a discernible enthalpy change (i.e. a 96 per cent (wt/wt) mixture of compound **2**). The transition temperatures and associated enthalpies of the cooling cycles are given in table 2. The DSC data obtained generally support the optical microscopy results. In the case of the mixture with 24 per cent (wt/wt) of compound **2**, the initial N*–TGB A* transition was easily detected, but, the accompanying small shoulder is probably due to the TGB A*–S_A^* transition. The enthalpy of the TGB A*–S_A^* transition therefore proved impossible to measure due to its proximity to the earlier N*–TGB A* event. No evidence was obtained to prove that the twist inversion (N_{RH}^*–N_{∞}^*–N_{LH}^*) observed optically in the sample with 96 per cent (wt/wt) of compound **2** was accompanied by a measurable enthalpy change; this is in agreement with results obtained for twist inversions in other systems [7, 12].

4. Discussion

It is apparent from the results reported that the electronic nature of the substituents at the chiral centres of compounds **1** and **2** govern the twist sense of the mesophase and are directly responsible for the formation of the induced TGB A* phase and the twist inversion phenomenon shown in the phase diagram (see figure 2). Clearly the propanonitrile (**1**) has a very much higher twisting power than the alkoxypropane (**2**); this is evident from the imbalance of the N* regions on either side of the N^*_∞ line, as only a relatively small quantity of compound **1** is required to cause the inversion in helical twist sense. The highly twisting nature of the propanonitrile (**1**) is also the reason for the formation of the TGB A* phase which mediates the N^*_{LH}–S^*_A transition at compositions ranging from *c* 5–80 per cent (wt/wt) of compound **2** (95–20 per cent (wt/wt) of compound **1**). As the composition of compound **1** is increased across the phase diagram, the right-handed helicity (N^*_{RH}) is gradually, but rapidly, annihilated to give the N^*_∞ point; the helicity of the system then inverts and becomes left-handed as the proportion of compound **1** increases still further (N^*_{LH}). Remembering that compound **1** has a much higher twisting power, the N^*_{LH} region will have a correspondingly high degree of form chirality (certainly more so than the N^*_{RH} region), and therefore on cooling from this highly chiral twisted nematic state towards the smectic A* phase region the formation of a small band of TGB A* phase is observed. Here the helical twist of the N^*_{LH} region is incorporated into a 'layered' smectic phase. It is currently believed that the smectic phase must have relatively weak layer ordering to enable a helical twist distortion to first penetrate and then become incorporated into the phase structure [13, 14]. This is supported to some degree by enthalpimetric data obtained for the N*–S^*_A phase sequences of the pure compounds and the N*–TGB A*–S^*_A sequences for the binary mixtures of **1** and **2**. The values of enthalpy change are as follows ($\mathrm{cal\,g^{-1}}$); compound **2**, 0·59; 96 per cent (wt/wt) compound **2**, 0·63; 24 per cent (wt/wt) compound **2**, 0·13; and compound **1**, 0·12. An N*–S^*_A transition occurs in three of these examples and with the exception of pure compound **1**, they have higher enthalpies than the N*–TGB A*–S^*_A transition. These observations further support Renn and Lubensky's prediction that the N*–S^*_A transition may under certain circumstances be mediated by the formation of an intermediary TGB A* phase [15]. It should be pointed out that another example of an induced TGB A* phase in mixtures is thought to have been previously noted in a mixture of sterol based esters [16]. It is possible to draw an analogy between the presence of this induced TGB A* phase and the expulsion and penetration of magnetic fields in type II superconductors, above and below their lower and upper critical fields (H_{C1} and H_{C2}). The stabilization of the TGB A* phase may only occur when the chirality of the binary mixture has a value between the respective lower and upper critical fields for this system. In a highly twisting mixture, the pitch may exceed the upper critical field and the mixture assumes a chiral nematic state. Conversely, for a much lower twisting mixture, the pitch may be lower than the lower critical field; therefore the mixture will assume a smectic state. This may in part explain why a highly twisting compound (**1**) shows no TGB A* phase despite its low enthalpy for its N*–S^*_A transition ($0{\cdot}12\,\mathrm{cal\,g^{-1}}$).

5. Conclusions

It has been demonstrated that the helical twist senses of the propanonitrile (**1**) and the alkoxypropane (**2**) are governed by the electronic nature of the substituents at the chiral point in each compound. Additionally, the highly twisting nature of compound **1** is believed to be responsible for the formation of the induced band of TGB A* phase and for the twist inversion phenomenon as observed in the phase diagram.

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