# Highly twisting enantiomeric radial multiyne dopants for discotic liquid-crystalline systems

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The synthesis and dopant properties of both the (R,R,R,R,R)- and (S,S,S,S,S)-hexadecyloxy {pentakis[4-(1-methylheptyloxy)phenylethynyl]} benzene enantiomers are described. Although the materials were found not to be liquid-crystalline, it was found possible to induce left [for the (R,R,R,R,R)-enantiomer] and right handed [for the (S,S,S,S,S)-enantiomer] chiral discotic nematic phases  $(N_D^*)$  as well as being only the second instance of the observation of discotic blue phases  $(BP_DIII \text{ and } BP_DII)$  in binary mixtures with the hexayne host, hexakis(4-nonylphenylethynyl)benzene; a phase diagram is presented. The helical pitch and helical twisting power of the dopants was measured by use of the modified Cano method, and revealed far higher twisting powers than previously reported pentaynes. In addition the temperature dependent and angular dependent selective reflection spectra are reported, along with average refractive index approximations, which enable the pitch length of the chiral discotic nematic phase  $(N_D^*)$  to be estimated to be of the order of 0.36 to 0.35 µm.

Just as the effect of chirality on the properties of calamitic liquid-crystalline systems has been extensively explored and documented over the last decade,<sup>1</sup> a similar development of discotic liquid-crystalline systems is becoming an increasingly more prominent feature of current liquid crystalline research. This is in no small part due to the discovery of the following series of effects: discotic cholesteric or chiral nematic phases ( $N_D^*$ ) in a variety of triphenylenes and truxene cored discogens,<sup>2</sup> observation of ferroelectric switching in chiral columnar phases,<sup>3-6</sup> the formation of induced discotic blue phases<sup>7</sup> and the observation of both selective reflection and helix inversion in a pure chiral discotic nematic mesogen.<sup>8</sup> These observations will undoubtably provide the impetus for further systematic research into the influence of chirality on the physical properties of discotic mesogens.

Our work has centred on the development of highly chiral pentayne compounds, certain forms of which have been well documented in recent years and many of which are known to show discotic nematic phases;<sup>9-13</sup> such materials offer the potential for the formation and study of the still novel chiral discotic nematic phase. Most of the known chiral multiynes synthesised to date belong to two classes: (i) consisting of pentaynes with one chiral alkyl chain (1 and 2) or (ii) as chiral pentaynes with one achiral alkyl chain (3 and 4), these are shown in Fig. 1. These materials all utilize either 2-methylbutanol or 3,7-dimethyloctanol (from  $\beta$ -citronellol) as the chiral moiety, in each instance the chiral centre is located either one or two carbon atoms away from the ether oxygen atom. In an attempt to increase the macroscopic chirality of the system represented by compounds 3 and 4, we chose to employ (R)or (S)-octan-2-ol as the terminal chiral group; this moiety is well known for its ability to generate tightly twisting and highly chiral phases in calamitic systems. In such systems the chiral centre is directly attached to the liquid-crystalline core via an oxygen atom, and is thought to result in a higher degree of restricted rotation leading to molecular frustration and therefore higher chirality.14,15

The two materials selected for synthesis are (R,R,R,R,R)and (S,S,S,S,S)-hexadecyloxy{pentakis[4-(1-methylheptyloxy)phenylethynyl]}benzene (5a and b) (Fig. 2). It was hoped that

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Fig. 1 Different forms of chiral multiynes



Fig. 2 Chiral hexadecyloxy{pentakis[4-(1-methylheptyloxy)phenylethynyl}benzenes, where \* = (R)- for 5a and (S)- for 5b

# Experimental

#### Synthesis

The route employed to prepare the chiral radial multiynes (5a and **b**) is shown in Scheme 1. The (R)- and (S)-ethynylbenzene side chains were prepared firstly by the Mitsunobu alkylation of 4-iodophenol (6) using diethyl azodicarboxylate (DEAD) and triphenylphosphine with (S)- and (R)-octan-2-ol to give the ethers 7a and 7b in good yield.<sup>16</sup> Compounds 7a and 7b were then coupled to trimethylsilylacetylene using tris(triphenylphosphine)palladium(II) chloride, copper(I) iodide and triphenylphosphine as catalyst under anhydrous basic conditions; the trimethylsilyl protected intermediates (8a and 8b) were deprotected using basic aqueous methanol to give the chiral ethynylbenzenes (9a and 9b) as pure orange liquids. The final stage multiple couplings of 9a and 9b with pentabromo-(hexadecyloxy)benzene (10) were achieved using tris (triphenylphosphine)palladium(II) chloride, copper(I) iodide and triphenylphosphine in anhydrous refluxing triethylamine under a nitrogen atmosphere. The final products were all isolated by rigorous purification by flash chromatography. The chemical structures of compounds 5a and 5b and intermediates were confirmed by a combination of <sup>1</sup>H NMR, <sup>13</sup>C NMR (DEPT) and IR spectroscopy and EI MS, the spectroscopic

details of both the chiral pentaynes (**5a** and **5b**) are given below. In the <sup>1</sup>H NMR assignments 1M7 refers to the 1methylheptyloxy substituents. More comprehensive experimental details of these reactions have been reported previously.<sup>8</sup>

## (*R*,*R*,*R*,*R*,*R*)-Hexadecyloxy{pentakis[4-(1-methylheptyloxy)phenylethynyl]}benzene (5a)

Yield 930 mg (25%);  $R_{\rm f}$  0.29 (1:1, toluene-hexane);  $\delta_{\rm H}$ (400 MHz; CDCl<sub>3</sub>; TMS) 0.88 (18 H, t, terminal CH<sub>3</sub>s), 1.32-1.48 (80 H, m, CH<sub>2</sub>s of alkyl chains and CH<sub>3</sub> branches on 1M7 chains), 1.60 (6 H, m, alkyl chain CH<sub>2</sub>s), 1.76 (5 H, m, 1M7 chains), 1.92 (2 H, quintet, OCH<sub>2</sub>CH<sub>2</sub>alkyl), 4.32 (2 H, t,  $OCH_2C_{15}C_{31}$ ), 4.39 (5 H, sextet, methine H in 1M7 groups), 6.86 (10 H, m, aromatic Hs), 7.52 (10 H, m, aromatic Hs);  $\delta_{\rm C}(270 \text{ MHz}; \text{ CDCl}_3, \text{ TMS})$  14.08 (q, methyl C), 14.12 (q, methyl C), 19.67 (q, methyl C), 22.60, 22.69, 25.49, 26.40, 29.27, 29.38, 29.70, 29.74, 30.61, 31.79, 31.93, 36.42 (t, multiple methylene C), 73.94 (d, methine C), 74.62 (t, phenyl-O-CH<sub>2</sub>), 83.47, 86.05, 86.58 (s, outer ethynyl C), 97.01, 99.11, 99.25 (s, inner ethynyl C), 115.12, 115.16, 15.38, 115.71 (d, phenyl C-H), 119.87, 123.86, 128.34 (s, phenyl C-ethynyl), 133.15, 133.18, 133.33 (d, phenyl C-H), 158.53, 158.63, 158.73, 159.92 (s, phenyl C-O);  $v_{max}(film)/cm^{-1}$  3505, 3010, 2960, 2410, 1760, 1520, 1440, 1220, 940; m/z (EI) 1460 (M<sup>+</sup>+1), 1459 (M<sup>+</sup>).



Scheme 1 Synthetic route to chiral hexadecyloxy{pentakis[4-(1-methylheptyloxy)phenylethynyl]}benzenes ( $\S$ = not isolated or purified). *Reagents and conditions*: i, (R)- or (S)-octan-2-ol, DEAD, PPh<sub>3</sub>, THF, N<sub>2</sub>, room temp.; ii, HC=CSi(CH<sub>3</sub>)<sub>3</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, PPh<sub>3</sub>, Et<sub>3</sub>N, N<sub>2</sub>, room temp.; iii, KOH, MeOH, H<sub>2</sub>O; iv, HCl, H<sub>2</sub>O; v, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, PPh<sub>3</sub>, Et<sub>3</sub>N, N<sub>2</sub>, 100–110 °C

## (S,S,S,S,S)-Hexadecyloxy{pentakis[4-(1-methylheptyloxy)phenylethynyl]}benzene (5b)

Yield 400 mg (13%);  $R_{f}$  0.29 (1:1, toluene-hexane);  $\delta_{\rm H}(400 \text{ MHz}; \text{ CDCl}_3, \text{ TMS})$  1.04 (18 H, t, terminal CH<sub>3</sub>s), 1.31-1.64 (80 H, m, alkyl chain CH<sub>2</sub>s), 1.74 (6 H, m, alkyl chain CH<sub>2</sub>s), 1.90 (5 H, m, 1M7 chains), 2.06 (2 H, quintet, OCH<sub>2</sub>CH<sub>2</sub>alkyl), 4.48 (2 H, t, OCH<sub>2</sub>C<sub>15</sub>H<sub>31</sub>), 4.52 (5 H, sextet, methine H in 1M7 groups), 7.00 (10 H, m, aromatic Hs), 7.66 (10 H, m, aromatic Hs);  $\delta_{\rm C}(270 \text{ MHz}; \text{ CDCl}_3, \text{ TMS})$  14.08 (q, methyl C), 14.12 (q, methyl C), 19.67 (q, methyl C), 22.59, 22.69, 25.48, 26.39, 29.27, 29.38, 29.67, 29.70, 29.74, 30.61, 31.78, 31.92, 36.42 (t, multiple methylene C), 73.95 (d, methine C), 74.62 (t, phenyl-O-CH<sub>2</sub>), 83.47, 86.04, 86.57 (s, outer ethynyl C), 97.01, 99.10, 99.25 (s, inner ethynyl C), 115.12, 115.16, 115.38, 115.71 (d, phenyl C-H), 119.86, 123.86, 128.34 (s, phenyl C-ethynyl), 133.14, 133.18, 133.32 (d, phenyl C-H), 158.52, 158.63, 158.73, 159.82 (s, phenyl C-O);  $v_{max}(film)/cm^{-1}$  3010, 2960, 2420, 1750, 1620, 1520, 1230, 940; m/z (EI) 1460 (M<sup>+</sup> + 1), 1459 (M<sup>+</sup>).

# Measurements

The nominal molecular weights of compounds **5a** and **5b** (m/z = 1459.0493) were confirmed by electron ionisation mass spectrometry (Finnigan MAT 95Q spectrometer), the samples being directly injected at an inlet temperature of 390 °C. Two peaks having an approximate ratio to one another of 1:1 were observed at m/z 1459 and m/z 1460; the former corresponding to the molecular ion and the latter the M<sup>+</sup> + 1 ion peak, the presence of which is unsurprising considering that the molecule has the molecular formula  $C_{102}H_{138}O_6$  and will contain the natural abundance of <sup>13</sup>C atoms (1.108%).

Binary mixtures of compounds 5a and 5b and the appropriate discotic host were prepared by accurately weighing the desired amounts onto (or into) tared microscope coverslips (for phase diagrams) or DSC pans (Cano pitch measurements) using a Mettler ME22 microbalance in conjunction with a Mettler BE22/BA25 digital balance display. The mixtures were then intimately mixed whilst in their isotropic states. The

transition temperatures were then checked for consistency before use using a Leica Laborlux 12POL S microscope equipped with a Mettler FP82 hotstage and FP80 temperature controller; all reported transition temperatures were recorded at heating and cooling rates of 5 deg min<sup>-1</sup>.

The helical pitch lengths of specific mixtures were measured using the modified Cano-Granjean method using a convex lens and glass plate.<sup>17</sup> The temperature of the discotic chiral nematic sample was controlled by the use of a Haake F3 thermostat and copper heating block placed on an optical microscope. The concentric disclination lines obtained at a given temperature were recorded using a Sony video graphic printer UP-811, enabling the radius of the concentric disclinations to be determined with reference to a microscopic scale.

Selective reflection spectra at normal incidence of light were recorded using a Photoresearch PR-703 A diode array spectrometer mounted on a Leitz Ortholux II-Pol microscope, the chiral discotic nematic phases' temperature being controlled using a Linkam TM90 hot stage, whilst being constrained in an EHC (Japan) indium tin oxide (ITO)-polyimide coated cells ( $d = 4.05 - 4.37 \,\mu$ m). Planar alignment was achieved by application of an ac electric field (160 V peak to peak at 50 kHz). Angle dependent spectra were recorded using the above spectrometer, a Flexilux 150 HL universal white light source both equipped with right or left handed circular polarizers. These were mounted so that an angle  $\theta$  could be swept out ( $\theta_{max} \approx \pm 45$  deg) from the normal to the cell. The temperature of the EHC cell was maintained using a heated copper block and a Haake F3 thermostat. Planar alignment was achieved in exactly the same manner as described before.

# Results

#### Mesogenic behaviour

The chiral pentaynes **5a** and **5b** are not mesogenic, even rapid cooling to approximately -60 °C failed to reveal any phase or even result in crystallization. In hindsight, this is perhaps not surprising, as another chiral pentayne, (*S*,*S*,*S*,*S*,*S*)-hexadecy-



13, K 92 ND 107 I (°C)

Fig. 3 Structures of the discotic nematic hosts

loxy {pentakis[4-(3, 7-dimethyloctyloxy)phenylethynyl]}benzene (4) shows a discotic chiral nematic phase  $(N_D^*)$  with a very low clearing point ( $N_D$ \*–I 234 °C) <sup>8</sup> As the compounds 5a and 5b contain five chiral 1-methylheptyloxy side chains, it may be appreciated that the proximity of the chiral branch to the discotic nucleus [both moieties separated by one atom (oxygen)], contrasts to compound 4's five 3,7-dimethyloctyloxy chains, the chiral branch being some three atoms distant from the core, and is thought to lead to a considerable destabilization of attractive interactions which might promote a discotic phase, ultimately resulting in a huge depression of clearing point Nevertheless, in order to assess compounds 5a and 5b's liquidcrystalline character, they were formulated into binary mixtures of varying composition using the known discotic nematic host, hexakıs(4-nonylphenylethynyl)benzene (11) (see Fig 3)<sup>18</sup> Fig 4, shows the phase diagram for various compositions of 5a in compound 11

At low concentrations of **5a**, up to *ca* 15 wt%, an enantiotropic discotic chiral nematic phase ( $N_D^*$ ) is observed The phase is characterized by the presence of oily streaks and domains of clearly defined pitch disclinations in the planar texture after the samples' coverships had been mechanically disturbed [remember that the discotic hexayne host (**11**) prefers to adopt a homeotropically aligned texture<sup>18</sup>] The handedness of the helical axis of the discotic chiral nematic phase was determined by both observation of the direction of dispersion of white light on rotation of the microscopes upper polarizer and by observing the selectively reflected light from a sheared sample through both right and left handed circular polarizers Both methods reveal that the (*R*,*R*,*R*,*R*)-pentayne (**5a**) has a discotic chiral nematic phase with a left handed helix

At higher concentrations of dopant 5a, say between 15 and 23 wt%, the enantiotropic phase behaviour disappears, and is replaced by the appearance of monotropic discotic blue phases  $(BP_D)$  and the discotic chiral nematic phase before crystallizing The higher temperature blue phase appears as an amorphous blue haze on slow cooling from the isotropic liquid and may be classified unambiguously as being the BP<sub>D</sub>III or 'fog phase' Continued cooling of  $BP_DIII$  at low cooling rates (*i e*  $02^{\circ}$ C min<sup>-1</sup>) results in the appearance of a second form of blue phase in the form of highly coloured (blue, green, orange, red) platelets Careful control of the temperature over a period of time can result in the growth of well defined platelets which are suitable for identification by Kossel analysis <sup>19</sup> It is however, perhaps worth noting that the host material (11) shows a glassy transition at ca 58 °C, which rather fortuitously has enabled the blue phase structure of other discotic systems to be frozen in thereby avoiding the crystallization of the sample This is of importance as it enables Kossel analysis to be carried out without the need for accurate and careful temperature

anch to independent response of the selective reflection of reflected light on single crystals of this blue phase, another feature of BPII <sup>20</sup> Further clarification of this point is currently on going No liquid-crystalline behaviour was noted for binary mixtures beyond a composition of ca 23–24 wt% **5a**, these mixtures give normal melting behaviour

Slow cooling of all compositions from the  $N_D^*$  phase results in crystallization of the samples, however, it was noticed that there are least two crystal forms Crystallization first occurs in the appearance of distorted hexagonal like crystals, these eventually give way to the formation of a more thermodynamically stable crystal form which is characterized by the appearance of long lance like structures which grow throughout the microscopic field of view This has been confirmed by DSC analysis of selected binary mixture compositions

control Preliminary Kossel analysis, revealed the presence of

[110] and [100] hkl lines and appears to indicate that this lower

temperature discotic blue phase has a simple cubic lattice, ie

It is  $BP_DII$  This is further supported by the temperature

A similar phase diagram was obtained for the (S,S,S,S,S)pentayne (5b), with the obvious difference that the induced discotic nematic phase has a right handed helical axis

# Pitch length and helical twisting power measurements

The pitch length of a discotic chiral nematic phase  $(N_D^*)$  may be conveniently measured using the modified Grandjean–Cano method, which involves the measurement of the distance of concentric disclination lines  $(r_n \text{ and } r_{n+1})$  observed when the a discotic chiral nematic sample is constrained between a convex lens (of known radius of curvature, R) and glass plate, each having been treated by undirectional rubbing to give planar alignment, the pitch length (p) being calculated from the relationship<sup>9</sup> shown in eqn (1)

$$p/2 = \sqrt{(R^2 - r_n^2)} - \sqrt{(R^2 - r_{n+1}^2)}$$
(1)

However, as the two chiral pentaynes (5a and 5b) are not liquid crystalline, they first had to be formulated into binary mixtures with a suitable discotic nematic host  $(N_D)$  Previous investigations on chiral multiynes have revealed that radially symmetric multiynes tend to give homeotropic alignment, whilst pentaynes give planar alignment above a certain critical sample thickness<sup>8</sup> <sup>18</sup> <sup>21</sup> Understandably, the pentayne undecyloxy[pentakis(4-pentylphenylethynyl)]benzene (12)(see Fig  $3)^{22}$  was initially selected for use as a discotic nematic host for dopants 5a and 5b because of its preferred alignment and its structural similarity to the dopants (it is a well known fact that similarity between chiral dopants and hosts in calamitic systems results in effective chirality transfer and early studies appear to suggest that this is also true for discotic systems) <sup>23-25</sup> Table 1 lists the low weight percentage mixtures of compounds 5a and 5b in the discotic nematic host 12 along with their transition temperatures and helical twist senses as determined by optical microscopy As would be expected for binary mixtures containing low concentrations of a chiral dopant (<10 wt $\%^{23}$ ) the temperature dependence of the inverse pitch  $(p^{-1})$  of the mixtures **a-f** is essentially linear within experimental error, this is show in Fig. 5, where the (R,R,R,R,R)or left handed mixtures are denoted as being negative (-ve)and the (S,S,S,S,S) binary mixtures are right handed and denoted as being positive (+ve) It is immediately apparent that despite slight differences in weight percentages of mixtures of opposite twist sense that the pitch lengths are comparable No twist inversion behaviour was noted for any of the six binary mixture compositions Rotation of the microscopes analyser during these experiments confirmed the helical twist senses determined previously by microscopy, that is that the (R,R,R,R,R)-form (5a) is left handed and that the (S,S,S,S,S)form (5b) is right handed



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The helical twisting power (HTP or  $\beta$ ) which is defined as



Table 1 Composition and thermodynamic properties of chiral discotic nematic mixtures of compounds 5a and 5b in pentayne host discotic nematic compound 12

| mixture | absolute<br>configuration |                  |        |                      |                           |                    |
|---------|---------------------------|------------------|--------|----------------------|---------------------------|--------------------|
|         |                           | wt% <sup>b</sup> | mp–Iso | Iso-N <sub>D</sub> * | N <sub>D</sub> *-recryst. | sense <sup>c</sup> |
| 8       | (R,R,R,R,R)               | 1.17             | 77.1   | 91.7                 | 58.1                      | LH                 |
| b       | (R,R,R,R,R)               | 1.88             | 76.5   | 90.0                 | 58.2                      | LH                 |
| c       | (R,R,R,R,R)               | 2.99             | 76.4   | 81.6                 | 56.4                      | LH                 |
| d       | (S.S.S.S.S)               | 1.17             | 76.7   | 91.6                 | 60.4                      | RH                 |
| e       | (S, S, S, S, S)           | 1.85             | 76.9   | 89.6                 | 63.0                      | RH                 |
| f       | (S,S,S,S,S)               | 2.97             | 75.1   | 87.4                 | 62.0                      | RH                 |

<sup>a</sup> Transition temperatures recorded at heating and cooling rates of 5 deg min<sup>-1</sup>.

 $^{\circ}$  wt% of dopant (R,R,R,R,R) 5a or (S,S,S,S,S) 5b in the host undecyloxy[pentakis(4-phenylethynyl)]benzene (12).

<sup>c</sup> Determined by optical microscopy on a binary mixture of dopants 5a and 5b in undecyloxy[pentakis(4-nonylphenylethynyl)]benzene (12).



Fig. 5 Temperature dependence of the reciprocal pitch length of mixtures of dopants 5a and 5b in the discotic nematic host undecyloxy[pentakis(4-pentylphenylethynyl)]benzene (12) (Key: filled symbols refer to compound 5b,  $\blacksquare = 1.17$  wt%,  $\blacklozenge = 1.85$  wt% and  $\blacklozenge = 2.97$  wt%. Unfilled symbols refer to compound 5a,  $\square = 1.17$  wt%,  $\bigcirc = 1.88$  wt% and  $\diamondsuit = 2.99$  wt%.)



Fig. 6 Temperature dependence of helical twisting power of mixtures of dopants 5a and 5b in the discotic nematic host undecyloxy[pen-takis(4-pentylphenylethynyl)]benzene (12) (Key: filled symbols refer to compound 5b,  $\blacksquare = 1.17$  wt%,  $\blacklozenge = 1.85$  wt%,  $\blacklozenge = 2.97$  wt%. Unfilled symbols refer to compound 5a,  $\square = 1.17$  wt%,  $\bigcirc = 1.88$  wt%,  $\diamondsuit = 2.99$  wt%.)

being the reciprocal of the product of the pitch length and concentration  $[(pc)^{-1}]^{23}$  which for convenience the concentration (c) is measured in wt% may then be calculated from this pitch length data. The temperature dependence of helical twisting power of the six mixtures (**a**-**f**) of the two chiral dopants (**5a** and **5b**) is plotted in Fig. 6, and shows that within experimental error at such low concentrations (1.17-2.99 wt%) the helical twisting power is essentially independent of the concentration of dopant over the experimental temperature range (ca. 90-65 °C). At a temperature of ca. 75 °C the helical

twisting power (HTP) of compounds **5a** and **5b** in the discotic nematic host **12** is *ca.* 19 mm<sup>-1</sup> wt%<sup>-1</sup>.

Remarkably, it was found possible to obtain concentric Cano disclination lines for mixtures of 5a and 5b in the hexayne discotic nematic host compound 11; previously, planar alignment was believed to be impossible due to the hexaynes preference for homeotropically aligned systems. It should be noted that the concentric disclination patterns were considerably harder to obtain for mixtures of 5a/b in compound 11 than in compound 12, the disclination lines become indistinct with decreasing temperature, making measurement somewhat difficult.<sup>‡</sup> The compositions and transition temperatures of these mixtures are listed in Table 2.

The temperature dependences of the reciprocal pitch  $(p^{-1})$ and helical twisting power  $[(pc)^{-1}]$  are plotted in Figs. 7 and 8, similar sign/helical handedness conventions have been used to Figs. 5 and 6. The appearance of the temperature dependence of reciprocal pitch is similar to the plot for the system 5a/b-compound 12 (Fig. 5), with the obvious difference that the chiral discotic nematic phase range is much longer. More interestingly, the values of helical twisting power show considerably higher values, despite the scattering of experimental data at lower temperatures. At a temperature of ca. 75 °C, the helical twisting power of this 5a/b-compound 12 system is ca. 29 mm<sup>-1</sup> wt%<sup>-</sup> <sup>1</sup>, a factor of some 1.5 times larger than the 5a/b-compound 11 binary system. Quite clearly the preferred orientation of the host discotic nematic phase played an unexpected role in the transfer of chirality from the host molecule to the bulk of the liquid-crystalline phase.

It is interesting to contrast the nature of the dependence of helical twisting power  $[(pc)^{-1}]$  on temperature of compound **5a** in a series of pentaynes (**12** and **13**<sup>26</sup>) and hexayne (**11**) discotic nematic hosts, formulated into binary mixtures of comparable compositions (2.98–3.19 wt% of compound **5a**), this is shown in Fig. 9. The plot clearly shows that for these mixtures, the pentayne–hexayne system (2.98 wt% **5a** in **11**) shows considerably higher twisting powers at all temperatures (ranging from *ca.* 30 to 45 mm<sup>-1</sup> wt%<sup>-1</sup>) than the pentayne–pentayne (2.99 wt% **5a** in **12**) and pentayne–twin pentayne (3.19 wt% **5a** in **13**) systems. It is also immediately apparent that the pentayne–pentayne and pentayne–twin-pentayne lines are closely related in appearance, this is believed to reflect the similarity of both systems twist elastic constants (K<sub>2</sub>).

It is also clear that the pentaynes **5a** and **5b** have helical twisting powers which are at least comparable to the previously reported helical twisting powers values for cellobiose derivatives in discotic nematic host  $11^7$  and are certainly far higher than for other chiral pentaynes in discotic nematic host  $13.^8$ 

<sup>&</sup>lt;sup>‡</sup> It is worth noting that preliminary experiments using trimethylsilyl chloride as a surface alignment agent for the lens and glass plate, appears to markedly improve the quality of the concentric disclination lines. See also reference 8.

Table 2 Composition and thermodynamic properties of chiral discotic nematic mixtures of compounds 5a and 5b in hexayne host discotic nematic compound 11

| mixture | absolute<br>configuration |                  | transition temperatures/°C <sup>a</sup> |                      |                           |                                     |
|---------|---------------------------|------------------|---|----------------------|---------------------------|-------------------------------------|
|         |                           | wt% <sup>b</sup> | mp–Iso                                  | Iso–N <sub>D</sub> * | N <sub>D</sub> *-recryst. | helical twist<br>sense <sup>c</sup> |
| g       | (R,R,R,R,R)               | 1.17             | 60.5                                    | 82.6                 | 39.0                      | LH                                  |
| ĥ       | (R,R,R,R,R)               | 1.85             | 60.6                                    | 81.2                 | 39.0                      | LH                                  |
| i       | (R,R,R,R,R)               | 2.98             | 60.3                                    | 79.7                 | 39.4                      | LH                                  |
| i       | (S, S, S, S, S)           | 1.15             | 60.1                                    | 82.9                 | 39.9                      | RH                                  |
| k       | (S,S,S,S,S)               | 1.79             | 60.9                                    | 81.7                 | 40.1                      | RH                                  |
| 1       | (S, S, S, S, S, S)        | 3.00             | 60.6                                    | 79.2                 | 38.9                      | RH                                  |

<sup>a</sup> Transition temperatures recorded at heating and cooling rates of 5 deg min<sup>-1</sup>. <sup>b</sup> wt% of dopant (R,R,R,R,R) **5a** or (S,S,S,S) **5b** in the host undecyloxy[hexakis(4-nonylphenylethynyl)]benzene (11).

<sup>c</sup> Determined by optical microscopy on a binary mixture of dopants 5a and 5b in hexakis(4-nonylphenylethynyl)benzene (11).



Fig. 7 Temperature dependence of the reciprocal pitch length of mixtures of dopants 5a and 5b in the discotic nematic host hexakis(4nonylphenylethynyl)benzene (11) (Key: filled symbols refer to compound 5b  $\blacksquare = 1.17$  wt%,  $\bullet = 1.85$  wt% and  $\bullet = 2.98$  wt%. Unfilled symbols refer to compound 5a,  $\Box = 1.15$  wt%,  $\bigcirc = 1.79$  wt% and  $\dot{\diamond} = 3.00 \text{ wt\%.}$ 



Fig. 8 Temperature dependence of helical twisting power of mixtures of dopants 5a and 5b in the discotic nematic host hexakis(4nonylphenylethynyl)benzene (12) (Key: filled symbols refer to compound 5b,  $\blacksquare = 1.17$  wt%,  $\bullet = 1.85$  wt% and  $\bullet = 2.98$  wt%. Unfilled symbols refer to compound 5a,  $\Box = 1.15$  wt%,  $\bigcirc = 1.79$  wt% and  $\diamond = 3.00 \text{ wt}\%$ .)

## Selective reflection measurements

The temperature dependent selective reflection and angular dependent spectra were recorded using a 20.9 wt% sample of 5a in the hexayne discotic nematic host 11; the latter's negative dielectric anisotropy and preference for homeotropic surface alignment aiding the formation of a planar aligned chiral discotic nematic phase on the application of an electric field.<sup>7,8</sup> It was found that on the application of an applied electric field, that a field induced phase transition eliminates the blue phases, resulting in a direct Iso-N<sub>D</sub>\* transition at 45 °C. Plots of the temperature dependence of the selectively reflected



Fig. 9 Dependence of compound 5a's helical twisting power on the nature of discotic nematic host [(O) 3.19 wt% 5a in twin pentayne 13; (⊞) 2.99 wt% 5a in pentayne 12 and (●) 2.98 wt% 5a in hexayne 11]

component of incident white light and angular dependence are shown in Figs 10 and 11 respectively.

However, to accurately estimate the pitch lengths at such temperatures it is necessary to determine the average refractive index  $(\tilde{n})$  of the discotic nematic phase. The average refractive index of both the isotropic liquid  $(\tilde{n}_{iso})$  and the chiral discotic nematic phase  $(\tilde{n}_{ND}*)$  are normally given by the relationships shown in eqns. (2) and (3)

$$\tilde{n}_{\rm iso} = \sqrt{1/3(n_{\rm ||}^2 + 2n_{\perp}^2)}$$
(2)

$$\tilde{n}_{\rm ND*} = \sqrt{1/2(n_{\rm H}^2 + n_{\perp}^2)} \tag{3}$$

However, both  $\tilde{n}_{iso}$  and  $\tilde{n}_{ND^*}$  were determined for a series of temperatures by using least squares numerical analysis to



Fig. 10 Temperature dependence of selectively reflected wavelengths of light of a 20.9 wt% binary mixture of 5a in hexayne host 11 (cell thickness 4.32 µm, 160 V peak to peak, 50 kHz)



Fig. 11 Angular dependence of selective reflection of a 20.9 wt% binary mixture of 5a in host hexayne 11 (T 42.5 °C, cell thickness  $4.05 \mu\text{m}$ , 130 V peak to peak, 40 kHz)

calculate the ratio of optical path length of an empty cell (assuming  $n_{arr} = 1$ ),  $d_0$ , to that of a cell filled with the sample,  $d_{ND*}$ , by observing the wavelength maxima of interference patterns of incident light in transmissive mode [eqn. (4)]

Average refractive index, 
$$\tilde{n} = d_0/d_{\rm ND*}$$
 (4)

The refractive index was found to vary slightly on cooling from the isotropic liquid, this is shown in Fig. 12, the refractive indices of the isotropic liquid and chiral discotic nematic phase ranging from ca. 1.71 to 1.74.

The values of average refractive index calculated from the above data for particular temperatures were then used to calculate estimated pitch lengths for the selective reflection maxima recorded in Fig. 10. The maxima of the selective reflection peaks were determined at each temperature at half the height of the peak, the results are shown as reciprocal of pitch in Fig. 13. The reciprocal pitch length varies in an approximately linear manner, corresponding to a pitch length range of *ca.* 0.36 to 0.35  $\mu$ m, although two high temperature points fall away probably because of the proximity to the clearing point transition.

## **Discussion and conclusions**

One of the first questions which needs to be asked, is whether it is possible to apply the well known selection rules relating helical twist sense to absolute configuration, parity and the electronic nature of the substituents at the chiral centre to discotic systems.<sup>27,28</sup> Using these empirical rules it is possible to classify compounds **5a** and **5b** in the following manner {abs. config, parity [odd or even (n+1)], electronic influence (+ I or -I) and helical twist sense}; **5a**: (R), o, + I, left handed helix; **5b**: (S), o, + I, right handed helix. Both assignments have



Fig. 12 Temperature dependence of average refractive index of a 20.8 wt% binary mixture of 5a in hexayne discotic host 11 (recorded in a 4.37  $\mu$ m cell at 120 V peak to peak and 10 kHz)



Fig. 13 Temperature dependence of reciprocal pitch length  $(p^{-1})$  for a 20.9 wt% binary mixture of compound 5a in hexayne host 11

been confirmed to be true by experiment. Digressing slightly, these rules also appear to apply to the other chiral discotic nematics (S)-2-methylbutyloxy[pentakis(4-butylphenylethynyl)]benzene  $(1)^8$  and (S,S,S,S,S)-hexadecyloxy{pentakis [4-(3,7-dimethyloctyloxy)phenylethynyl]} benzene (**4**):<sup>8</sup> which may be classified as: 1; (S), e, +I, left handed helix; 4; (S), o, +I, right handed helix. However, the rule fails for (S)-3,7-dimethyloctyloxy [pentakis (4-pentylphenylethynyl)] benzene (2)<sup>8</sup> which by applying the rules is classified as: 3; (S), o, +I, right handed helix. This compound is reported as having a left handed helix, a result for which no obvious explanation can be made. In summary, although the rules are essentially empirical and developed from calamitic systems which frequently possess only one chiral centre, it may be concluded that they may be employed usefully for discotic systems with care and subsequent confirmation.

Comparing the twisting powers of compounds 5a and 5b with compounds 1, 2 and 3, is conveniently achieved by comparing the pc values ( $\mu m$  wt%; the smaller the value of pc the greater the twisting power), reveals that 5a in the hexayne host 11, has a pc value of ca. 8  $\mu m$  wt%. This corresponds to a far higher helical twisting power than previously reported pentayne compounds 1, 2 and 3, which have pc values of 2500, 830 and 38  $\mu m$  wt% in the pure compound respectively.

The materials 5a and 5b are unique for two reasons, firstly, they are only the second known examples of compounds which are capable of generating discotic blue phases (BP<sub>D</sub>) in a suitable discotic nematic host system.<sup>7</sup> The observed discotic blue phases have been tentatively assigned as BP<sub>D</sub>III and BP<sub>D</sub>II. And secondly, they are enantiomeric, which in principle will enable the precise formulation of racemic (R,S)- and enantiomeric (R)- or (S)- mixtures which are essential in the study of phase diagrams of blue phases.<sup>29</sup> The use of such binary mixtures has enabled us to vary the chirality of the system without a change in the thermodynamic properties of the system (*i.e.* twist elastic constant,  $k_2$ ), and observe a linear relationship between the reciprocal pitch and concentration, pitch being measured by the modified Cano method at low concentration and selective reflection at high concentration.<sup>30</sup>

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