Novel glass-forming liquid crystals. III Helical sense and twisting power in chiral nematic systems

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Novel glass-forming liquid crystals. III Helical sense and twisting power in chiral nematic systems

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Based on nematic and chiral precursors comprising of acetylenic, phenyl, naphthyl and terminal cyano groups in conjugation and cyclohexane as the central core, a series of novel nematic and chiral nematic glass-forming liquid crystals with a $T_g \geqslant 60°C$ were synthesized for an investigation of handedness and helical twisting power, HTP, as functions of chemical structure. Three chiral building blocks with a single asymmetric carbon centre were employed: (S)-(−)-1-phenylethanol, (S)-(−)-α-methyl-2-naphthalenemethanol, and (S)-(−)-1-phenylethylamine, were all found to yield a left-handed cholesteric mesophase. With reference to (S)-(−)-1-phenylethanol, the HTP value was found to be nearly doubled in the presence of a strong anchoring plane furnished by a naphthyl group surrounding the asymmetric carbon centre, but reduced by one third in the presence of intermolecular hydrogen bonding through the amide group. All these observations were properly accounted for by a molecular interaction model of a steric nature while allowing for hydrogen bonding. Consistent with previous observations on naturally occurring (−)-cholesterol, (+)-estrone was found to give a left-handed cholesteric mesophase and an HTP value a quarter of that of (S)-(−)-1-phenylethanol under otherwise identical structural settings, both remaining unaccounted for from a molecular point of view. The cyclohexane ring to which chiral as well as nematic precursors are attached was found to improve miscibility with cyclohexane-based nematic hosts and to elevate the T_g of the blends with an improved morphological stability but a very modest increase in HTP, all in comparison to chiral precursors as the dopant. The optical elements prepared on a single glass substrate and between a pair of substrates using the presently reported materials showed broad selective wavelength reflection bands with a monodomain feature characterized by pronounced side band oscillations.

1. Introduction

Glass forming, low molar mass liquid crystals (GLMLCs) with a glass transition temperature, T_g, above the ambient represent a new emerging class of advanced organic materials showing a potential for being readily processed into uniformly thin films because of their low melt and solution viscosities. In recent years, these materials have been seriously considered for linear and non-optical applications, such as efficient light polarization [1], optical information storage [2,3], optical communication and information processing [4], and frequency conversion [5–7]. Normally, low molar mass organics tend to crystallize over time, giving rise to a polycrystalline character that is detrimental to contact at an interface and is undesirable because of light scattering from grain boundaries. Intensive research in the recent past [8–16] has produced numerous GLMLCs with a varying degree of morphological stability as assessed by the tendency of the quenched glass to crystallize upon heating beyond its T_g. Nonetheless, fundamental understanding of vitrification in low molar mass organics in general is still lacking at present. It remains challenging to design molecular systems representing a subtle balance between encouraging liquid crystalline mesomorphism and discouraging solid crystallinity, resulting in GLMLCs with a relative high T_g. At the same time, the ability to molecularly engineer functional materials is critical to the development of advanced optical technologies. In a recent series of publications [17, 18], we have reported the design and synthesis of GLMLCs based on a novel molecular design concept in which mesogenic groups are attached to excluded-volume moieties as a way to depress crystallization. In addition, morphological stability [19] and its dependence on stereochemistry [20] have been quantitatively evaluated through the measurement of spherulitic growth rate as a function of temperature between T_g and

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T_m, the crystalline melting point. It was demonstrated that GLMLCs can be made as morphologically stable as typical slowly crystallizing polymers, for example, polystyrene. Hence, the proposed concept validated with relevant experiments is potentially capable of generating morphologically stable, glass forming functional materials for a wide variety of applications.

The main theme of the present study is on chiral nematic (i.e. cholesteric) liquid crystals; we are particularly interested in the issues of helical sense (i.e. handedness), as defined by the sense of the reflected circularly polarized light [21], and helical twisting power, HTP. From the structure point of view, handedness is defined by the sense in which the director of the nematic sublayer is twisted helically into a supramolecular structure, and HTP is a measure of the effectiveness of chiral twisting along the helical axis [22]. For all the theoretical [23, 24] and empirical [25, 27] research committed over the past several decades, fundamental understanding of handedness and HTP in both low molar mass and polymeric systems still leaves much to be desired. Specifically, it is difficult to relate physical parameters invoked in theories to real chemical systems. As an alternative approach, chiral/nematic molecular interaction models of a steric origin have been constructed to elucidate handedness in low molar mass [28, 29] as well as side chain polymeric systems [30]. In what follows, an attempt will be made to furnish new insights into the chiral nematic mesomorphism via the synthesis and characterization of novel GLMLCs that also hold promise for practical applications. The experimentally determined handedness and HTP will be interpreted using a molecular interaction model in which hydrogen bonding is permitted to dictate the spatial accessibility around an asymmetric carbon centre.

2. Experimental

2.1. Reagents and chemicals

Bis(triphenylphosphine)palladium(II) chloride (98 per cent), 2-(4-bromophenoxy)ethanol (98 per cent), 3,4-dihydro-$2H$-pyran (97 per cent), (trimethylsilyl)acetylene (98 per cent), pyridinium toluene-4-sulphonate, PPTS 98 per cent), diethyl azodicarboxylate, DEAD (> 90 per cent), triphenylphosphine, PPh$_3$ (99 per cent), (S)-(−)-1-phenylethanol (99 per cent), (R)-(+)-1-phenylethylamine (98 per cent), (S)-(−)-1-phenylethylamine (98 per cent) (R)-(+)-α-methyl-2-naphthalenemethanol (98 per cent), (+)-estrone (99 per cent), 4-bromobenzonitrile (99 per cent), 6-methoxy-2-naphthonitrile (98 per cent), caesium carbonate (99·9 per cent), 6-bromo-2-naphthol (97 per cent), copper(I) iodide (99·999 per cent), thionyl chloride (99 per cent), trifluoromethanesulphonic anhydride, 4-iodobenzoyl chloride (97 per cent), 2-iodoethanol (99 per cent), 4-(dimethylamino)pyridine, DMAP (99 per

cent), 1,3,5-cyclohexanetricarboxylic acid (95 per cent, cis-isomer), and silica gel (40 µm flash chromatography packing), were all used as received from the Aldrich Chemical Company. The solvent THF (100·0 per cent, J. T. Baker) was dried by refluxing over sodium spheres in the presence of benzophenone, and methylene chloride (> 99·5 per cent, J. T. Baker) was dried by distillation over calcium hydride. Cholesteric cyclosiloxane samples with a selective reflection wavelength in the visible region were used as received from Consortium für Elektrochemische Industrie GmbH in Germany. The cis-isomer of 1,3,5-cyclohexanetricarboxylic acid was readily converted into the trans-isomer following the published procedures [31].

2.2. Synthesis of glass forming low molar mass molecular materials

The chemical structures of model compounds designed for the present study are as depicted in figure 1. The procedures for the synthesis of compounds (N-1), (C-1), (C-2), (C-7) and (C-8) have been described previously

(N-1)
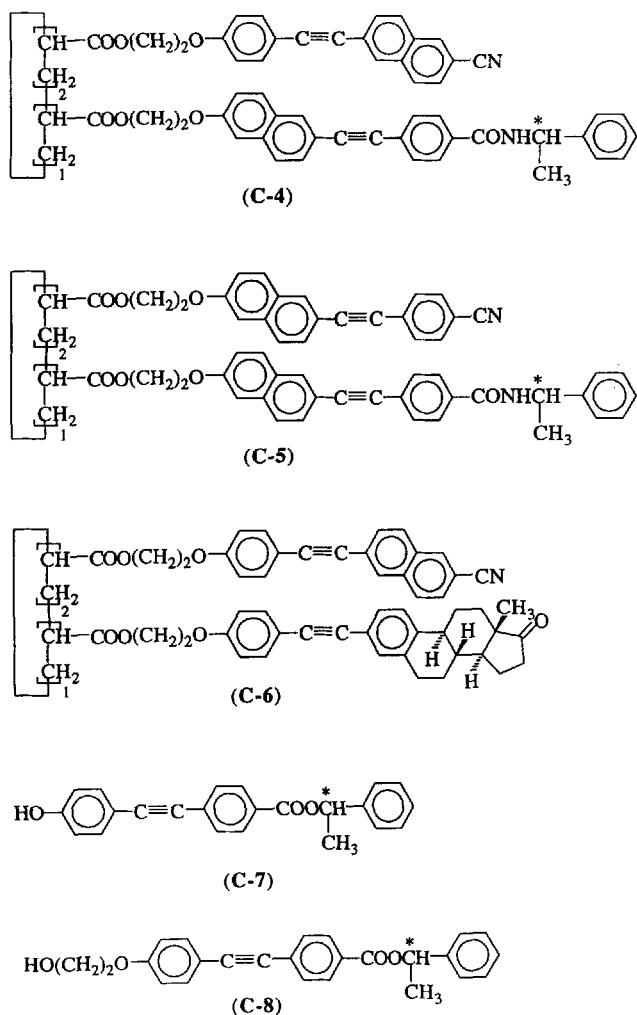

(N-2)

(C-1)

(C-2)

(C-3)
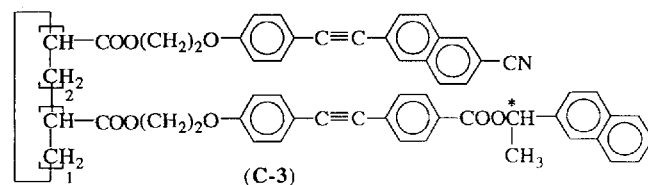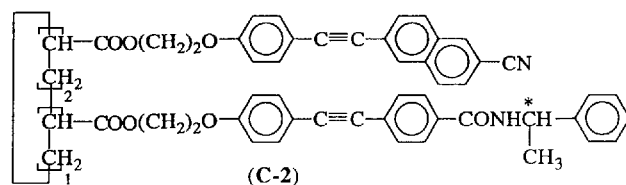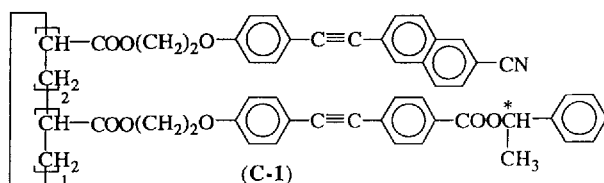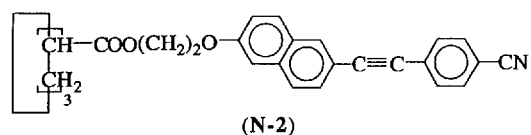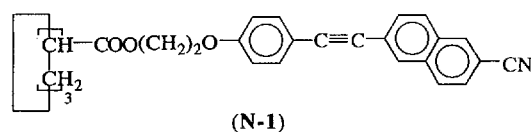
Figure 1. Chemical structures of the nematic and chiral compounds synthesized for the present investigations of handedness and helical twisting power in glass forming low molar mass chiral nematics.

[18] and will not be repeated here, but the results of elemental analysis and proton NMR spectral data essential to the elucidation of the chemical structures will be presented in what follows for all the compounds synthesized for the present study. Schemes 1 to 5 were devised for the preparation of (N-2) and (C-3) to (C-6) following the experimental procedures as described below.

2.2.1. Compound (N-2)

(N-2-1): A solution of iodoethanol (30·0 g, 0·175 mol) and dihydropyran (31·8 ml, 0·349 mol) in anhydrous methylene chloride (50 ml) containing pyridinium toluene-4-sulphonate, PPTS, (4·39 g, 17·5 mmol) was stirred at room temperature for 5 h. The solution was diluted with methylene chloride (50 ml) and washed several times with half-saturated brine to remove the catalyst. Upon evaporation of the solvent *in vacuo*,

vacuum distillation (2 mmHg at 60°C) was accomplished to yield compound (N-2-1) (31·8 g, 71 per cent).

(N-2-2): To a solution containing 6-bromo-2-naphthol (10 g, 44·8 mmol) and caesium carbonate (17·5 g, 53·8 mmol) in dimethylformamide (20 ml) was added dropwise compound (N-2-1) (13·8 g, 53·8 mmol) at 80°C. The reaction mixture was allowed to stirred at 80°C for 4 h before dilution with methylene chloride (400 ml). The solution was washed with water and dried over anhydrous MgSO₄. The solvent was removed *in vacuo*, and the crude product was recrystallized from ethanol to give compound (N-2-2) (13·3 g, 85 per cent).

(N-2-3): Dimethylformamide (40 ml) and diethylamine (20 ml) were added successfully into a mixture of compound (N-2-2) (10·0 g, 28·5 mmol), (trimethyl-silyl)acetylene (8·1 ml, 57·0 mmol), bis(triphenylphosphine)palladium dichloride (0·4 g, 0·57 mmol), and copper (I) iodide (0·21 g, 1·14 mmol). The mixture was stirred for 3 h at room temperature under argon. The solution was then diluted with water for extraction with methylene chloride (3 × 200 ml). The combined extracts were washed with water and then dried over anhydrous MgSO₄. The solvent was then evaporated *in vacuo*. The residue was purified by flash chromatography with methylene chloride as the eluent to yield an oily intermediate. This intermediate and anhydrous potassium carbonate (1·0 g) were dissolved in 300 ml methanol, and the solution stirred for 2 h. The solvent was then evaporated off *in vacuo*, and the residue was dissolved in 200 ml methylene chloride followed by washing with water and drying over anhydrous MgSO₄. Another oily intermediate was obtained after evaporation of the solvent. To this new intermediate were successively added tetrahydrofuran (30 ml), water (15 ml) and acetic acid (60 ml). After stirring at 60°C for 24 h, the mixture was diluted with methylene chloride (400 ml), washed with water and dried over anhydrous MgSO₄. The solvent was removed *in vacuo*, and the residue was purified by flash chromatography with methylene chloride/acetone (20 : 1) as the eluent to obtain compound (N-2-3) (4·3 g, 71 per cent).

(N-2-4): To a mixture of compound (N-2-3) (1·5 g, 7·1 mmol), 4-bromobenzonitrile (1·3 g, 7·1 mmol), bis(triphenylphosphine)palladium dichloride (0·1 g, 0·14 mmol) and copper(I) iodide (0·05 g, 0·28 mmol) were added dimethylformamide (10 ml) and diethylamine (5 ml) successively. The mixture was stirred for 3 h at room temperature under argon. The solution was diluted with water for extraction with methylene chloride (3 × 200 ml). The combined extracts were washed with water and then dried over anhydrous MgSO₄. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography with methylene chloride as the eluent to yield compound (N-2-4) (1·3 g, 59 per cent).

(N-2) to a stirred solution containing compound (N-2-4)
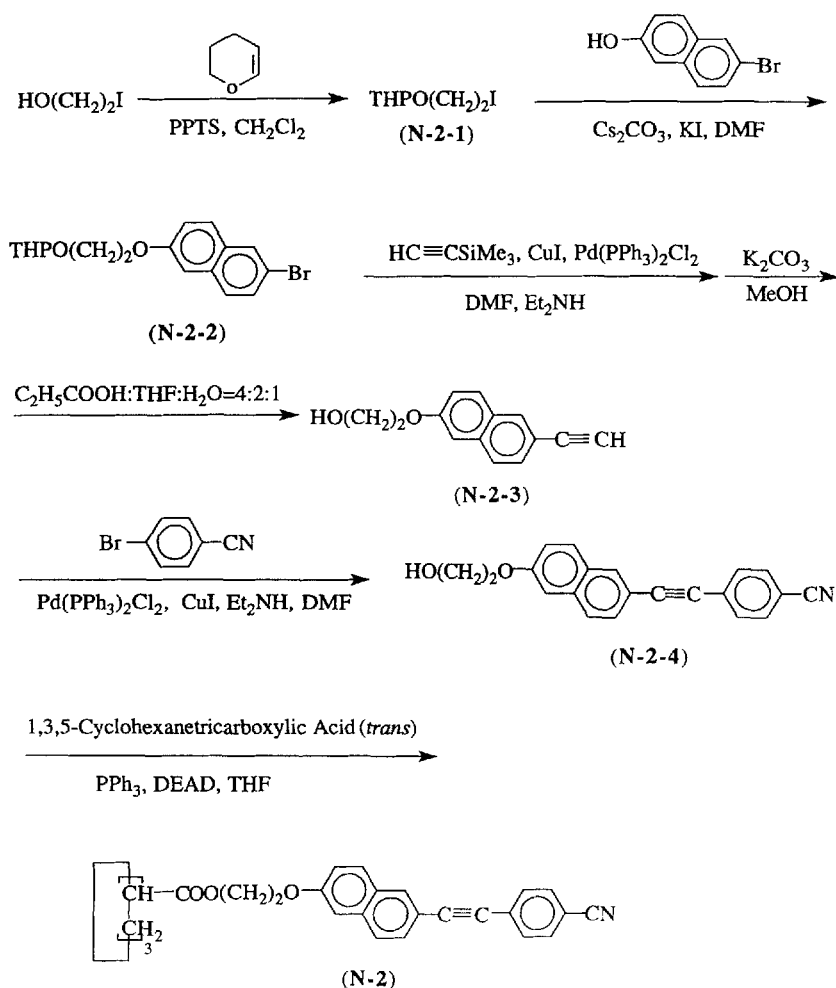
Scheme 1.   Synthetic routes for compound (N-2).

(0·5 g,   1·60 mmol),   triphenylphosphine   (0·419 g,
1·60 mmol), and 1,3,5-cyclohexanetricarboxylic acid
(trans-isomer, 0·105 g, 0·48 mmol) in dry tetrahydrofuran
(10 ml) was added dropwise a solution of diethyl azodicar-
boxylate (0·196 ml, 1·60 mmol) in dry tetrahydrofuran
(10 ml) under an argon atmosphere. The reaction mixture
was stirred for 3 h before evaporating off the solvent in
vacuo. The residue was purified by flash chromatography
with methylene chloride/acetone (40 : 1) as the eluent. The
crude product was dissolved in methylene chloride (2 ml)
and precipitated from methanol to give compound (N-2)
(0·49 g, 91 per cent). Proton NMR (CDCl₃, δ): 1·61–3·10
(m, 9 H, –CH₂CH– on cyclohexane ring), 4·24–4·32 (m,
6 H, –CH₂O–), 4·48–4·57 (m, 6 H, –CO₂CH₂–), 7·10–8·00
(m, 30 H, aromatic). Elemental analysis for C₇₂H₅₁O₉N₃
(1102·21): Calculated C, 78·45, H, 4·66, N, 3·81; Found
C, 77·85, H, 4·95, N, 3·78 per cent.

2.2.2. Compound (C-2)
    Proton NMR (CDCl₃, δ): 1·55–3·02 (m, 9 H, –CH₂CH–

on cyclohexane ring; 3 H, –NHCH(CH₃)–), 4·21 (m, 6 H,
–CH₂O–), 4·48–4·54 (m, 6 H, –CO₂CH₂–), 5·39 (m, 1 H,
NHCH(CH₃)–), 6·39 (d, 1 H, –NHCH(CH₃)–), 6·91–8·20
(m, 33 H, aromatic). Elemental analysis for C₇₆H₅₉O₁₀N₃
(1174·31): Calculated C, 77·73, H, 5·06, N, 3·58; Found
C, 77·21, H, 5·24, N, 3·59 per cent.

2.2.3. Compound (C-3)
    (C-3-1): To a solution of 4-iodobenzoyl chloride (1·6 g,
6·1 mmol) and (R)-(+)-α-methyl-2-naphthalenemeth-
anol (1·0 g, 5·81 mmol) in tetrahydrofuran (20 ml) was
added triethylamine (1·6 ml, 11·6 mmol) at room tempera-
ture. The mixture was stirred for 4 h before dilution with
methylene chloride (200 ml). The solution was washed
with water and then dried over anhydrous MgSO₄. After
removing the solvent in vacuo, the solid product (C-3-1)
emerged from the residual viscous liquid (2·3 g, 98 per
cent).
    (C-3-2): Dimethylformamide (30 ml) and diethylamine
(15 ml) were added successively to a mixture of 2-(4-bro-
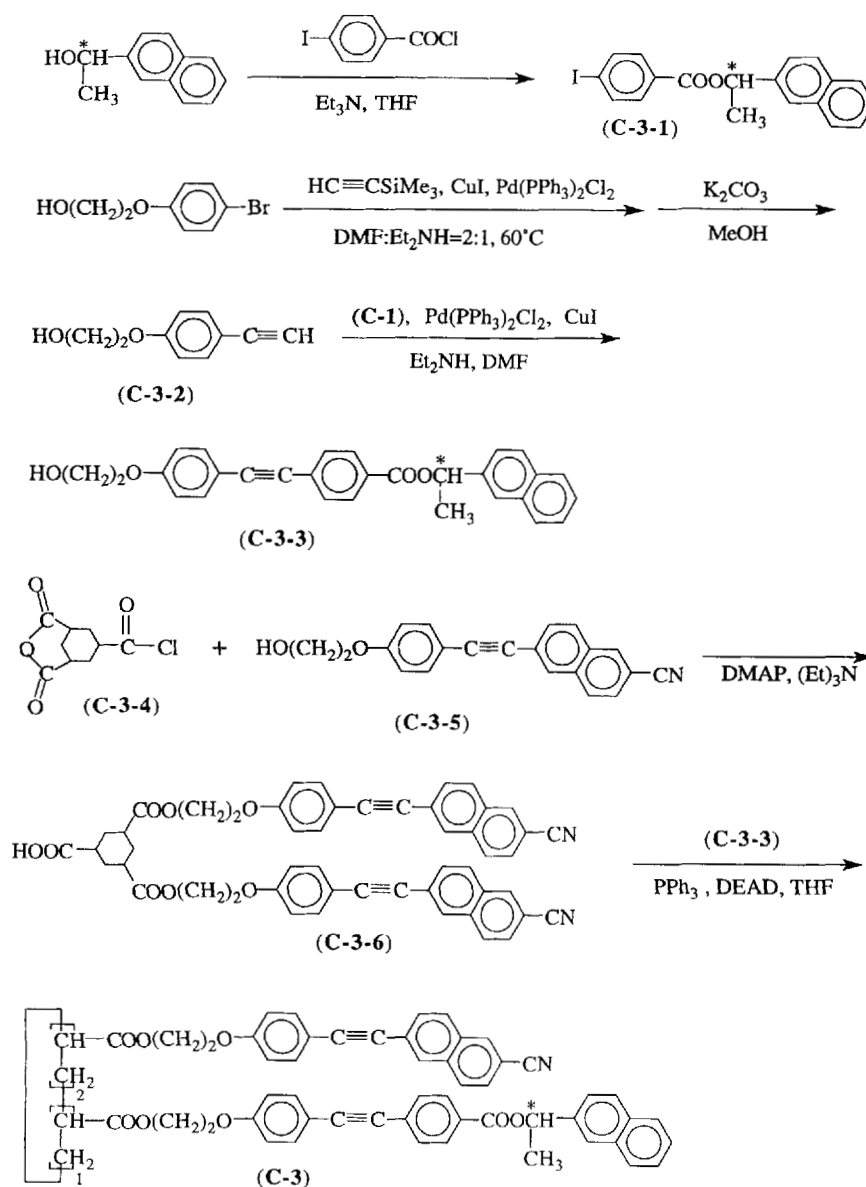
Scheme 2. Synthetic routes for compound (**C-3**).

mophenoxy)ethanol (5·75 g, 26·6 mmol), (trimethylsilyl)acetylene (7·49 g, 53·0 mmol), bis(triphenylphosphine)palladium (II) chloride (0·73 g, 0·53 mmol) and copper(I) iodide (0·20 g, 1·06 mmol). The mixture 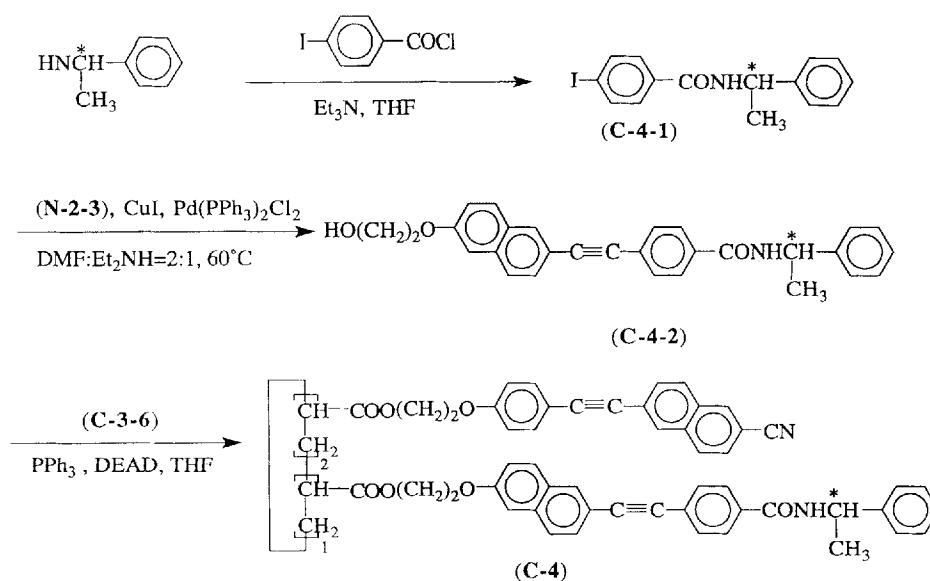was stirred for 4 h at room temperature under argon. The solution was diluted with water for extraction with methylene chloride (3 × 100 ml). The combined extracts were washed with an aqueous solution of sodium chloride and then dried over anhydrous MgSO₄.The solvent was evaporated off *in vacuo*, and the residue was purified by flash chromatography with methylene chloride as the eluent to yield an intermediate. This intermediate and anhydrous potassium carbonate (1·0 g) were dissolved in

200 ml methanol, and the solution was stirred for 2 h. The solvent was then evaporated off *in vacuo*, and the residue was dissolved in 200 ml methylene chloride following by washing with water and drying over anhydrous MgSO₄. After evaporating off the solvent *in vacuo*, the crude product was recrystallized from ethanol to produce compound (**C-3-2**) (3·1 g, 72 per cent).

(**C-3-3**): To a mixture of compound (**C-3-1**) (2·3 g, 5·72 mmol), (**C-3-2**) (0·93 g, 5·72 mmol), bis(triphenylphosphine)palladium (II) chloride (0·08 g, 0·114 mmol) and copper(I) iodide (0·04 g, 0·228 mmol) were added dimethylformamide (10 ml) and diethylamine (5 ml) successively. The mixture was stirred for 4 h at

Scheme 3.   Synthetic routes for compound (C-4).

room temperature under an argon atmosphere. The solution was diluted with water for extraction with methylene chloride (3 × 80 ml). The combined extracts were washed with an aqueous solution of sodium chloride and then dried over anhydrous MgSO₄. The solvent was evaporated off *in vacuo*, and the residue was purified by flash chromatography with methylene chloride as the eluent to yield compound (C-3-3) (1·57 g, 63 per cent).

(C-3-4), (C-3-5), and (C-3-6): See reference [18] for experimental procedures.

(C-3): To a stirred solution containing compound (C-3-3) (0·27 g, 0·62 mmol), compound (C-3-6) (0·5 g, 0·62 mmol), and triphenylphosphine (0·16 g, 0·62 mmol) in dry tetrahydrofuran (10 ml) was added dropwise a solution of diethyl azodicarboxylate (0·076 ml, 0·62 mmol) in dry tetrahydrofuran (10 ml) under an argon atmosphere. The reaction mixture was stirred for 3 h before evaporating off the solvent *in vacuo*. The solid residue was purified by flash chromatography with methylene chloride/acetone (40:1) as the eluent. The crude product was dissolved in methylene chloride (2 ml) for precipitation from methanol to give compound (C-3) (0·55 g, 72 per cent). Proton NMR (CDCl₃, δ): 1·55–3·01 (m, 9 H, –CH_2CH– on cyclohexane ring; 3 H, –CO₂CH(CH_3)–), 4·20 (m, 6 H, –CH_2O), 4·46–4·52 (m, 6 H, –CO₂CH_2–), 6·32 (m, 1 H, –CO₂CH(CH₃)–), 6·90–8·20 (m, 35 H, aromatic). Elemental analysis for C₈₀H₆₀O₁₁N₂ (1225·36): Calculated C, 78·41, H, 4·94, N, 2·29; Found C, 78·21, H, 5·18, N, 2·28 per cent.
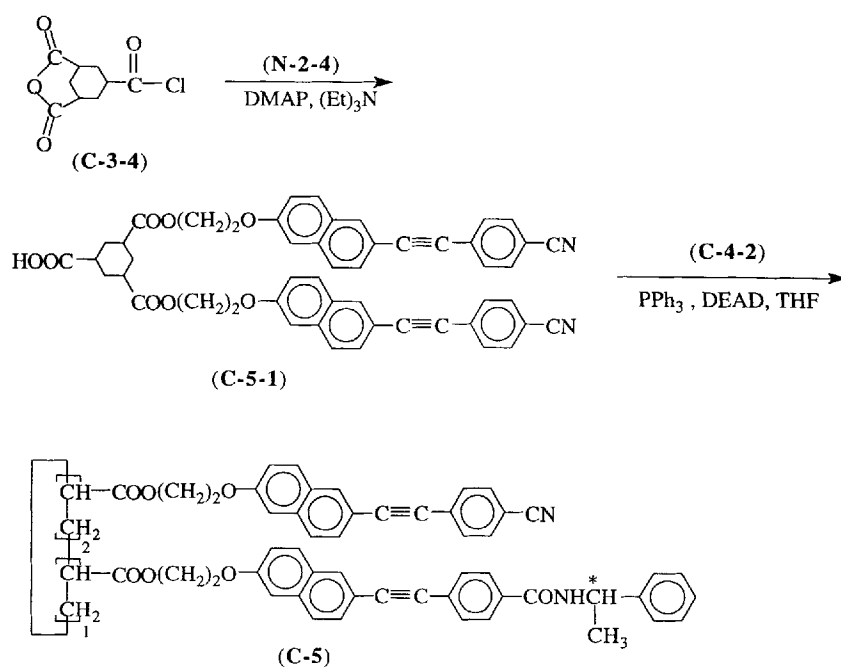
2.2.4. *Compound* (C-4)

(C-4-1): To a solution of 4-iodobenzoyl chloride (10 g, 37·53 mmol) and (R)-(+)-1-phenylethylamine (4·55 g,

37·53 mmol) in tetrahydrofuran (40 ml) was added triethylamine (3·8 ml, 37·53 mmol) at room temperature. The mixture was stirred for 4 h before dilution with methylene chloride (500 ml). The solution was washed with water and then dried over anhydrous MgSO₄. After removing the solvent *in vacuo*, the crude product was recrystallized from methylene chloride to obtain needle-like crystals of compound (C-4-1) (11·0 g, 83 per cent).

(C-4-2): Dimethylformamide (10 ml) and diethylamine (5 ml) were added successively to a mixture comprising compound (N-2-3) (1·5 g, 7·08 mmol), (C-4-1) (2·98 g, 8·49 mmol), bis(triphenylphosphine)palladium(II) chloride (0·1 g, 0·14 mmol), and copper(I) iodide (0·05 g, 0·28 mmol). The mixture was stirred for 4 h at room temperature under argon. The solution was diluted with water for extraction with methylene chloride (3 × 100 ml). The combined extracts were washed with an aqueous solution of sodium chloride and then dried over anhydrous MgSO₄. The solvent was evaporated *in vacuo*, and the residue was purified by flash chromatography with methylene chloride/acetone (20:1) as the eluent. The crude product was recrystallized from ethanol/acetone (5:1) to produce compound (C-4-2) (1·57 g, 51 per cent).

(C-4): To a stirred solution containing compound (C-4-2) (0·13 g, 0·30 mmol), compound (C-3-6) (0·22 g, 0·27 mmol), and triphenylphosphine (0·08 g, 0·30 mmol) in dry tetrahydrofuran (10 ml) was added dropwise a solution of diethyl azodicarboxylate (0·037 ml, 0·30 mmol) in dry tetrahydrofuran (5 ml) under an argon atmosphere. The reaction mixture was stirred for 3 h before evaporating off the solvent *in vacuo*. The solid residue was purified by flash chromatography with methylene chloride/acetone (40:1) as the eluent. The

Scheme 4. Synthetic routes for compound (C-5).

2.2.5. *Compound* (C-5)

(C-5-1): Dry triethylamine (0·267 ml, 1·92 mmol) was added to a solution of compound (C-3-4) (0·21 g, 0·96 mmol), compound (N-2-4) (0·6 g, 1·92 mmol) and 4-(dimethylamino)pyridine (DMAP) (0·012 g, 0·096 mmol) in dry THF (15 ml). Upon removing the solvent *in vacuo*, the solid residue was purified by flash chromatography with methylene chloride/methanol (9:1) as the eluent to give compound (C-5-1) (0·47 g, 61 per cent).
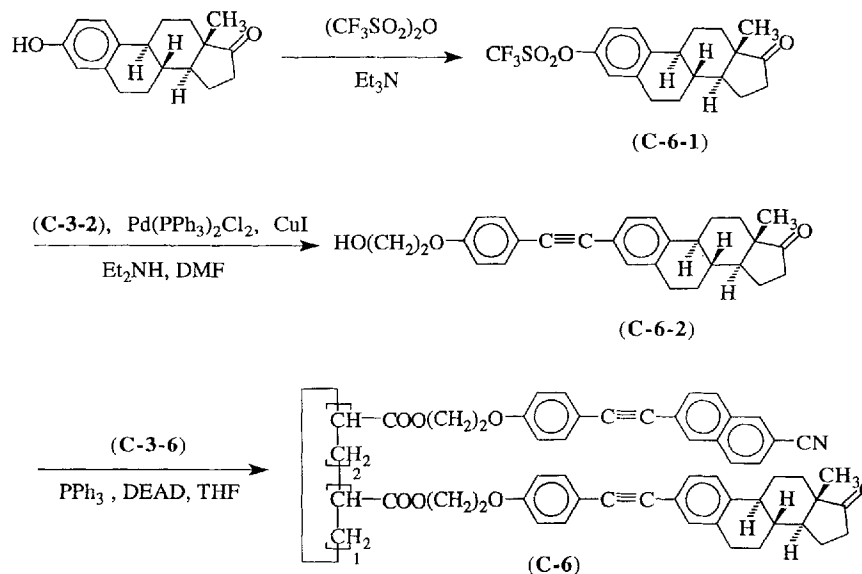
(C-5): To a stirred solution containing compound (C-5-1) (0·32 g, 0·40 mmol), compound (C-4-2) (0·21 g, 0·48 mmol), and triphenylphosphine (0·13 g, 0·48 mmol) in dry tetrahydrofuran (10 ml) was added dropwise a solution of diethyl azodicarboxylate (0·058 ml, 0·48 mmol) in dry tetrahydrofuran (5 ml) under an argon atmosphere. The reaction mixture was stirred for 3 h before evaporating off the solvent *in vacuo*. The solid residue was purified by flash chromatography with

crude product was dissolved in methylene chloride (2 ml) for precipitation from methanol to give compound (C-4) (0·28 g, 83 per cent). Proton NMR (CDCl₃, δ): 1·55–3·01 (m, 9 H, –CH_2CH– on cyclohexane ring; 3 H, – NHCH(CH_3)–), 4·18–4·31 (m, 6 H, –CH_2 O–), 4·48–4·55 (m, 6 H, –CO₂CH_2–), 5·40 (m, 1 H, –NHCH(CH₃)–), 6·42 (d, 1 H, –NHCH(CH₃)–), 6·93–8·20 (m, 35 H, aromatic). Elemental analysis for $C_{80}H_{61}O_{10}N_3$ (1224·37): Calculated C, 78·48, H, 5·02, N, 3·43; Found C, 78·24, H, 5·27, N, 3·42 per cent.

methylene chloride/acetone (40:1) as the eluent. The crude product was dissolved in methylene chloride (2 ml) for precipitation from methanol to give compound (C-5) (0·41 g, 84 per cent). Proton NMR (CDCl₃, δ): 1·55–3·01 (m, 9 H, –CH_2CH– on cyclohexane ring; 3 H, –NHCH(CH_3)–), 4·26–4·33 (m, 6 H, –CH_2O–), 4·46–4·56 (m, 6 H, –CO₂CH_2–), 5·39 (m, 1 H, –NHCH(CH₃)–), 6·40 (d, 1 H, –NHCH(CH₃)–), 7·08–8·00 (m, 35 H, aromatic). Elemental analysis for $C_{80}H_{61}O_{10}N_3$ (1224·37): Calculated C, 78·48, H, 5·02, N, 3·43; Found C, 78·17, H, 5·29, N, 3·44 per cent.

2.2.6. *Compound* (C-6)

(C-6-1): To a stirred solution of (+)-estrone (5·0 g, 18·49 mmol) in dry pyridine was added dropwise trifluoromethanesulphonic anhydride (3·73 ml, 22·19 mmol) at 0°C under an argon atmosphere. The mixture was stirred at room temperature for 4 h before pouring into water for extraction with methylene chloride (200 ml). The extract was washed with water and dried over anhydrous MgSO₄. The solvent was removed *in vacuo*, and the residue was recrystallized from ethanol to give compound (C-6-1) (6·4 g, 86 per cent).

(C-6-2): Dimethylformamide (30 ml) and diethylamine (15 ml) were added successively to a mixture of compound (C-3-2) (0·55 g, 3·40 mmol), (C-6-1) (1·5 g, 3·73 mmol), bis(triphenylphosphine)palladium(II) chloride (0·05 g, 0·075 mmol) and copper(I) iodide (0·03 g, 0·15 mmol). The mixture was stirred for 4 h at room temperature under argon. The solution was diluted with water for extraction

Scheme 5.   Synthetic routes for compound (C-6).

with methylene chloride (3 × 80 ml). The combined extracts were washed with aqueous solution of sodium chloride and then dried over anhydrous MgSO$_4$. The solvent was evaporated off *in vacuo*, and the residue was purified by flash chromatography with methylene chloride/acetone (20:1) as the eluent. The crude product was recrystallized from ethanol to produce compound (C-6-2) (0·33 g, 24 per cent).

(C-6): To a stirred solution containing compound (C-6-2) (0·269 g, 0·65 mmol), compound (C-3-6) (0·5 g, 0·62 mmol), and triphenylphosphine (0·16 g, 0·65 mmol) in dry tetrahydrofuran (10 ml) was added dropwise a solution of diethyl azodicarboxylate (0·076 ml, 0·65 mmol) in dry tetrahydrofuran (5 ml) under an argon atmosphere. The reaction mixture was stirred for 3 h before evaporating off the solvent *in vacuo*, and the solid residue was purified by flash chromatography with methylene chloride/acetone (40:1) as the eluent. The crude product was dissolved in methylene chloride (2 ml) for precipitation from methanol to give compound (C-6) (0·65 g, 87 per cent). Proton NMR (CDCl$_3$, δ): 1·48–3·01 (m, 27 H, –CH_2CH–, –(CH_3)–, –CH_2CH_2–, –CH– on cyclohexane and estrone rings), 4·20 (m, 6 H, –CH_2O–), 4·44–4·52 (m, 6 H, –CO$_2$CH_2–), 6·87–8·22 (m, 27 H, aromatic). Elemental analysis for C$_{79}$H$_{66}$O$_{10}$N$_2$ (1203·39): Calculated C, 78·84, H, 5·53, N, 2·33; Found C, 78·54, H, 5·73, N, 2·31 per cent.

2.2.7. *Compound* (C-7)

Proton NMR (CDCl$_3$, δ): 1·72 (d, 3 H, –NHCH(CH_3)–), 6·18 (m, 1 H, –CO$_2$CH(CH$_3$)–), 6·86–8·09 (m, 13 H, aromatic). Elemental analysis for C$_{23}$H$_{18}$O$_3$ (342·39):

Calculated C, 80·68, H, 5·30, N, 0·00; Found C, 80·55, H, 5·54, N, 0·00 per cent.

2.2.8. *Compound* (C-8)

Proton NMR (CDCl$_3$, δ): 17·2 (d, 3 H, –NHCH(CH_3)–), 4·00 (m, 2 H, –CH_2O–), 4·14 (m, 2 H, –CO$_2$CH_2–), 6·15 (m, 1 H, –CO$_2$CH(CH$_3$)–), 6·88–8·07 (m, 13 H, aromatic). Elemental analysis for C$_{25}$H$_{22}$O$_4$ (386·44): Calculated C, 77·70, H, 5·74, N, 0·00; Found C, 77·67, H, 5·89, N, 0·00 per cent.

2.3. *Characterization techniques*

A Hitachi high performance liquid chromatography, HPLC, system comprising of an L-2000 metering pump and an L-4200 UV–Vis absorbance detector equipped with an LiChrosorb® column (RP-18, 10 μm) was employed to determine the number of components and purity of the products. The purity levels of all final products were found to be better than 99 per cent based on HPLC analysis. Chemical structures of glassy nematics and chiral nematics were elucidated with elemental analysis (performed by Oneida Research Services, Inc. in Whitesboro, New York), the FTIR (Nicolet 20 SXC) and proton NMR (QE-300, GE) spectroscopic techniques. The chiral mol fractions in the chiral nematic systems were determined via an integration of appropriate proton NMR signals (typically 1 wt% in CDCl$_3$). Thermal transition temperatures were determined by differential scanning calorimetry, DSC (Perkin–Elmer DSC-7 or a nitrogen purge of 50 cc/min) with mesophase textures identified under a polarizing optical microscope (Leitz Orthoplan-Pol) equipped with a hot stage (FP82, Mettler) plus a central

processor (FP80, Mettler). For the determination of selective reflection wavelength, a spectrophotometer (Perkin–Elmer Lambda 9) was employed to gather a UV–Vis–NIR spectrum at room temperature on an optical element containing a chiral nematic material with a thickness on the order of 10 μm sandwiched between a pair of glass substrates (Corning 7059 near zero alkali baria alumina borosilicate glass with a refractive index of 1·53 at 589·3 nm). The optical element was first heated above the· clearing temperature of the material followed by shearing to induce alignment and subsequently annealed at 95 per cent of its clearing temperature for 24 h. An Abbé refractometer (Bellingham and Stanley, Model 60/HR), with a sodium lamp ($\lambda = 589\cdot3$ nm), was employed to measure the average refractive indices of compounds (N-1), (N-2), and (C-1) to (C-8) at room temperature. Typically, a sample was sandwiched between a high index glass plate (SF$_6$, $n = 1\cdot81$) and a low index glass plate (CaF$_2$, $n = 1\cdot43$). The random orientation of mesogenic molecules in the cell was verified by rotation under a polarized optical microscope. The cholesteric sense (i.e. handedness) was determined by comparing to commercially available low molar mass nematic and chiral compounds mixed at the molar ratio that gives a desired λ_R value with known handedness. For example, CB-15 and E7 available from BDH Chemicals Ltd. were blended to give right-handed chiral nematics.

3. Results and discussion

The thermotropic and optical properties of all the nematic and chiral compounds plus the blends between them are summarized in the table. All systems appeared to be morphologically stable in that no crystallization was detectable on heating across T_g and up to T_c with the only exception of (C-8), which was found to undergo a glass transition at 10°C and crystallization at 76°C followed by melting at 94°C on second and subsequent heating scans at a standard rate of 20°C min^{-1}. The observed values of n_{avg} and λ_R as a function of chiral mol fraction, x, defined as the number of moles of chiral side arms divided by the total number of nematic and chiral side arms, were employed to calculate HTP using the formula $HTP = n_{avg}[d\lambda_R{}^{-1}/dx]$ as x approaches 0. Note that nematic hosts (N-1) and (N-2) doped with chiral compounds (C-1) to (C-6) yield glassy chiral nematic blends with T_gs all above 60°C and T_cs decreasing from those of nematic hosts (both above 190°C) with an increasing x value. Chiral dopants (C-7) and (C-8) were included to assess the effect of the cyclohexane ring on the HTP, and their plasticizing effect, i.e. depression of T_g, was anticipated in view of their relatively low molecular weights. In what follows, let us make use of the data compiled in the table to gain new insights into the two key issues governing cholesteric mesomorphism, namely, the

handedness and HTP as functions of chemical structure.

As indicated earlier in the Introduction, an interpretation of the handedness and HTP in terms of chemical structure in thermotropic chiral nematics has remained as challenging at the present time for all the theoretical and experimental investigations performed during the past several decades. Both theories and experiments have revealed the intricate nature of these two parameters as related to chemical structure. For instance, handedness appears to be a consequence of the interaction between light and matter; a subtle change in chemical structure may lead to an inversion of handedness. Moreover, the magnitude of the HTP appears to be a consequence of chiral/nematic molecular interactions; for a given chiral dopant, the HTP value may vary significantly with the nematic host. Nevertheless, evidence abounds which suggests that within a limited scope, handedness can be properly accounted for through geometric considerations. The essence of this approach is that the cholesteric mesophase is composed of a stack of nematic sublayers twisted by chiral moieties. Specifically, the sense of chiral twisting appears to be explicable from the perspective of steric hindrance as well as intermolecular hydrogen bonding, where applicable, under the constraint of retaining the energetically favoured face-to-face arrangement of linearly extended, planar molecules.

Let us accept these premises and proceed to depict in figure 2 (*a*) a chiral pendant group with a single asymmetric carbon centre as encountered in the present work. Besides the hydrogen atom projecting away from the viewer, three groups surrounding the asymmetric carbon centre can be identified: quasiplanar rigid core (consisting of a benzene and a naphthalene ring connected by an acetylenic group), anchoring plane (consisting of a benzene or a naphthalene ring), and a methyl group which performs chiral twisting. For an absolute configuration S characterizing the chiral building blocks: (S)-(−)-1-phenylethanol, (S)-(−)-α-methyl-2-naphthalenemethanol, and (S)-(−)-1-phenylethylamine, the chiral/nematic steric interaction as shown in figure 2 (*b*) is predicted to give rise to a left-handed (LH) cholesteric mesophase, as defined by the handedness of the reflected circularly polarized light [21]. Conversely, an absolute configuration R should give rise to a right-handed (RH) cholesteric mesophase. As demonstrated in the table, these predictions are borne out in all the chiral nematic systems with the exception of (+)-estrone containing four asymmetric carbon centres, which was found to yield a LH (C-6)/(N-1) blend, as reported previously for chiral nematic systems derived from naturally occurring (−)-cholesterol [32]. Unlike the chiral side arms comprising of a single asymmetric carbon centre, the handedness of the cholesteric mesophase presented by steroidal compounds remains baffling from a molecular perspective.

Thermotropic and optical properties of nematic compounds (N-1) and (N-2) as well as their induced cholesteric systems.

System	$x^{\dagger}$	λ_R/nm	T_g/°C	T_c/°C	ΔC_p/W g^{-1}	ΔH_c/J g^{-1}	n_{avg}	Absolute configuration of chiral precursor	Handedness of cholesteric mesophase	10^{-4} HTP/nm^{-1}
N-1	0·00	na	60	197	0·13	2·72	1·70			
N-2	0·00	na	65	191	0·12	2·46	1·71			
C-1/N-1	0·33	‡	61	77	0·16	0·34	1·68	S	LH	203 ± 3
	0·16	508	62	135	0·15	1·00				
	0·12	713	62	155	0·15	1·51				
	0·08	1024	62	169	0·15	1·36				
C-2/N-1	0·33	§	76	na	0·14	na	1·68	S	LH	133 ± 2
	0·20	610	68	124	0·11	0·87				
	0·14	930	61	140	0·12	2·32				
	0·09	1450	62	162	0·11	1·25				
C-3/N-1	0·33	§	70	na	0·12	na	1·68	R	RH	387 ± 2
	0·08	545	60	164	0·10	2·29				
	0·06	720	60	171	0·11	1·97				
	0·04	1070	61	182	0·11	2·19				
C-4/N-1	0·33	‡	77	106	0·11	0·40	1·68	R	RH	125 ± 3
	0·20	650	68	137	0·11	0·78				
	0·14	980	63	153	0·11	1·06				
	0·09	1650	63	176	0·11	1·42				
C-5/N-2	0·33	‡	81	106	0·12	0·47	1·68	R	RH	137 ± 3
	0·20	580	70	132	0·11	1·30				
	0·14	880	68	147	0·11	1·20				
	0·09	1525	66	163	0·14	0·69				
C-6/N-1	0·33	930	79	182	0·13	1·84	1·68	‖	LH	53 ± 2
	0·25	1225	72	179	0·12	1·68				
	0·20	1770	70	189	0·16	1·02				
C-7/N-1	1·00	§	28	na	0·20	na	1·67	S	LH	171 ± 3
	0·16	633	50	128	0·12	1·03				
	0·12	800	51	149	0·13	1·62				
	0·08	1160	52	163	0·13	1·21				
C-8/N-1	1·00	§	10¶	na	0·19	na	1·65	S	LH	189 ± 1
	0·16	553	51	144	0·13	1·29				
	0·12	733	47	150	0·13	1·38				
	0·08	1145	50	164	0·13	1·55				

† x is defined as the number of chiral side arms divided by the total number of nematic and chiral side arms in the blend.
‡ Showing cholesteric oily streaks under polarizing optical microscope, but no selective reflection peaks available for determination of λ_R because of the close proximity of T_c to T_g.
§ Non-mesogenic.
¶ DSC heating scan shows a crystallization and melting at 76 and 94°C, respectively, in addition to the glass transition.
‖ Unspecified.

Based on the molecular interaction model depicted in figure 2, a further attempt was made to rationalize the difference in the calculated the HTP values between (C-1), (C-2) and (C-3) doped into the same nematic host (N-1). First, the HTP value of (C-2) is about 66 per cent that of (C-1), which can be accounted for in terms of intermolecular hydrogen bonding present in (C-2). To aid in the visualization of helical twisting, figure 3 was prepared for the same absolute configuration S as in figure 2 at both

asymmetric carbon centres while allowing for intermolecular hydrogen bonding through the two amide groups. Although left-handedness appears to prevail, the favourable face-to-face alignment of the top nematic layer with both the rigid core and the anchoring plane in the underlying chiral side arm, as shown in figure 2 (b), is diminished by the methyl group projecting up from the plane as shown in figure 3. Therefore, the HTP depicted in figure 3 is expected to be less than that shown in
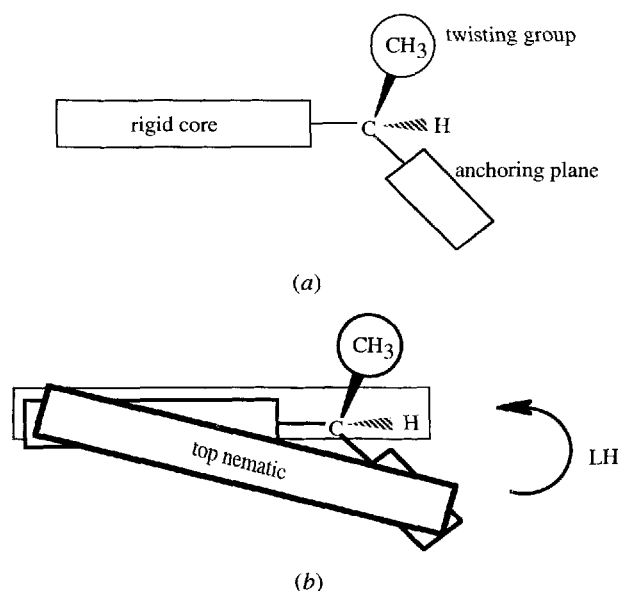
Figure 2. Chiral/nematic molecular interaction model of a steric origin: (a) Chiral side arm with an absolute configuration *S* at the asymmetric carbon centre; (b) Helical twisting of the top nematic sublayer by the methyl group protruding from an asymmetric carbon centre with an absolute configuration *S*.
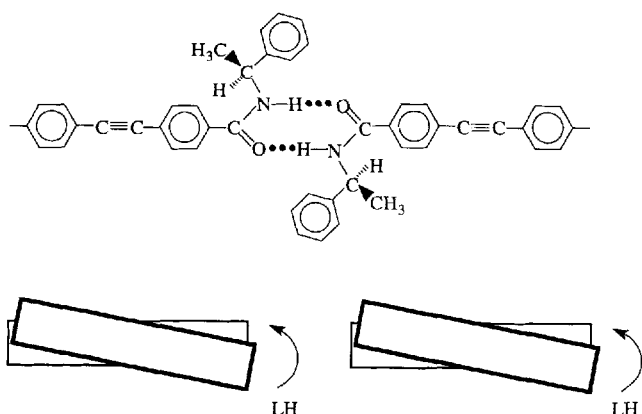

Figure 3. Intermolecular hydrogen bonding through the amide group visualized to reduce the extent of helical twisting in comparison to what is depicted in figure 2 (b).

figure 2 (b) simply because the top nematic layer has to stay clear of the methyl group. On the other hand, the HTP value of (C-3) is near double that of (C-1), presumably because of the stronger anchoring plane furnished by the naphthalene ring compared to the benzene ring, thereby forcing the chiral twisting methyl group to protrude farther into the space otherwise accessible to the top nematic layer (see figure 2). Specifically, the relatively freely rotating benzene ring allows the protruding methyl group to stay more clear of the top nematic layer, thereby diminishing the HTP of (C-1) in comparison to (C-3) for the same

nematic (N-1). Still puzzling is the observation that (+)-estrone yields the least HTP of all given its relatively bulky molecular volume. On the other hand, (+)-estrone shows the least effect on depressing T_cs of all the chiral nematic systems from those of the nematic hosts $(T_{c,n})$, as revealed in terms of $T_c/T_{c,n}$ plotted as a function of x in figure 4.

Besides chiral nematic cyclohexane derivatives, (C-1) to (C-6), precursors (C-7) and (C-8) to (C-1) were also explored as chiral dopants in nematic host (N-1). It is noted that the HTP values of (C-7) and (C-8) are comparable to, although somewhat less than, that of (C-1) in the nematic host (N-1). This observation suggests that the cyclohexane ring present in (C-1) does not appear to significantly enhance the HTP, which is consistent with our previous observation that the HTP values in side chain polymers do not always exceed those of low molar mass analogues [33]. Additionally, it can be argued that the hydrogen bonding sites in molecules of (C-7) and (C-8) are so far
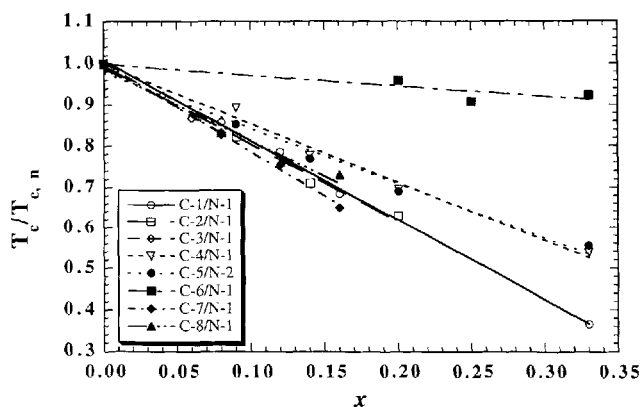

Figure 4. The effect of chiral mol fraction, x, on depressing the clearing temperature of chiral nematics, T_c, from that of nematic hosts, $T_{c,n}$.
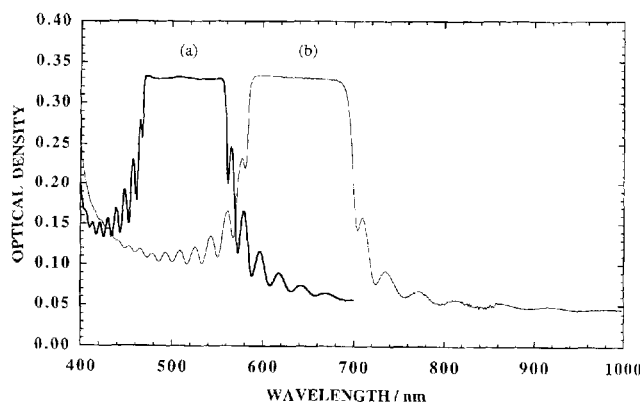

Figure 5. Selective wavelength reflection bands of chiral nematics: (a) C-1/N-1 on a single glass substrate; (b) C-7/N-1 sandwiched between a pair of glass substrates, both with a chiral mol fraction $x = 0.16$.

removed from the asymmetric carbon centres that it does not appear to diminish the HTP as observed in (**C-2**). Above all, one should not overlook the merits of a cyclohexane ring as part of the chiral dopant, including improved miscibility with the nematic hosts (**N-1**) and (**N-2**) and improved morphological stability of the glassy blends against crystallization. As (**C-2**), (**C-4**), and (**C-5**) were blended with (**N-1**) and (**N-2**), it was discovered that the HTP values are rather insensitive to the placement of the benzene and naphthalene rings relative to the acetylenic group in the rigid cores present in both the nematic and chiral side arms.

Finally, to illustrate the ease of processing low molar mass chiral nematics, a single substrate and a sandwiched optical element were prepared using the (**C-1**)/(**N-1**) and (**C-7**)/(**N-1**) blends, respectively, both with a chiral mole fraction $x = 16$. The selective reflection bands gathered from UV–Vis scans using an unpolarized light source at normal incidence are reproduced in figure 5 to illustrate the quality of the finished optical elements. Note the pronounced side band oscillations indicative of the monodomain character [34] of the cholestric mesophase achieved with the presently reported chiral nematic systems. Furthermore, the bandwidths observed in figure 5 turns out to be about twice as much as those achieved with commercially available chiral nematic cyclosiloxanes, whose chemical structures and properties are as shown in figure 23 of reference [9], at the same centre wavelength (λ_R), which is expected of the high optical birefringence value of the 1-phenyl-2-(6-cyanonaphth-2-yl)ethyne group [35] as the nematogen in (**N-1**), as opposed to biphenyl as the nematiogen in cyclosiloxanes.

4. Summary

Nematic and chiral precursors containing acetylenic, phenyl, and naphthyl groups in conjugation were attached to 1,3,5,-cyclohexanetricarboxylic acid as an excluded-volume core to produce glass forming chiral nematic liquid crystals with a $T_g \geqslant 60^{\circ}$C. Two key parameters governing cholesteric mesophase formation were experimentally determined, and the following observations have emerged from the present study:

(i) In the given nematic hosts, chiral building blocks (*S*)-(−)-1-phenylethanol, (*S*)-(−)-α-methyl-2-naphthalenemethanol, and (*S*)-(−)-1-phenylethylamine were found to give a left-handed cholesteric mesophase with an inversion of absolute configuration leading to the opposite handedness.

(ii) The HTP presented by (*S*)-(−)-α-methyl-2-naphthalenemethanol was found to nearly double that by (*S*)-(−)-1-phenylethanol presumably because of a restricted rotation around the C–C

single bond imposed by the naphthalene ring in comparison to the benzene ring.

(iii) Intermolecular hydrogen bonding present in (*S*)-(−)-1-phenylethylamine through the amide group was found to reduce its HTP by one third compared to that of (*S*)-(−)-1-phenylethanol.

(iv) A molecular interaction model allowing for hydrogen bonding was shown to be capable of qualitatively accounting for all the above observations.

(v) (+)-Estrone was found to give a left-handed cholesteric mesophase and an HTP of about a quarter of that of (*S*)-(−)-1-phenylethanol, consistent with naturally occurring (−)-cholesterol as previously reported but remaining unaccounted for from a molecular standpoint.

(vi) The cyclohexane ring was found to play an essential role in promoting glass formation and morphological stability in chiral nematic blends, although it did not appear to contribute to a significant increase in the HTP.

(vii) Optical elements prepared with the presently reported chiral nematic liquid crystals on a single glass substrate and between a pair of substrates showed broad selective wavelength reflection bands accompanied by pronounced side band oscillations characteristic of a monodomain cholesteric mesophase, suggesting a relative ease of alignment in thin films.

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