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Synthesis and characterisation of nematic liquid crystals containing a *trans*-decalin ring

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The synthesis and mesomorphic behaviour of a series of liquid crystals incorporating a *trans*-decalin ring and two aromatic rings linked by esters are reported. Structures of the new compounds were confirmed by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. A single crystal of compound **18** was prepared to confirm the *trans*-conformation of the decalin ring. Liquid crystalline properties were investigated by differential scanning calorimetry and polarising optical microscopy. All of the synthesised compounds except **17e** are found to show only an enantiotropic nematic phase over a wide temperature range.

Keywords: *trans*-decalin liquid crystal; nematic synthesis

1. Introduction

Increasing interest in electro-optical displays requires thermotropic nematic liquid crystals (*1*). Since no single liquid crystal (LC) compound can meet the diverse demands of display modes, LC mixture materials are often widely used in LC displays (LCDs). Thus, LC mixtures are required to have high clearing points and broad thermal range nematic phases. It has been reported that the replacement of aromatic rings with decalin rings often has advantageous effects on giving nematic phases with high crystal–nematic (Cr–N) transition temperatures, broad temperature range nematic phases and low viscosity (*2–5*).

The fluorine atom is generally used in the design of LC molecules to obtain many interesting effects, such as stronger dipole moment, lower viscosity and higher chemical stability (*6–8*). This kind of fluorine-containing LC materials has been widely used in nematic mixtures for TFT LCDs. Thus, incorporating a fluorine atom into *trans*-decalin-containing molecules could result in some novel LCs to meet the need of LC mixtures for application in LCDs with high clearing point, wide thermal range of nematic phase and appropriate melting point. To our knowledge, little literature and few patents have been reported in the field of fluorinated LCs with decalin rings. In addition, the conformation of decalin has only been deduced approximately by ^{1}H NMR analysis in the reported literature (*9–13*).

As a continuation of our work on decalin-based systems, in this paper we describe the synthesis, thermal and optical properties of a new kind of LC incorporating *trans*-decalin and two aromatic rings with ester linkages. The target compounds are divided into two groups. One group comprises non-fluorine-containing LCs (series **11** and **12**), which possess an alkoxy chain terminal substituent on an aromatic core and an alkyl chain terminal substituent on a *trans*-decalin ring. The other group of LCs (series **16** and **17**) contains fluorine atom or trifluoromethyl substituents instead of the corresponding alkoxy chains.

The aim of our work was to improve the synthetic method of preparing the *trans*-decalin ring and to investigate the mesomorphic properties of this kind of LC containing 6-equatorial-alkyl-*trans*-decalin, bound to two aromatic rings by an ester linkage.

2. Experimental

Synthesis

The synthetic method for the preparation of the *trans*-decalin (**5**) is shown in Scheme 1. Reaction of pyrrolidine enamines (**2**) with methyl vinyl ketone in refluxed benzene gave the key 6-alkyl-$\Delta^{1,9}$-2-octalone (**3**) in high yields (*14–16*). Synthesis of *trans*-6-alkyl decalin-2-ol (**5**) was accomplished by the reduction by $LiAlH_4$ of 6-alkyl-2-decalone (**4**), which was prepared from 6-alkyl-$\Delta^{1,9}$-2-octalone by a Birch reduction with lithium in ethylenediamine (EDA) and further oxidation with Jones reagent (*17–22*). As the Birch reduction of α,β-unsaturated ketones (**3**) is known to be highly stereoselective, mainly giving the thermodynamically stable configurations of equatorial substituents and the *trans* ring connection in the decalin system (*23–26*), the geometry of the reduction products (**4**) is deduced to be *trans*-decalin with an equatorial arrangement of substituent in the 6-position and the cyclohexane rings in *trans*-decalin

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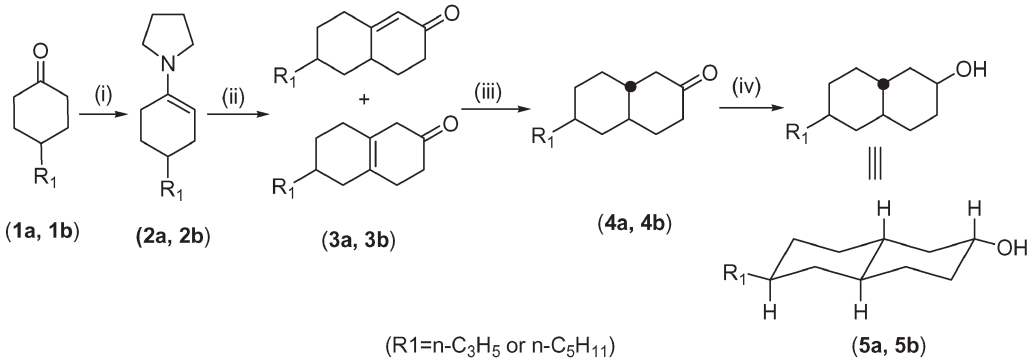


Scheme 1. Synthesis of *trans*-decalin **5**. Reagents and conditions: (i) pyrrolidine, C_6H_6; (ii) methyl vinyl ketone, C_6H_6; (iii) (a) Li, $NH_2CH_2CH_2NH_2$, (b) CrO_3, H_2SO_4; (iv) $LiAlH_4$, THF.

are fused by two equatorial bonds. ^1H and ^{13}C NMR spectra studies of **4** also confirmed its pure *trans*-configuration. Further reduction of 2-decalone (**4a**, **4b**) with $NaBH_4$ or $LiAlH_4$ stereoselectively gave mainly the alcohol with equatorial arrangement, according to the ^1H NMR spectra analysis. However, using $LiAlH_4$ reductive reagent gave a much higher stereoselectivity (over 90%) in the reduction of decalone, whereas lower stereoselectivity (below 75%) was obtained when $NaBH_4$ was used (*27–29*). Thus, $LiAlH_4$ was used in the reduction of the decalone and the ratios of equatorial:axial configurations of *trans*-6-alkyldecalin-2-ol and *cis*-6-alkyldecalin-2-ol in **5a** and **5b** were found be 91:9 and 90:10, respectively.

The *trans*-6-alkyldecalin-2-ol was reacted with the fluorine-containing or non-fluorine-containing mesogenic benzoates to form the target esters (**11a**–**11d**, **12a**–**12d**, **16a**–**16d** and **17a**–**17d**), based on the modified literature procedures shown in Scheme 2. Stereochemically pure target compounds, obtained by repeated recrystallisation from EtOH, were characterised via detailed ^1H NMR studies and also by X-ray diffraction (XRD).

In order to produce the necessary acids to synthesise the final compounds (**11a**–**11d**, **12a**–**12d**), methyl hydroxybenzoate (**6**) was alkylated using various 1-bromoalkanes and potassium carbonate in a Williamson ether synthesis to produce the methyl esters (**7a**–**7d**) (*30*). Then, 4-alkoxybenzoic acids (**8a**–**8d**) were obtained by saponification of the methyl esters (**7a**–**7d**). Esterification using *N*,*N*-dicyclohexylcarbodiimide (DCC), *N*,*N*-dimethylaminopyridine (DMAP) with 4-hydroxybenzaldehyde gave the corresponding benzaldehydes (**9a**–**9d**) (*31*), which were further oxidised to corresponding benzoic acids (**10a**–**10d**) by Jones reagent without purification. The last step involved the esterification of **10a**–**10d** with 6-equatorial-alkyl-*trans*-decalin-2-ol (**5a**, **5b**), giving the non-fluorine-containing target compounds (**11a**–**11d** and **12a**–**12d**). The fluorine-containing model esters were synthesised in a similar manner. Detailed analysis of ^1H, ^{13}C and ^{19}F NMR spectra confirmed the stereochemical purity of the prepared compounds.

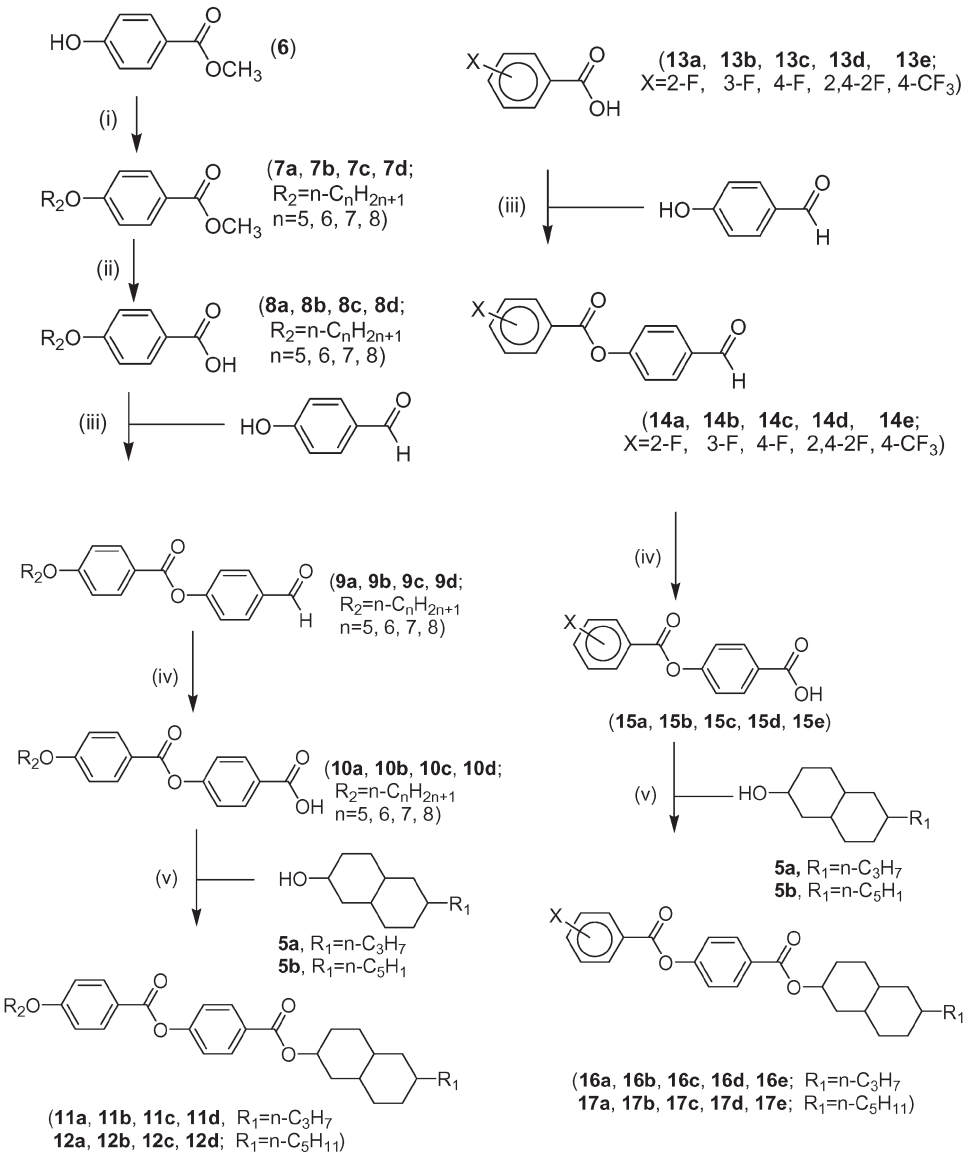
Characterisation of materials

IR spectra were recorded on an Avatar 370 FT-IR spectrometer. ^1H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AV-500 spectrometer using tetramethylsilane (TMS) or $CFCl_3$ as an internal reference. Elemental analyses were performed using an Elemental Vario EL III instrument. The transition temperatures and associated enthalpy changes were determined by differential scanning calorimetry (DSC, Net2stch STA409PC, Germany) using a scanning rate of $5^\circ C\,min^{-1}$. The mesophases were identified according to the textures observed under an Orthlux-II POLBK polarising optical microscope. Single-crystal XRD was performed with graphite-monochromatic Mo K_α radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex CCD diffractometer at $T = 273(2)$ K. The structures were solved by direct method with SHELXS-97 program and refined by full matrix least-squares on F2 with SHELXL-97 program. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated position.

Synthesis of intermediates and products

*General procedure for synthesis of 6-alkyl-α,β-unsaturated 2-decalone (**3**).*

4-Alkylcyclohexanone (0.2 mmol) and pyrrolidine (0.3 mmol) in 100 ml benzene were placed in a flask with a constant water separator. The mixture was refluxed and the water, which distilled out with the refluxing benzene, was removed at intervals. After refluxing for about 24 h, the mixture was evaporated



Scheme 2. Synthesis of target esters. Reagents and conditions: (i) K_2CO_3, $CH_3CH_2COCH_3$; (ii) NaOH, H_2O, CH_3CH_2OH; (iii) DCC, DMAP, CH_2Cl_2; (iv) CrO_3, H_2SO_4; (v) DCC, DMAP, CH_2Cl_2.

under reduced pressure to remove the superfluous pyrrolidine and benzene. The residue was further mixed with methyl vinyl ketone (0.24 mmol) and anhydrous benzene and refluxed for 24 h. A buffer solution made up of acetic acid (25 ml), sodium acetate (18 g) and water (25 ml) was then added and the refluxing was continued for another 4 h. The organic layer was separated and washed with 10% hydrochloric acid and aqueous sodium bicarbonate. After removal of benzene, the residue was distilled under reduced pressure. The distillation was fractionated by column chromatography to afford the product **3**.

For 6-propyl-4,4*a*,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (**3a**), yield 58%. ^{1}H NMR ($CDCl_3$): δ 0.80–2.60 (m, 19H), 5.83 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 14.3, 20.0, 29.3, 33.2, 35.3, 36.5, 36.6, 37.6, 38.8, 41.0, 124.2, 167.4, 200.1.

For 6-pentyl-4,4*a*,5,6,7,8-hexahydro naphthalen-2(3*H*)-one (**3b**), yield 62%. ^{1}H NMR ($CDCl_3$): δ 0.80–2.50 (m, 23H), 5.85 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 14.3, 22.9, 26.8, 33.1, 33.4, 35.3, 36.2, 36.9, 37.3, 38.9, 39.2, 41.0, 124.2, 167.4, 200.3.

*General procedure for synthesis of 6-alkyl-2-decalone (**4**).*

A mixture of EDA (150 ml) and lithium wire (4 g, 0.12 ml) was stirred in a water-ice bath for 30 min. Then, a solution of α,β-enone **3** (0.1 mmol) in DME

(50 ml) was added dropwise. After stirring for another 2 h, the mixture was quenched by aqueous NH_4Cl, extracted by ether, dried with anhydrous $MgSO_4$ and the solvent was removed by an evaporator. The residue was dissolved in acetone and treated by Jones reagent and then with *i*-PrOH until the colour was discharged. After extraction by ether, the combined extract was removed by vacuum to give the crude product, which was further fractionated by column chromatography.

For 6-propyl-2-decalone (**4a**), yield 69%. ^{1}H NMR ($CDCl_3$): δ 0.61 (q, 1H, CH), 0.80–2.40 (m, 21H). ^{13}C NMR ($CDCl_3$): δ 14.4, 20.1, 32.4, 33.7, 34.2, 37.3, 39.5, 39.6, 41.5, 41.6, 43.5, 48.6, 212.0.

For 6-pentyl-2-decalone (**4b**), yield 73%. ^{1}H NMR ($CDCl_3$): δ 0.61 (q, 1H, CH), 0.80–2.40 (m, 25H). ^{13}C NMR ($CDCl_3$): δ 14.5, 22.9, 26.8, 32.9, 33.5, 33.7, 34.2, 37.5, 37.8, 39.5, 39.6, 41.5, 43.5, 49.2, 212.3.

General procedure for the synthesis of trans-*6-alkyldecalin-2-ol (**5**).*

To a solution of one equivalent of 6-alkyl-2-decalone in dried ether, 1.2 equivalent of $LiAlH_4$ was added gradually. After stirring at ambient temperature for 30 min, the mixture was quenched by water and extracted by ether. The extract was dried by anhydrous $MgSO_4$ and the solvent was removed by vacuum. Purification by column chromatography gave the product **5**.

For *trans*-6-propyldecalin-2-ol (**5a**), yield 95%. ^{1}H NMR ($CDCl_3$): δ 0.55 (q, 1H, CH), 0.80–2.00 (m, 21H), 3.59 (m, 1H, O*CH*). ^{13}C NMR ($CDCl_3$): δ 14.4, 22.0, 32.0, 33.0, 33.7, 35.7, 37.5, 39.8, 40.1, 41.2, 42.0, 42.9, 70.7.

For *trans*-6-pentyldecalin-2-ol (**5b**), yield 97%. ^{1}H NMR ($CDCl_3$): δ 0.55 (q, 1H, CH), 0.80–2.00 (m, 25H), 3.59 (m, 1H, OCH). ^{13}C NMR ($CDCl_3$): δ 14.3, 22.9, 26.8, 32.1, 32.3, 33.2, 33.7, 35.9, 37.5, 37.9, 40.2, 41.3, 42.1, 43.1, 71.0.

*General procedure for synthesis of 4-*n*-alkoxybenzoxybenzoic acid (**10a–10d**) and fluorinated benzoxybenzoic acid (**15a–15e**).*

A solution of one equivalent of the synthesised 4-*n*-alkoxybenzoic acid (*32*), 4-hydroxybenzaldehyde, DCC and DMAP in dichloromethane was stirred at room temperature for 10 h. The whole mixture was filtered and the filtrate was distilled by vacuum. Then the residue dissolved in acetone was treated by Jones reagent and further purified by recrystallisation from ethanol to afford the product (**10a**–**10d**). The fluorinated benzoxybenzoic acids (**15a**–**15e**) were obtained by the means described above. All the structural characterisations for **10** and **15** were identical to literature data (*33, 34*).

General procedure for synthesis of the target trans-*decalin derivatives (series **11, 12, 16 and 17**).*

One equivalent of the above benzoic acids (**10**, **15**), 6-*n*-alkyl-*trans*-decalin-2-ol (**5a**, **5b**), DCC and DMAP were added in dichloromethane and stirred at room temperature for 10 h. The whole mixture was filtered and the filtrate was distilled by vacuum. The crude product was fractionated by column chromatography and further recrystallised from EtOH to afford the products.

For *trans*-decalin derivative **11a**: yield 62%. IR (KBr): ν_{max} (cm^{-1}) 2919, 2850, 1730, 1709, 1604, 1511, 1463, 1267. ^{1}H NMR ($CDCl_3$): δ 0.63 (q, 1H, CH), 0.80–2.20 (m, 31H), 4.05 (t, 2H, OCH_2), 4.96 (m, 1H, OCH), 6.97 (d, 2H, 2 arom. H), 7.27 (d, 2H, 2 arom. H), 8.10 (d, 2H, 2 arom. H), 8.14 (d, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$): δ 14.0, 14.4, 20.0, 22.5, 28.1, 28.8, 31.7, 32.0, 32.9, 33.5, 37.4, 39.0, 39.7, 39.9, 41.1, 42.0, 68.4, 74.1, 114.4, 121.1, 121.7, 128.4, 131.1, 132.4, 154.6, 163.8,164.5, 165.4. Elemental analysis: found, C 75.73, H 8.36; calculated, C 75.86, H 8.36%.

For **12a**: yield 71%. IR (KBr): ν_{max} (cm^{-1}) 2918, 2849, 1730, 1710, 1600, 1512, 1463, 1268. ^{1}H NMR ($CDCl_3$): δ 0.62 (q, 1H, CH), 0.80–2.20 (m, 35H), 4.05 (t, 2H, OCH_2), 4.97 (m, 1H, OCH), 6.97 (d, 2H, 2 arom. H), 7.27 (d, 2H, 2 arom. H), 8.10 (d, 2H, 2 arom. H), 8.13 (d, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$): δ 14.2, 14.3, 22.6, 22.9, 26.8, 28.3, 28.9, 31.8, 32.1, 32.3, 33.1, 33.7, 37.5, 37.8, 39.1, 40.1, 41.2, 42.1, 68.5, 74.2, 114.5, 121.2, 121.8, 128.5, 131.2, 132.5, 154.8, 163.9, 164.6, 165.5. Elemental analysis: found, C 76.40, H 8.72; calculated, C 76.37, H 8.67%.

For **16a**: yield 73%. IR (KBr): ν_{max} (cm^{-1}) 2921, 2851, 1743, 1713, 1607, 1507, 1454, 1276. ^{1}H NMR ($CDCl_3$): δ 0.65 (q, 1H, CH), 0.80–2.20 (m, 21H), 5.00 (m, 1H, OCH), 7.27 (m, 4H, 4 arom. H), 7.65 (m, 1H, 1 arom. H), 8.14 (m, 3H, 3 arom. H). ^{13}CNMR ($CDCl_3$): δ 14.5, 20.1, 31.8, 32.1, 33.0, 33.7, 37.6, 39.1, 39.8, 40.0, 41.2, 42.1, 74.3, 117.6, 121.7, 124.4, 128.9, 131.3, 132.7, 135.7, 154.2, 161.5, 162.4, 163.6, 165.4. ^{19}F NMR ($CDCl_3$): δ −107.8. Elemental analysis: found, C 73.92, H 7.14; calculated, C 73.95, H 7.13%.

For **16b**: yield 74%. IR (KBr): ν_{max} (cm^{-1}) 2905, 2848, 1741, 1708, 1596, 1445, 1261. ^{1}H NMR ($CDCl_3$): δ 0.63 (q, 1H, CH), 0.80–2.20 (m, 21H), 4.97 (m, 1H, OCH), 7.29 (m, 2H, 2 arom. H), 7.37 (q, 1H, 1 arom. H), 7.51 (m, 1H, 1 arom. H), 7.88 (m, 1H, 1 arom. H), 8.00 (d, 1H, 1 arom. H), 8.12 (q, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$): δ 14.5, 20.1, 31.8, 32.1, 33.0, 33.7, 37.6, 39.1, 39.8, 40.0, 41.2, 42.1, 74.3,

117.3, 121.1, 121.7, 126.1, 129.0, 130.5, 131.3, 131.4, 154.3, 161.8, 163.7, 165.4. ^{19}F NMR ($CDCl_3$): δ −111.6. Elemental analysis: found, C 73.82, H 7.16; calculated, C 73.95, H 7.13%.

For **16c**: yield 72%. IR (KBr): ν_{max} (cm^{-1}) 2911, 2848, 1732, 1706, 1602, 1509, 1452, 1272. ^{1}H NMR ($CDCl_3$): δ 0.65 (q, 1H, CH), 0.80–2.20 (m, 21H), 4.97 (m, 1H, OCH), 7.20 (m, 2H, 2 arom. H), 7.27 (m, 2H, 2 arom. H), 8.12 (m, 2H, 2 arom. H), 8.22 (m, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$): δ 14.5, 20.1, 31.8, 32.1, 33.0, 33.7, 37.6, 39.1, 39.8, 40.0, 41.2, 42.1, 74.3, 116.1, 121.7, 125.5, 128.8, 131.3, 133.0, 154.4, 163.8, 165.4, 167.5. ^{19}F NMR ($CDCl_3$): δ −103.8. Elemental analysis: found, C 74.03, H 7.15; calculated, C 73.95, H 7.13%.

For **16d**: yield 76%. IR (KBr): ν_{max} (cm^{-1}) 2924, 2848, 1745, 1708, 1604, 1505, 1261. ^{1}H NMR ($CDCl_3$): δ 0.62 (q, 1H, CH), 0.80–2.20 (m, 21H), 4.98 (m, 1H, OCH), 6.96 (m, 1H, 1 arom. H), 7.02 (m, 1H, 1 arom. H), 7.28 (t, 2H, 2 arom. H), 8.10 (m, 3H, 3arom. H). ^{13}C NMR ($CDCl_3$): δ 14.5, 20.1, 31.8, 32.1, 33.0, 33.7, 37.6, 39.1, 39.8, 40.0, 41.2, 42.1, 74.3 (OCH); 105.8, 112.1, 114.3, 121.7, 129.0, 131.3, 134.6, 154.0, 161.5, 163.5, 165.4, 167.5. ^{19}F NMR ($CDCl_3$): δ −99.8, −102.2. Elemental analysis: found, C 71.14, H 6.59; calculated, C 71.03, H 6.62%.

For **16e**: yield 69%. IR (KBr): ν_{max} (cm^{-1}) 2924, 2848, 1745, 1708, 1604, 1505, 1261. ^{1}H NMR ($CDCl_3$): δ 0.63 (q, 1H, CH), 0.80–2.20 (m, 21H); 4.98 (m, 1H, OCH), 7.30 (m, 2H, 2 arom. H), 7.79 (d, 2H, 2 arom. H), 8.14 (m, 2H, 2 arom. H), 8.32 (d, 2H, 2 arom. H). ^{13}C NMR($CDCl_3$): δ 14.5, 20.1, 31.8, 32.0, 33.0, 33.6, 37.5, 39.1, 39.8, 40.0, 41.2, 42.1, 74.3, 121.6, 125.5, 125.8, 129.1, 130.7, 131.4, 132.5, 154.1, 135.3 (CF_3), 163.6, 165.3. ^{19}F NMR ($CDCl_3$): δ −63.2. Elemental analysis: found, C 68.73, H 6.47; calculated, C 68.84, H 6.40%.

3. Results and discussion

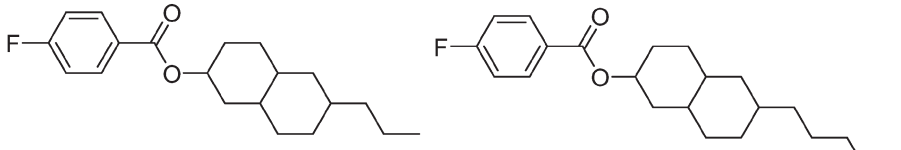
The conformation of decalins

Before synthesising the target esters (series **11**, **12**, **16** and **17**) with two aromatic rings, the esters (**18**, **19**) with only one aromatic ring had already been designed and synthesised (Figure 1). A comparison between decalinol **5a** and ester **18** was made to determine the stereochemical purity and conformation of the decalin ring on the basis of ^{1}H NMR spectra (Figure 2). The ^{1}H NMR spectra of decalinol **5a** (Figure 2(a)) shows a mixture of *trans*/*cis* isomers (91:9) after reduction of decalone by $LiAlH_4$ from **4**. The chemical shifts of **5a** at δ=0.54 (C*H*), 3.60 (O*CH*) were assigned to the axial C-6 and C-2 methine protons, indicative of equatorially substituted *trans*-decalin, whereas the peaks at δ=0.66, 4.11 indicated the C-6, C-2 methine protons in *cis*-substituted decalin. The shift of the C-6 methine proton at δ=0.66 in *cis*-decalin to δ=0.54 in *trans*-decalin was ascribed to the shielding effect from the neighbouring C–C σ bonds. Figure 2(b) shows the existence of two axial C-6, C-2 methane protons at δ=0.54, 4.95 in the *trans*-decalin derivative (**18**). No equatorial C-6 methine proton could be found around δ=0.66. This indicated the absence of *cis*-substituted decalin isomer and the high stereochemical purity of the *trans*-substituted decalin.

In order to confirm the absolute conformation of the *trans*-decalin system and the arrangement of the alkyl and ester groups, we also grew a single crystal of compound **18** by slow evaporation from EtOH/EtOAc solution. X-ray crystallographic analysis of **18** unambiguously assigned the absolute configuration of the *trans*-decalin fused rings. The two axial methine protons at C11, C16 in X-ray crystallography (Figure 3) show that the fused cyclohexane adopts the *trans* configuration and chair conformation. Another two axial methine protons at C8, C13 indicate the equatorial arrangement of *trans*-substitution on the *trans*-decalin system. The analyses of the X-ray crystallographic data are summarised in Table 1. These XRD data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 679605). To our knowledge, this is the first report of the absolute structure of the *trans*-conformation in a LC analogue by XRD analysis.

Mesomorphic properties

The mesomorphic properties of the *trans*-decalin derivatives were studied by DSC and polarising



Compound (**18**) Compound (**19**)

Figure 1. Structure of esters **18** and **19**.

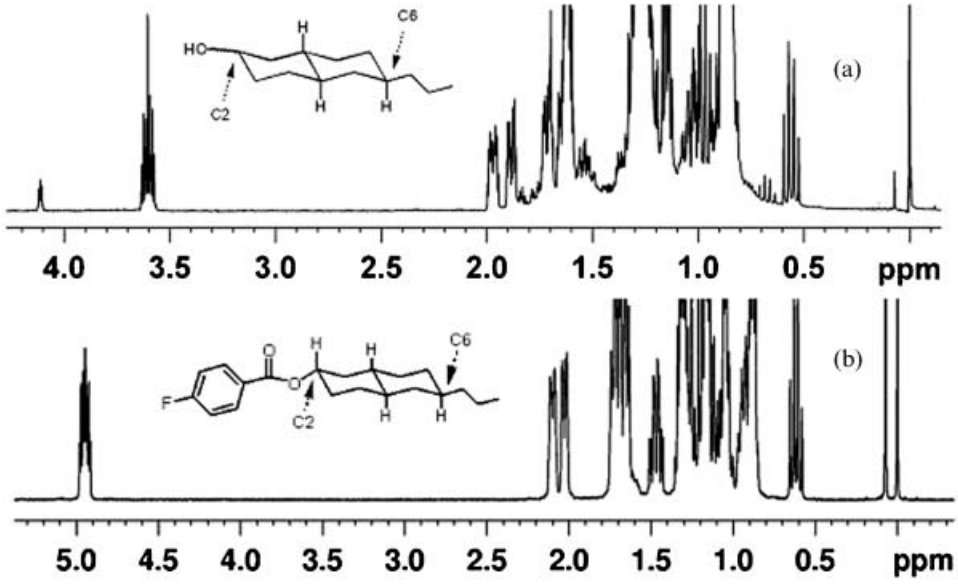


Figure 2. ^{1}H NMR comparison between decalin-2-ol **5a** and ester **18**.

optical microscopy (POM). The mesomorphic behaviour of **18** and **19**, which possess only one aromatic ring, are found to be suppressed by the lack of rigidity of the mesogenic core. Ester **18** simply melts at 78°C to form an isotropic liquid; so does ester **19** at 81°C. No monotropic mesophases could be observed on cooling before recrystallisation occurred.

For the non-fluorine-containing compounds in series **11** and **12**, which have two aromatic rings linked by an ester group, all the compounds are found to exhibit only an enantiotropic nematic phase of very low viscosity. When the samples were cooled from the isotropic phase, they clearly presented typical schlieren textures with two- and four-point brushes characteristic of the nematic phase. The results of DSC measurements are in reasonable agreement with those determined by POM observations. For example, only two endothermic peaks at 92.4°C and 201.4°C on first heating could be found in the DSC measurements for **12d** (Figure 4) and a nematic phase was observed under the polarising optical microscope. The optical, thermal and thermodynamic data for these compounds (**11a**–**11d**, **12a**–**12d**) are summarised in Table 2. Series **11** exhibit both slightly higher clearing temperatures and lower melting temperatures than the corresponding analogues of series **12**. In addition, **11b** and **12b** exhibit the most thermodynamically stable phase of the series. Shorter or longer alkoxy chains attached at the end of the molecular structure tend to slightly destabilise the nematic phase. The enthalpy changes of the nematic to isotropic transition are within the expected order of magnitude (1–2 kJ mol^{-1}).

The analogous model esters of series **16** and **17** containing terminal fluorine atoms instead of terminal alkoxy chains were synthesised in an attempt to introduce a group of strong polarity, such as F or CF_3. Observation under the polarising microscope indicated that all the compounds, except **17e**, exhibit a nematic phase with typical schlieren texture (figure 5(a)). Compound **17e** exhibited a focal-conic texture assigned as a smectic A (SmA) phase (figure 5(b)). The phase transition temperatures and mesomorphic behaviour of these fluorine-containing LCs are summarised in Table 3. The clearing

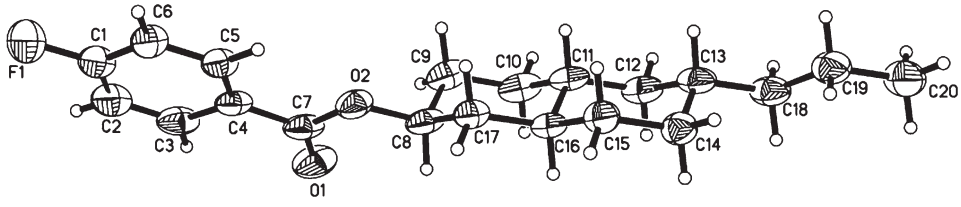


Figure 3. The X-ray crystallographic structure of ester **18**.

Table 1. Crystal parameters, selective bond lengths (Å) and bond angles (°) of ester **18**.

Crystal data:			
$C_{20}H_{27}FO_2$		$\gamma=100.085(6)^\circ$	
$M_r=318.42$		$V=892.6(7)$ Å^3	
Triclinic, $P\bar{1}$		$Z=2$	
$a=5.668(2)$ Å		Mo K_α	
$b=9.382(4)$ Å		$\mu=0.08$ mm^{-1}	
$c=17.461(7)$ Å		$T=273(2)$ K	
$\alpha=100.135(6)^\circ$		$0.30\times0.30\times0.10$ mm	
$\beta=95.294(6)^\circ$		H-atom parameters constrained	
$R[F^2>2\sigma(F^2)]=0.057$		$\Delta\rho_{max}=0.11$ e Å^{-3}	
$wR(F^2)=0.192$		$\Delta\rho_{min}=-0.11$ e Å^{-3}	
$S=1.04$			
F(1)–C(1)	1.355(4)	C(10)–C(11)–C(12)	113.5(3)
O(1)–C(7)	1.210(3)	C(10)–C(11)–C(16)	110.3(3)
O(2)–C(7)	1.343(3)	C(12)–C(11)–C(16)	111.2(3)
O(2)–C(8)	1.454(3)	C(11)–C(12)–C(13)	113.6(3)
C(8)–C(17)	1.500(4)	C(14)–C(13)–C(12)	109.4(3)
C(8)–C(9)	1.516(4)	C(14)–C(13)–C(18)	112.8(3)
C(9)–C(10)	1.524(4)	C(12)–C(13)–C(18)	112.6(3)
C(10)–C(11)	1.516(4)	C(11)–C(10)–C(9)	112.6(3)
C(11)–C(12)	1.520(4)	C(10)–C(11)–C(12)	113.5(3)
C(11)–C(16)	1.527(4)	C(10)–C(11)–C(16)	110.3(3)
C(12)–C(13)	1.525(4)	C(12)–C(11)–C(16)	111.2(3)
C(13)–C(14)	1.518(4)	C(11)–C(12)–C(13)	113.6(3)
C(13)–C(18)	1.526(4)	C(14)–C(13)–C(12)	109.4(3)
C(14)–C(15)	1.525(3)	C(14)–C(13)–C(18)	112.8(3)
C(15)–C(16)	1.523(4)	C(12)–C(13)–C(18)	112.6(3)
C(16)–C(17)	1.525(3)	C(11)–C(10)–C(9)	112.6(3)
C(18)–C(19)	1.509(5)	C(10)–C(11)–C(12)	113.5(3)
C(19)–C(20)	1.524(4)	C(13)–C(14)–C(15)	112.5(3)
C(7)–O(2)–C(8)	118.3(3)	C(16)–C(15)–C(14)	112.2(2)
C(6)–C(1)–F(1)	119.2(4)	C(15)–C(16)–C(17)	113.0(2)
C(6)–C(1)–C(2)	122.8(4)	C(15)–C(16)–C(11)	110.8(3)
F(1)–C(1)–C(2)	118.0(3)	C(17)–C(16)–C(11)	111.3(2)
O(2)–C(8)–C(17)	107.4(3)	C(8)–C(17)–C(16)	112.7(3)
O(2)–C(8)–C(9)	109.9(3)	C(8)–C(17)–H(17A)	109.1
C(17)–C(8)–C(9)	111.5(3)	C(19)–C(18)–C(13)	115.1(3)

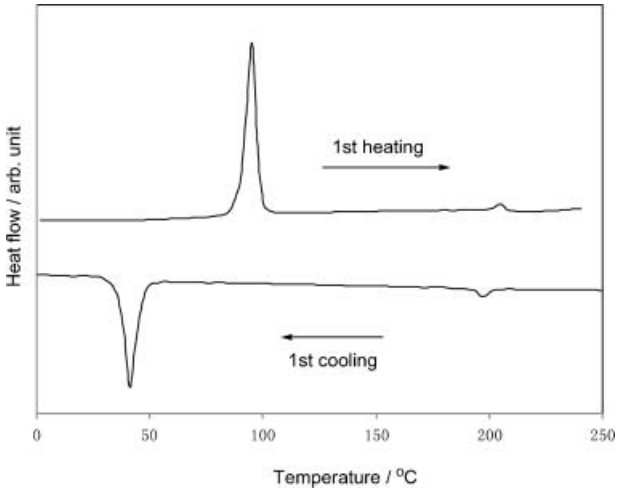


Figure 4. DSC curves of ester **12d** on first heating and cooling run.

Table 2. Transition temperatures (°C) and enthalpies of esters **11a**–**11d** and **12a**–**12d**.

Compound	Transition	Temperature	ΔH/kJ mol^{-1}
11a ($m=3$, $n=5$)	Cr–N	100.3	32.3
	N–I	214.0	1.30
11b ($m=3$, $n=6$)	Cr–N	89.0	24.0
	N–I	215.4	1.16
11c ($m=3$, $n=7$)	Cr–N	87.2	29.1
	N–I	208.1	1.24
11d ($m=3$, $n=8$)	Cr–N	91.2	31.5
	N–I	201.8	1.25
12a ($m=5$, $n=5$)	Cr–N	88.5	33.3
	N–I	211.1	1.35
12b ($m=5$, $n=6$)	Cr–N	88.9	36.1
	N–I	215.3	1.73
12c ($m=5$, $n=7$)	Cr–N	79.1	29.2
	N–I	203.1	1.40
12d ($m=5$, $n=8$)	Cr–N	92.4	44.7
	N–I	201.2	1.77

temperatures decrease and the liquid crystallinity becomes thermodynamically unstable when a fluorine atom is introduced in a lateral position. Fluorinated compounds **16c**, **16e** and **17c**, **17e** with a more linear geometry, which contain F or CF_3 substituents in the 4-position of the aromatic ring, respectively, exhibit higher clearing temperatures than the analogues compounds possessing lateral fluorine atoms. Compared with the non-fluorine-containing LCs of series **11**, **12**, the enthalpy changes associated with nematic–isotropic (N–I) transition in the fluorinated LCs, **16, 17**, are smaller and below 1kJ mol^{-1}.

4. Conclusion

We have prepared a series of *trans*-decalin-containing calamitic LCs. By analysis of single-crystal XRD, the conformation of the decalin system was confirmed to be trans and the arrangement of substituents is equatorial, which indicates the linear structure of the synthesised LCs. Mesomorphic studies showed that all the target compounds have enantiotropic nematic phases over a wide temperature range except compound **17e**, which contains CF_3 on the aromatic ring, which exhibits a smectic A phase. These results suggest that these LCs based on *trans*-decalin may be candidates as LC materials in LCDs.

Acknowledgments

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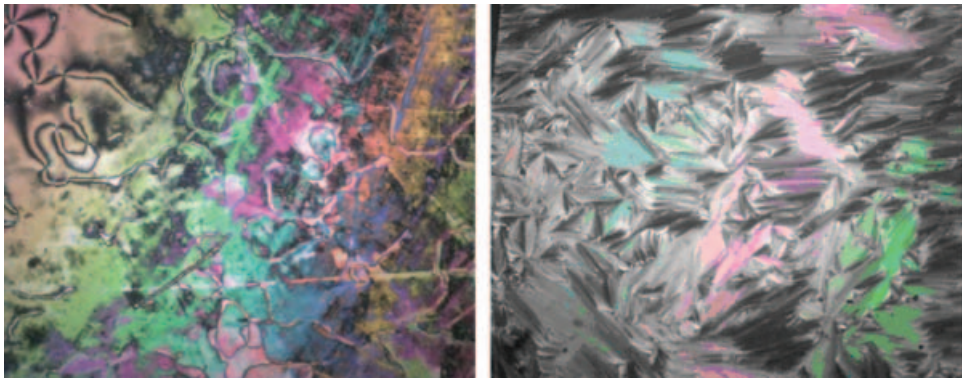

(a) (b)

Figure 5. Polarising optical textures (× 200) for esters **16b** (a) at 140°C and **17e** (b) at 180°C.

Table 3. Transition temperatures (°C) and enthalpies of esters **16a**–**16d** and **17a**–**17d**.

Compound	Transition	Temperature	ΔH/kJ mol^{-1}
16a (Ar=2-FC_6H_4, m=3)	Cr–N	106.9	47.3
	N–I	145.8	0.75
16b (Ar=3-FC_6H_4, m=3)	Cr–N	110.0	73.4
	N–I	153.4	0.74
16c (Ar=4-FC_6H_4, m=3)	Cr–N	89.5	54.3
	N–I	206.9	0.70
16d (Ar=2,4-$F_2C_6H_3$, m=3)	Cr–N	97.9	63.7
	N–I	207.3	0.91
16e (Ar=4-$CF_3C_6H_4$, m=3)	Cr–N	145.5	78.3
	N–I	205.0	0.89
17a (Ar=2-FC_6H_4, m=5)	Cr–N	88.1	58.9
	N–I	141.8	0.78
17b (Ar=3-FC_6H_4, m=5)	Cr–N	101.5	65.0
	N–I	160.9	1.42
17c (Ar=4-FC_6H_4, m=5)	Cr–N	113.7	65.5
	N–I	213.1	0.70
17d (Ar=2,4-$F_2C_6H_3$, m=5)	Cr–N	94.4	53.5
	N–I	197.0	0.86
17e (Ar=4-$CF_3C_6H_4$, m=5)	Cr–SmA	128.5	67.3
	SmA–I	201.9	1.02

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