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Four-unit linking groups

V. Optically active dopants

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A number of diesters incorporating a four-unit linking group in the acid part (3-propyloxy, (*E*)-3-propenyloxy, and 4-butyl units) and an optically active centre in the diol part have been prepared. Structurally related three and four ring dioxolanes derived from the corresponding aldehyde precursors to the acids (i.e. also containing 3-propyloxy, (*E*)-3-propenyloxy, and 4-butyl groups) and the optically active tartaric acids have also been synthesized. The physical properties of these potential chiral dopants pertinent to electrooptic display device and thermochromic applications have been determined. These new chiral dopants are characterized by short pitches, good solubility in nematic hosts, excellent chemical, photochemical and thermal stability, etc. Most of these new optically active substances are well suited for at least one potential application for a chiral nematic mesophase with exactly defined properties made from a standard nematic mesophase and an optically active dopant. A small number of the new substances exhibit mesomorphic properties at elevated temperatures.

1. Introduction

Chiral dopants incorporating an optically active centre are used extensively in mixtures with nematic hosts for electrooptic display device applications. Chiral dopants have been used for many years to induce a certain handedness to prevent the formation of reverse twist in twisted nematic cells [1-5] as well as to compensate the temperature dependence of the threshold voltage of twisted nematic displays [6-8]. More recently such dopants have also been used to induce the desired angle of twist in supertwist display devices [9-14]. The magnitude of the d/p ratio used depends on the desired twist angle (θ) and varies between 0.3 and 0.7 for $180^\circ \leq \theta \leq 270^\circ$ (d is the cell thickness between the electrodes and p is the pitch of the induced cholesteric phase). It is impossible to adjust and stabilize the twist angle in highly twisted liquid crystal displays without such dopants. This can be elegantly combined with the compensation of the temperature dependence of the threshold voltage (V_c^0) of such supertwist displays [13, 14] to maintain the viewing characteristics, where otherwise compensation via the electronics would be required. For zero bias tilt angle the capacitive voltage (V_c^d) of the doped chiral nematic mixture is given by [15, 16]

$$V_c^d = V_c^0(1 + Fd/p)^{1/2}. \quad (1)$$

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The temperature dependence of the threshold voltage of the undoped mixture and the factor F is

$$V_c^0(T) = V_c^0(22^\circ\text{C}) + \frac{\partial V_c^0}{(\partial T/^\circ\text{C})}(T - 22)/^\circ\text{C}, \quad (2)$$

where

$$F = \frac{4k_{22}\theta}{\pi \left(k_{11} + \frac{k_{33} - 2k_{22}}{4} \right)}; \quad (3)$$

here k_{11} , k_{22} and k_{33} are the splay, twist and bend elastic constants, respectively. The optical threshold voltage is, to a good approximation, proportional to the capacitive threshold [17]. The voltage (V_c^0) decreases with increasing temperature (F is practically independent of temperature). Therefore the absolute value of the pitch has to decrease with increasing temperature. This can be achieved with two dopants of opposite, but unequal helical sense with different temperature dependencies [6–8] or by using one dopant incorporating two separate optically active centres of opposite sense, which also induce a pitch which contracts with increasing temperature [18].

Optically stable, chiral dopants with left as well as right handed short helical pitches are also of crucial importance for liquid crystal display applications using circularly polarized instead of linearly polarized light such as for the non-absorbing optical filters and polarizers in the recently presented polarised colour liquid crystal display projection concept [19–21]. The wavelength of light transmitted by the cholesteric layers must be independent of temperature over the device operating temperature range [18, 21]. The central wavelength λ_0 of selective reflection of a planar aligned cholesteric layer is given by

$$\lambda_0 = \frac{n_o + n_c}{2} = \bar{n}p \quad (4)$$

Both the pitch and the average refractive index \bar{n} are temperature dependent. Within the expressions [19]

$$\frac{1}{p(T)} = \sum_{i=1}^n c_i [A_i + B_i(T - 22)/^\circ\text{C} + C_i(T - 22)/^\circ\text{C}^2] \quad (5)$$

and

$$\frac{1}{\bar{n}} = a + b(T - 22)/^\circ\text{C} \quad (6)$$

we obtain

$$\frac{1}{\lambda_0(T)} = \sum_{i=1}^n c_i [A_i + B_i(T - 22)/^\circ\text{C} + C_i(T - 22)/^\circ\text{C}^2] [a + b(T - 22)/^\circ\text{C}], \quad (7)$$

where c_1 – c_n are the concentrations of the chiral dopants, and A_i , B_i , C_i , and a , b are expansion coefficients.

The temperature independence of λ_0 can be achieved, for example, by using two chiral dopants in a host nematic mixture for which

$$a(c_1B_1 + c_2A_2) = -b(c_1A_1 + c_2A_2). \quad (8)$$

holds [19]. In equation (7) it is the constants B_i which are essentially responsible for the temperature dependence of λ_0 . Therefore it is essential in this case to utilize two or more chiral dopants, whose pitches are additive (to achieve the small pitches required for selective reflection in the visible range) and whose temperature dependencies cancel each other as well as the temperature dependence of the optical birefringence of the mixture [19].

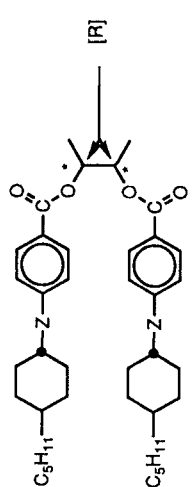
Chiral dopants of small pitch can also be utilized to create chiral nematic mixtures for use in non-destructive thermography requiring selective reflection of light in the visible spectrum. In this case a strong temperature dependence of the pitch and thus the colour of the selective reflection over a narrow temperature range is desired. Non-destructive thermography has developed significantly using stable chiral nematic materials in mixtures instead of unstable mixtures of cholesterol derivatives, where shelf-life and colour reproducibility were major problems [22–29]. Although the specifications for chiral nematic mixtures for cosmetic effects may be less stringent, they are essentially the same and based on the same effect.

The origin and application of induced chiral nematic mesophases consisting of a non-optically active nematic host and an optically active chiral dopant and their relationship to each other has been investigated as a phenomenon and as a tool for studies of chirality itself [30–34]. As part of a systematic investigation of structures incorporating the recently reported four-unit linking groups for electrooptic display applications [35–38] it was decided to prepare novel substances containing three of these new central linkages (3-propyloxy, (*E*)-3-propenyloxy, and 4-butyl units) and at least one optically active centre in order to assess their suitability as chiral dopants. Several diesters of commercially available diols are known to exhibit short pitches when mixed with nematic materials [6, 7, 14, 39, 40]. Therefore, structurally related diesters of benzoic acids incorporating the four-unit linking groups described previously were synthesized. A second avenue of approach adopted was the incorporation of the same four-unit linking groups in optically active dioxolane derivatives of the naturally occurring and commercially available tartaric acids.

The required 4-[3-(*trans*-4-pentylcyclohexyl)-1-propyloxy]benzoic acid, 4-[(*E*)-3-(*trans*-4-pentylcyclohexyl)allyloxy]benzoic acid and 4-[4-(*trans*-4-pentylcyclohexyl)-1-butyl]benzoic acid were prepared as already described [38] and then esterified with commercially available optically active diols. These were (*R,R*)-2,3-butanediol, *R*(–)-1-phenyl-1,2-ethanediol, (*R,R*)-1,2-diphenyl-ethanediol, and *R*(+)-1,1'-bis(2-naphthol) (which does not actually contain an optically active centre and is, thus, a rotomer) and their *S* antipodes. Only the *R* materials are discussed here as the *S* substances are naturally identical except for the sign of optical rotation and pitch. The optically active dioxolanes were prepared from commercially available tartaric acids and either the dimethyl acetals of the previously described 4-[3-(*trans*-4-pentylcyclohexyl)-1-propyloxy]benzaldehyde, 4-[(*E*)-3-(*trans*-4-pentylcyclohexyl)allyloxy]benzaldehyde and 4-[4-(*trans*-4-pentylcyclohexyl)-1-butyl]benzaldehyde [38] or directly from the aldehydes themselves as described in the Experimental.

2. Results and discussion

The melting point (T_{CI}) and the enthalpy of fusion (ΔH) for the diesters 1–4 of substituted benzoic acids incorporating the four-unit linking groups of interest (3-propyloxy, (*E*)-3-propenyloxy, and 4-butyl units) and optically active diols (i.e. (*R,R*)-2,3-butanediol, *R*(–)-1-phenyl-1,2-ethanediol, (*R,R*)-1,2-diphenyl-ethanediol, and *R*(+)-1,1'-bis(2-naphthol), respectively) are collated in tables 1–4. The optical

Table 1. Some physical data for the diesters **1** and for mixtures containing 1 wt% of the diesters **1** in the nematic mixture 3010.





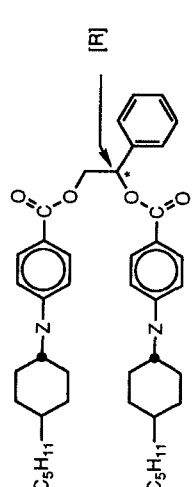
| Z | $T_{cl}/^{\circ}\text{C}$ | $\Delta H/\text{kJ mol}^{-1}$ | $[\alpha]_{389}^{20}/^{\circ}$ | Pitch/ μm | $A/10^{-2} \mu\text{m}^{-1}$ | $B/10^{-4} (\mu\text{m}^{\circ}\text{C})^{-1}$ | $C/10^{-6} \mu\text{m}^{-1} \text{C}^{-2}$ | $\Delta T_{NI}/^{\circ}\text{C}$ |
|--|---------------------------|-------------------------------|--------------------------------|----------------------|------------------------------|--|--|----------------------------------|
|  | 109 | — | -10.7 | 22.4 | 4.465 | -3.705 | -4.487 | |
|  | 128 | 44.6 | -15.4 | 37.1 | 2.69 | -2.292 | -0.211 | -0.7 |
|  | 95 | 35.4 | -3.0 | 32.8 | 3.05 | -4.00 | -2.36 | -1.3 |

Table 2. Some physical data for the diesters **2** and for mixtures containing 1 wt% of the diesters **2** in nematic mixture 3010.





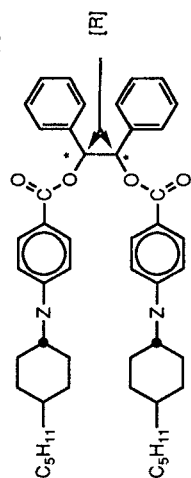
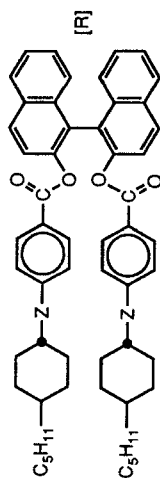
| Z | $T_{cl}/^{\circ}\text{C}$ | $\Delta H/\text{kJ mol}^{-1}$ | $[\alpha]_{389}^{20}/^{\circ}$ | Pitch/ μm | $A/10^{-2} \mu\text{m}^{-1}$ | $B/10^{-4} (\mu\text{m}^{\circ}\text{C})^{-1}$ | $C/10^{-6} \mu\text{m}^{-1} \text{C}^{-2}$ | $\Delta T_{NI}/^{\circ}\text{C}$ |
|--|---------------------------|-------------------------------|--------------------------------|----------------------|------------------------------|--|--|----------------------------------|
|  | 117 | 57.2 | -49.7 | -4.8 | -21.05 | -4.841 | 8.080 | |
|  | 101 | 46.6 | -8.9 | -4.26 | -23.5 | -5.870 | 6.250 | -0.3 |
|  | 103 | — | — | — | — | — | — | — |

Table 3. Some physical data for the diesters **3** and for mixtures containing 1 wt% of the diesters **3** in nematic mixture 3010.



| Z | $T_{Cl}/^{\circ}\text{C}$ | $\Delta H/\text{kJ mol}^{-1}$ | $[\alpha]_{589}^{20}/^{\circ}$ | Pitch/ μm | $A/10^{-2} \mu\text{m}^{-1}$ | $B/10^{-4} (\mu\text{m}^{\circ}\text{C})^{-1}$ | $C/10^{-6} \mu\text{m}^{-1} \text{C}^{-2}$ | $\Delta T_{NI}/^{\circ}\text{C}$ |
|---|---------------------------|-------------------------------|--------------------------------|----------------------|------------------------------|--|--|----------------------------------|
| | 75 | — | +55.0 | —2.8 | —35.73 | —5.297 | 4.063 | — |
| | 79 | — | +46.8 | —2.75 | —36.34 | —7.01 | —5.790 | —0.7 |
| | 91 | 29.7 | +53.0 | —2.68 | —37.33 | —3.08 | 10.10 | —0.8 |

Table 4. Some physical data for the diesters **4** and for mixtures containing 1 wt% of the diesters **4** in nematic mixture 3010.



| Z | $T_{Cl}/^{\circ}\text{C}$ | $\Delta H/\text{kJ mol}^{-1}$ | $[\alpha]_{589}^{20}/^{\circ}$ | Pitch/ μm | $A/10^{-2} \mu\text{m}^{-1}$ | $B/10^{-4} (\mu\text{m}^{\circ}\text{C})^{-1}$ | $C/10^{-6} \mu\text{m}^{-1} \text{C}^{-2}$ | $\Delta T_{NI}/^{\circ}\text{C}$ |
|---|---------------------------|-------------------------------|--------------------------------|----------------------|------------------------------|--|--|----------------------------------|
| | 50 | — | —5.0 | 1.8 | 55.42 | —11.475 | —17.82 | — |
| | 93 | 22.3 | —4.7 | 1.38 | 72.4 | —9.822 | —10.6 | —0.9 |
| | 0 | 30.4 | +4.8 | — | — | — | — | — |

rotation ($[\alpha]_{589}^{20}$) of each individual substance is also given. Tables 1–4 record the pitch, the constants responsible for temperature dependence (A , B and C) and clearing point depression ($\Delta T_{NI} - T_{NI}$) of chiral nematic mixtures consisting of a fixed concentration (1 wt%) of each individual chiral dopant and a standard nematic host mixture 3010 from F. Hoffmann-La Roche measured at a fixed temperature (25°C) (except, of course, the clearing point depression).

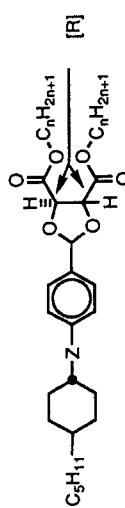
A salient feature of tables 1–4 is the direct relationship between increasing size of the groups attached to the diol groups (methyl, phenyl, biphenyl and bisnaphthyl) of the diesters 1–4 and decreasing values for the melting point (111°C, 107°C, 82°C and 48°C, on average, respectively), the pitch (+30.8 μm , –4.5 μm , –2.8 μm and +1.6 μm , on average, respectively) and to a lesser extent the enthalpy of fusion (40 kJ mol^{–1}, 51.9 kJ mol^{–1}, 29.7 kJ mol^{–1} and 26.4 kJ mol^{–1}, respectively). This is reflected in the amounts of each chiral dopant required to achieve selective reflection of light in the visible spectrum (< 100 per cent, 13 per cent, 9 per cent and 5 per cent, respectively) for the esters 1–4. These results are consistent with those for other structurally related esters [6, 7]. It is difficult to establish direct correlations between structure and the factors B and C and the optical rotation. However, it is clear that the sign of the optical rotation depends directly on the bridge Z and that the sign of the coefficients A and B remains constant for the same optically active moiety and is independent of Z . Within each series no variation due to the nature of the central linkage ($Z = \text{C}_3\text{H}_6\text{O}$, $\text{C}_3\text{H}_4\text{O}$ and C_4H_8) can be directly attributed. A surprising feature of the data in tables 1–4 is the small deviation in the clearing point observed for the diesters 1–4 (–1.0°C, –0.3°C, –0.8°C and –0.9°C, on average, respectively) which seems to be remarkably independent of the size of the diol substituents.

The same parameters collated in tables 1–4 for the diesters 1–4 are also listed for the related three ring dioxolanes 5–7 and the four ring dioxolanes 8 in tables 5 and 6, respectively. The length of the alkyl chain is also varied ($n = 1$ –4). The melting point (51°C, on average) of the three ring dioxolanes 5–7 incorporating the 3-propyloxy, (*E*)-propenyloxy-, and 4-butyl units ($Z = \text{C}_3\text{H}_6\text{O}$, $\text{C}_3\text{H}_4\text{O}$, and C_4H_8 , respectively) is lower than that (87°C, on average) of the analogous diesters 1–4, although the melting point (48°C, on average) of the bis-naphthyl-substituted diesters 4 is marginally lower. The pitch (5.6 μm , on average) of the dioxolanes 5–7 corresponds approximately to that (+4.5 μm , on average) of the phenyl-substituted diesters 2, although the melting point is significantly lower (–56°C, on average), which is also reflected in a higher solubility in the nematic host mixture. This also corresponds with the lower enthalpies of fusion for the dioxolanes 5–7 (32.4 kJ mol^{–1}, on average, where determinable) compared with those of the diesters 1–4 (38.0 kJ mol^{–1}, on average). The clearing point depression (ΔT_{NI}) caused by the three ring dioxolanes 5–7 are somewhat larger (–1.8°C, on average) than those of the diesters 1–4 (–0.8°C, on average).

The introduction of a second 1,4-disubstituted benzene ring into the dioxolanes 5 incorporating a propyloxy linking unit ($Z = \text{C}_3\text{H}_6\text{O}$) to yield the biphenyl dioxolanes 8 results not only in a significant increase in the melting point (+44°C, on average) but also in the appearance of liquid crystal mesophases (smectic A and chiral nematic). This had advantages for mixture preparation as the clearing point depression is minimal (–0.3°C, on average) although the solubility of the dioxolanes 8 remains surprisingly high by comparable pitch values (–6.5 μm and –7.2 μm , on average).

The temperature dependence of the pitch and the clearing point depressions induced by the dioxolanes 5–8 are almost exactly linear up to large concentrations of dopant, while the diesters 1–4 exhibit widely varying temperature dependencies. Thus

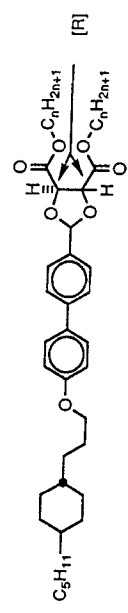
Table 5. Some physical data for the dioxolanes 5-7 and for mixtures containing 1 wt% of the dioxolanes 5-7 in nematic mixture 3010.



C_5H_{11} Z C_nH_{2n+1} [R]

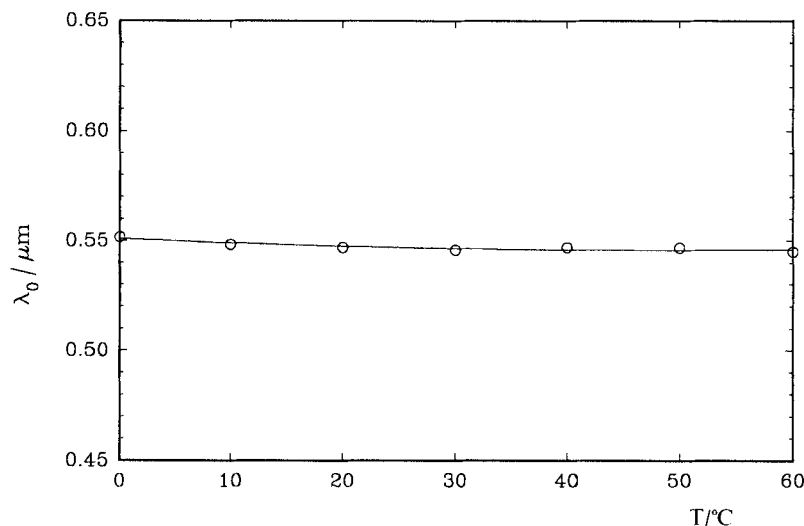
| Z | n | $T_{cl}/^{\circ}C$ | $\Delta H/kJ mol^{-1}$ | $[\alpha]_{589}^{20}/^{\circ}$ | Pitch/ μm | $A/10^{-2} \mu m^{-1}$ | $B/10^{-4} (\mu m^{\circ}C)^{-1}$ | $C/10^{-6} \mu m^{-1} C^{-2}$ | $\Delta T_{NI}/^{\circ}C$ |
|----------------|-------|--------------------|------------------------|--------------------------------|----------------|------------------------|-----------------------------------|-------------------------------|---------------------------|
| ~ ^o | 1 | 66 | 32.9 | -7.0 | -4.95 | -20.2 | 6.62 | -0.54 | -0.8 |
| | 2 | 57 | 31.9 | -11.1 | -5.35 | -18.7 | 7.08 | -1.12 | -0.7 |
| | iso-3 | 52 | 34.6 | -15.5 | -6.46 | -15.5 | 9.31 | 0.66 | -1.1 |
| | 4 | 42 | 43.8 | -11.0 | -9.43 | -10.6 | 2.25 | 1.53 | -1.8 |
| ~ ^o | 1 | 70 | 20.6 | -5.5 | -4.27 | -23.4 | 8.19 | -1.48 | -2.5 |
| | 2 | 55 | 30.5 | 5.8 | -5.55 | -18.0 | 8.25 | -3.26 | -1.7 |
| | iso-3 | 51 | 30.5 | -13.5 | -5.65 | -17.7 | 11.41 | -2.00 | -2.4 |
| | 4 | 40 | 26.4 | -8.8 | -5.42 | -18.4 | 9.55 | -2.53 | -2.0 |
| ~ ^o | 1 | 58 | 25.2 | -6.2 | -6.26 | -16.0 | 5.75 | -0.30 | -2.0 |
| | 2 | 40 | 26.3 | -10.3 | -7.39 | -13.5 | 5.45 | -0.10 | -2.0 |
| | iso-3 | 32 | 26.4 | -14.1 | -8.61 | -11.6 | 6.37 | -0.17 | -1.9 |
| | 4 | 23 | 26.4 | -10.9 | -9.77 | -10.2 | 6.43 | -2.39 | -2.2 |

Table 6. Some physical data for the dioxolanes 8 and for the mixtures containing 1 wt% of the dioxolanes 8 in nematic mixture 3010.



C_5H_{11} C_nH_{2n+1} [R]

| n | $T_{CS,NI}/^{\circ}C$ | $T_{SAC,NI}/^{\circ}C$ | $T_{ChI}/^{\circ}C$ | $\Delta H/kJ mol^{-1}$ | $[\alpha]_{589}^{20}/^{\circ}$ | Pitch/ μm | $A/10^{-2} \mu m^{-1}$ | $B/10^{-4} (\mu m^{\circ}C)^{-1}$ | $C/10^{-6} \mu m^{-1} C^{-2}$ | $\Delta T_{NI}/^{\circ}C$ |
|-------|-----------------------|------------------------|---------------------|------------------------|--------------------------------|----------------|------------------------|-----------------------------------|-------------------------------|---------------------------|
| 1 | 109 | 116 | — | 36.1 | +11.2 | -5.96 | -16.8 | 2.55 | -2.33 | -0.1 |
| 2 | 90 | (77) | (87) | 36.5 | +6.8 | -6.61 | -15.1 | 3.55 | -3.66 | -0.6 |
| iso-3 | 105 | — | — | 44.8 | +0.7 | -9.61 | -10.4 | 4.70 | -1.98 | -0.1 |
| 4 | 91 | — | — | 41.3 | — | -6.59 | -15.2 | 5.26 | -4.07 | -0.3 |



The temperature dependence of the wavelength of selective reflection, λ_0 .

some of the diesters **1–4** give rise to helix inversion in the induced cholesteric mesophases of some mixtures. These differences can be utilized to advantage in the conception and preparation of a wide variety of chiral nematic mixtures for use in many of the applications described in the Introduction.

Several of the diesters **1–4** have been used in conjunction with other chiral dopants in small concentrations to compensate the temperature dependence of the threshold voltage of supertwist displays whilst maintaining the other physical properties of the undoped nematic mixture constant [41]. Other examples of the diesters **1–4** with very small pitches have been used in low concentration to create wide range chiral nematic mixtures reflecting light in the visible part of the spectrum. Several of the dioxolanes **5–8** can be used when mixed with chiral dioxanes [42] of short pitch with the same handedness of optical rotation, but mutually opposed and cancelling B factors and an optimized host nematic mixture to yield chiral nematic mixtures ideally suitable for optical filter/polarizer applications [17, 19–21]. The planar texture of these new mixtures exhibits a wavelength of selective reflection which is virtually completely independent of temperature over the desired operating temperature range of the optical filter. An example of the non-temperature dependent selective reflection wavelength of such a chiral nematic mixture containing some of the new dioxolanes **5** ($n=1$, 5.0 wt% and $n=2$, 6.5 wt%) and two optically active dioxanes [42] (6.5 wt% and 5.0 wt%) is shown in the figure.

3. Experimental

The liquid crystal transition temperatures and/or the melting point of the compounds prepared and recorded in tables 1–6 were determined by optical microscopy using a Leitz Ortholux II POL-BK microscope in conjunction with a Mettler FP 82 heating stage and FP 80 control unit. All of the monotropic liquid crystal phases could be observed using a microscope and no virtual values (extrapolated) had to be determined. The liquid crystal transition temperatures and enthalpies of fusion were also determined using a Mettler DTA TA 2000.

The purity of the compounds was determined by thin layer chromatography, gas chromatography and DTA analysis. A Perkin-Elmer 8310 gas chromatograph and GP-100 graphics printer were used. 4 cm × 8 cm precoated TLC plates, SiO₂ SIL G/UV₂₅₄, layer thickness 0.25 mm (Macheray-Nagel, Düren, Germany) were utilized.

Column chromatography was carried out using silica gel 60 (230–400 mesh ASTM). Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Reactions were carried out under nitrogen unless water was present as solvent or reagent. All temperatures were measured externally unless otherwise stated. The ¹H NMR spectra were recorded at 60 MHz (Varian T-60), 80 MHz (Bruker WP-80) or 270 MHz (Bruker HX-270). Mass spectra were recorded on a MS9 (AEZ Manchester) spectrometer.

The pitch, temperature constants *A*, *B* and *C*, and the clearing point depression were measured in mixture 3010 from F. Hoffmann-La Roche Ltd (using the Grandjean-Cano wedge method for the pitch determination [43–45]).

3.1. (*R*)-Phenylethylene bis-4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]benzoate

A solution of *R*-(-)-1-phenyl-1,2-ethanediol (1 g, 0.007 mol), 4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]benzoic acid [38] (5 g, 0.015 mol), *N,N'*-dicyclohexylcarbodiimide (3 g, 0.016 mol), 4-dimethylaminopyridine (0.2 g) and dichloromethane (500 ml) was stirred at room temperature overnight, filtered to remove precipitate and evaporated down. The residue was purified by column chromatography on silica gel using toluene as eluent and recrystallization from ethanol (yield 3.6 g, 65 per cent). The melting point, optical rotation, enthalpy of fusion and other physical parameters of this diester and other diesters prepared using this general method are collated in tables 1–4.

3.2. 4-[3-(*trans*-4-Pentylcyclohexyl)propyloxy]benzaldehyde-dimethylacetal

A solution of 4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]benzaldehyde [38] (2.8 g, 0.0089 mol), trimethyl orthoformate (20 ml, 0.18 mol), and ammonium nitrate (0.1 g) was stirred at room temperature for one week, then poured into water (100 ml) and then extracted with diethyl ether (3 × 50 ml). The combined organic layers were washed with brine (2 × 50 ml), dried (MgSO₄), filtered and evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel with 7:3 hexane/ethyl acetate mixture as eluent (yield 3.0 g, 95 per cent).

3.3. Dimethyl(*R,R*)-2-(4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate

A solution of 4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]benzaldehyde-dimethylacetal (0.7 g, 0.0019 mol), *L*-(+)-dimethyl-tartrate (0.38 g, 0.0021 mol), pyridinium-(toluyl-4-sulphonate) (0.02 g) and toluene was heated for over 2 h so that the toluene/methanol mixture generated was continually distilled off. The solution was evaporated down and the residue purified by column chromatography on silica gel using a 7:3 hexane/ethyl acetate mixture as eluent and recrystallization from ethanol at –25°C. The melting point, enthalpy of fusion, optical rotation and several other physical properties of this dioxolane and other dioxolanes prepared using this general method are recorded in table 5.

3.4. 4-Cyano-4'-[3-(*trans*-4-pentylcyclohexyl)propyloxy]biphenyl

A solution of 3-(*trans*-4-pentylcyclohexyl)propane-1-ol [36] (15.9 g, 0.075 mol), 4-cyano-4'-hydroxybiphenyl (14.7 g, 0.075 mol), diethyl azodicarboxylate (13.0 g, 0.075 mol), triphenylphosphine (19.7 g, 0.075 mol) and tetrahydrofuran (250 ml) was stirred at room temperature overnight and then evaporated down. The solid residue was taken up in warm hexane (200 ml), filtered to remove precipitate (PPh₃O) and evaporated down once more. Purification of the residue by column chromatography on silica gel using 19:1 hexane/ethyl acetate mixture as eluent and then recrystallization from ethanol yielded the pure ether (24.5 g, 84 per cent), $T_{CSA} = 83^{\circ}\text{C}$; $T_{SAN} = 50^{\circ}\text{C}$; $T_{NI} = 167^{\circ}\text{C}$. IR (KBr): 2954, 2847, 2223, 1603, 1405, 823 cm^{-1} . MS: 389 (M^+), 195.

3.5. 4-Formyl-4'-[3-(*trans*-4-pentylcyclohexyl)propyloxy]biphenyl

A solution of diisobutyl aluminium hydride (20 per cent v/v) in toluene (200 ml) was added dropwise to a solution of 4-cyano-4'-[3-(*trans*-4-pentylcyclohexyl)propyloxy]biphenyl (10.2 g, 0.026 mol) at 0°C . After completion of the addition the reaction solution was allowed to regain room temperature slowly and was stirred at this temperature overnight. The reaction solution was cooled to 0°C and cold 1 N sulphuric acid (500 ml) was added carefully. The organic phase was separated off and the aqueous phase extracted with toluene (3×100 ml). The combined organic phases were washed with water (2×200 ml), dried (MgSO₄), filtered and finally evaporated down under reduced pressure. The residue was purified by recrystallization from ethyl acetate to give the pure aldehyde (6.6 g, 65 per cent), $T_{CSA} = 123^{\circ}\text{C}$; $T_{SAN} = 132^{\circ}\text{C}$; $T_{NI} = 156^{\circ}\text{C}$. IR (KBr): 2920, 2848, 2737, 1694, 1599, 1496, 1259, 1183, 1031, 819 cm^{-1} . MS: 392 (M^+), 198.

3.6. Dibutyl (*R,R*)-2-(4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]-4'-biphenyl)-1,3-dioxolane

Boron trifluoride diethyl etherate (0.05 ml) was added to a solution of 4-formyl-4'-[3-(*trans*-4-pentylcyclohexyl)propyloxy]biphenyl (1.0 g, 0.0026 mol), dimethyl (*R,R*)-2,3-bis(trimethylsiloxy)succinate [46] (1.25 g, 0.0030 mol) and ethylene chloride (40 ml) at 0°C and stirred at this temperature for 30 min. Trifluoro sulphonic acid (0.015 ml) was added and the resultant solution stirred at room temperature overnight, then added to water (100 ml). The organic layer was separated off and the aqueous layer extracted with dichloromethane (2×50 ml). The combined organic layers were washed with water (2×100 ml), dried (MgSO₄), filtered and finally evaporated down. Purification of the residue by column chromatography on silica gel with a 9:1 hexane/ethyl acetate mixture as eluent and recrystallisation from ethanol. The physical properties of this dioxolane and other dioxolanes prepared by this general method are collated in table 6.

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