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Synthesis and mesomorphic properties of oxadiazole esters derived from (*R*)-2-octanol, (*S*)-2-*n*-octyloxypropanol and (2*S*,3*S*)-2-chloro-3-methylpentanol

M. L. Parra[a]; P. I. Hidalgo[a]; E. Y. Elgueta[a]
[a] Facultad de Ciencias Químicas, Departamento de Química Orgánica, Universidad de Concepción, Casilla 160-C, Concepción, Chile

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Synthesis and mesomorphic properties of oxadiazole esters derived from (*R*)-2-octanol, (*S*)-2-*n*-octyloxypropanol and (2*S*,3*S*)-2-chloro-3-methylpentanol

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Facultad de Ciencias Químicas, Departamento de Química Orgánica, Universidad de Concepción, Casilla 160-C, Concepción, Chile

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A novel series of chiral liquid crystalline materials based on 1,3,4- and 1,2,4-oxadiazole derivatives were synthesised. These compounds contain a chiral chain derived from (*R*)-2-octanol (**Ia–Ic**), (*S*)-ethyl lactate (**IIa–IIc**) or (*S*)-isoleucine (**IIIa–IIIc**). Their liquid crystalline properties were studied by polarizing optical microscopy and differential scanning calorimetry. With the exception of compounds **IIa** and **IIb**, all of the new compounds exhibit an enantiotropic chiral nematic (cholesteric) phase. A monotropic chiral smectic C phase (ferroelectric) was also found in compounds **Ia**, **IIa** and **IIb**, whereas in compound **IIIa** an enantiotropic chiral smectic C phase was observed. Compounds **Ic**, **IIc**, **IIIb** and **IIIc** are purely chiral nematic (cholesteric) in character. In addition, a monotropic blue phase was observed in compounds **Ib** and **IIIa**.

Keywords: oxadiazole derivatives; cholesteric phases; blue phases; ferroelectric liquid crystals

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1. Introduction

The correlation between chemical structure and mesomorphic properties is one of the most important problems in the science of liquid crystals (LCs). Knowledge about the influence of different structural elements of the molecules on the physico-chemical characteristics of mesomorphic organic compounds allows chemists to synthesize LCs with the required properties.

Our interest in chiral calamitic LCs containing a five-membered heterocycle in the mesogenic core, especially materials displaying cholesteric (chiral nematic, N*) and ferroelectric (chiral smectic C, SmC*) mesophases, has led us to design new chiral molecules which incorporate the 1,3,4- and 1,2,4-oxadiazole heterocycles.

Examples of calamitic chiral LCs derived from five-membered have been reported and these include chiral 1,3,4-thiadiazole (*1–5*), chiral pyrazole and isoxazole (*6*) and chiral 1,2,3-triazole (*7, 8*) derivatives.

The 1,3,4- and 1,2,4-oxadiazole derivatives have also proved highly efficient in promoting mesomorphic properties, especially 1,3,4-oxadiazole derivatives. However, most of them are generally achiral calamitic molecules exhibiting nematic/smectic phases (*9–22*).

Previously, we have reported non-chiral mesomorphic 1,3,4-oxadiazole derivatives (*9, 23–25*) displaying a broad temperature range of tilted smectic phase and a new series of achiral *n*-alkoxy 1,2,4-oxadiazole-based compounds, where the *n*-alkoxy varied from 6 to 10 or 12 carbon atoms. The homologues with 6–10 carbon atoms in the *n*-alkoxy chain exhibited a nematic phase, whereas the homologue with 12 carbon atoms in the *n*-alkoxy chain displayed a smectic A–nematic (SmA–N) dimorphism (*26*). In addition, a variety of achiral mesogenic 1,2,4-oxadiazoles have been synthesized by Torgova *et al.* (*27*). Samulski and co-workers also reported a molecular system of nonlinear mesogens having an oxadiazole core, and their liquid crystallinity was examined by focusing on the biaxiality in smectic and nematic phases (*28, 29*).

In this work, as part of our continuing research on heterocyclic mesogens design, we describe the synthesis and mesomorphic properties of three novel series of chiral calamitic 1,3,4- and 1,2,4-oxadiazole derivatives. The chiral terminal chains are derived from (*R*)-2-octanol, (*S*)-ethyl lactate or (*S*)-isoleucine. The other terminal substituent is a thioalkyl chain (**Ia**, **IIa**, **IIIa**) or an alkoxy chain (**Ib**, **IIb**, **IIIb** and **Ic**, **IIc**, **IIIc**) with the number of carbon atoms kept constant at $n=12$.

The main aim of this work was to obtain chiral LCs with helical structure and cholesteric (N*) and ferroelectric (SmC*) phases and to study the effect of the nature of the chiral alkoxy chain and the effect of the heterocyclic moiety (1,3,4- and 1,2,4-oxadiazoles) on the mesomorphic properties. To the best of our knowledge, there have been no reports on the mesomorphic behaviour of chiral calamitic oxadiazole derivatives.

*Corresponding author. Email: mparra@udec.cl

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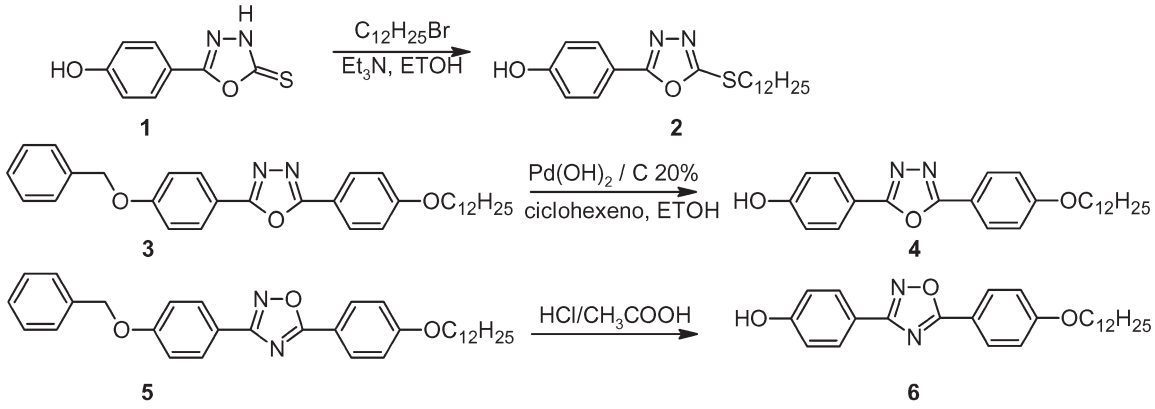

Scheme 1. Synthetic route for heterocyclic precursors **2**, **4** and **6**.

2. Synthesis

This study involved the synthesis and characterization of heterocyclic precursors **2**, **4** and **6** and chiral precursors **Q1–Q3** to prepare the target chiral mesogens **Ia–IIIc**.

The synthesis of compounds **2**, **4** and **6** is outlined in Scheme 1.

Synthesis and analytical data for thione **1** and oxadiazole derivatives **3** and **5** which are precursors of heterocyclic oxadiazoles **2**, **4** and **6**, have been reported previously (*24, 26*). The selective S-alkylation with *n*-dodecyl bromide of thione **1** leads to the phenolic oxadiazole **2**, according to the procedure reported in the literature (*10, 24*). The benzyl group in oxadiazoles **3** and **5** was removed using standard synthetic procedures (*6*) leading to the formation of the corresponding phenolic 1,3,4- and 1,2,4-oxadiazole (**4** and **6**, respectively).

Scheme 2 illustrates the synthesis of the chiral precursors **Q1–Q3**.

The chiral alcohols chosen as intermediates to prepare **Q1–Q3** were: (*R*)-2-octanol, (*S*)-2-*n*-octyloxypropanol and (2*S*,3*S*)-2-chloro-3-methylpentanol. The former was purchased from Merck while the latter were prepare using (*S*)-ethyl lactate and (*S*)-isoleucine as chiral precursors, according to methods described elsewhere (*30–35*).

The synthesis of the chiral 4-alkoxybenzoic acid chlorides (**Q1–Q3**) was achieved by Mitsunobu reaction (*36*) starting from methyl 4-hydroxybenzoate and the corresponding chiral alcohols, (*R*)-2-octanol, (*S*)-2-*n*-octyloxypropanol and (2*S*,3*S*)-2-chloro-3-methylpentanol. The resulting esters were saponified leading to the formation of corresponding chiral acids (**7–9**), followed by reaction with oxalyl chloride (*5*). It is known that the reaction of a phenol with primary or secondary alcohol in the presence of DIAD/triphenylphosphine (Mitsunobu reaction) produces an alkyl aryl ether. For reaction of secondary alcohols, there is inversion at the hydroxycarbon indicating that the reaction occurs by activation of the alcohol followed by SN^2 displacement by the phenol (*36*). Therefore, the Mitsunobu reaction between the methyl 4-hydroxybenzoate and (*R*)-2-octanol proceeded with inversion of the configuration at the chiral centre.

The chiral mesomorphic oxadiazoles **Ia-c–IIIa-c** (Scheme 3) were obtained by esterification of chiral precursors (**Q1–Q3**) with the corresponding phenolic oxadiazole derivatives (**2**, **4** and **6**) according to the procedure previously described (*9, 10*).

3. Results and discussion

Mesomorphic properties

The phase transitions of compounds of the **I–III** series were studied using polarizing optical microscopy (POM) and differential scanning calorimety (DSC). Phase transition temperatures observed by POM agree well with the corresponding DSC thermograms. The phase transitions and thermodynamic data for compounds of the **I–III** series are summarized in Table 1 and a graphical representation of the mesomorphic behaviour is presented in Figure 1, in which transition temperatures obtained both on heating and on cooling are presented.

In order to aid an analysis of their mesomorphic behaviour, the target compounds were grouped into three sets: compounds of set **Ia–Ic** contain a chiral chain derived from chiral 2-octanol, whereas compounds of sets **IIa–IIc** and **IIIa–IIIc** contain a chain derived from chiral ethyl lactate and chiral isoleucine, respectively. The other terminal substituent is an

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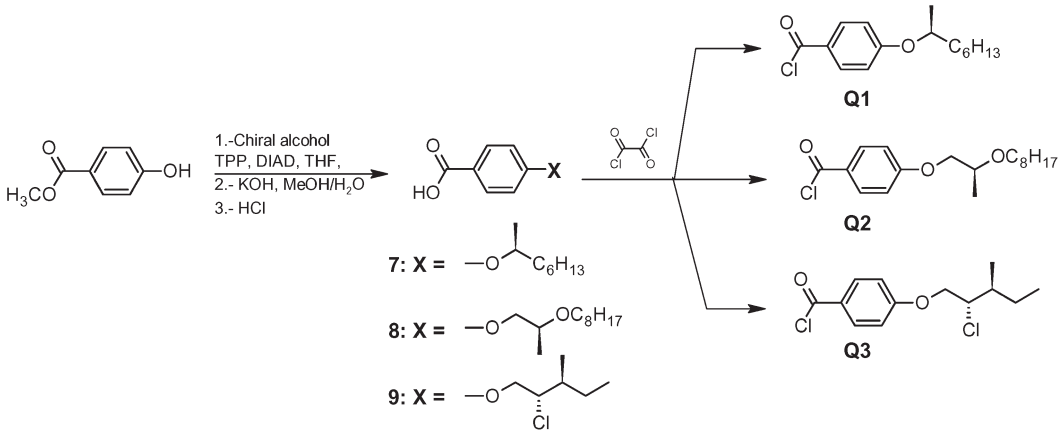
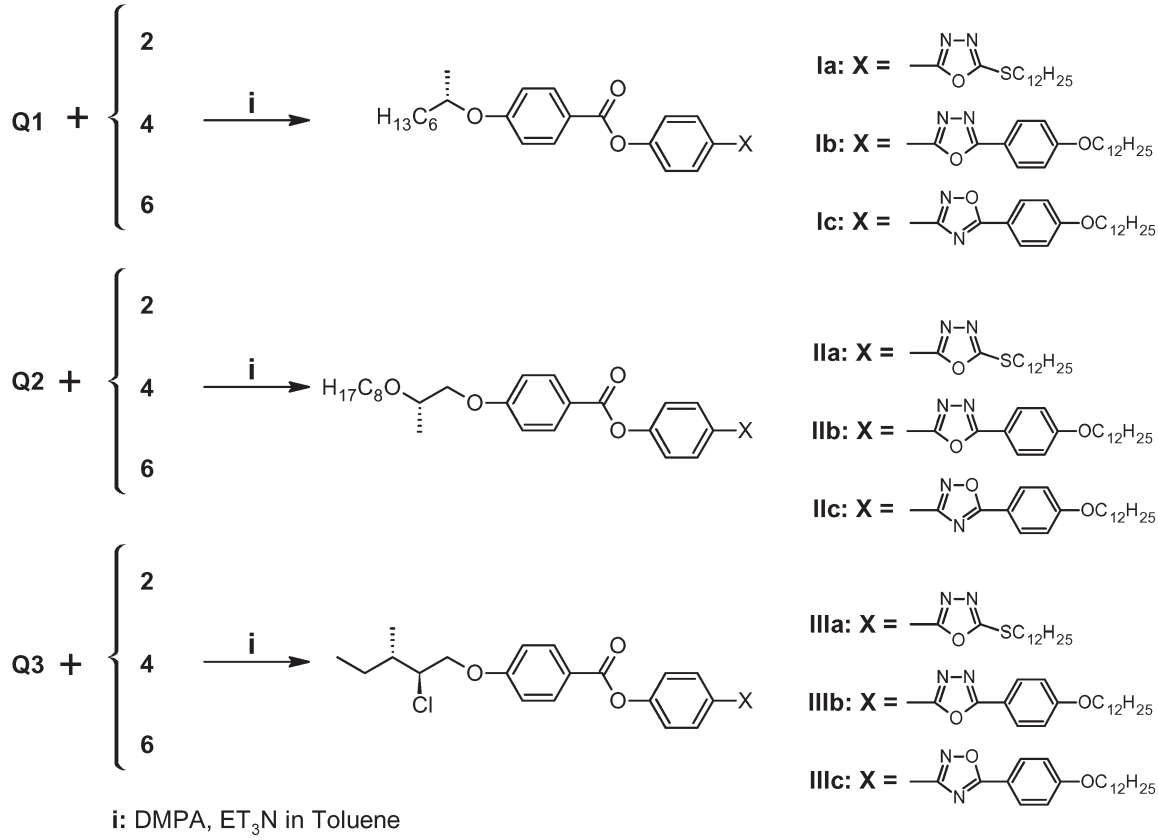


Scheme 2. Synthetic route for chiral precursors **Q1–Q3**.

achiral thioether chain in compounds **Ia–IIIa** and an achiral alkoxy chain in compounds **Ib–Ic**, **IIb–IIc** and **IIIb–IIIc** with the proviso that the total number of carbon atoms for both substituents (thioether and alkoxy chains) must remain as 12.

As can be seen from Table 1 and Figure 1, all the compounds in set **I** exhibit mesomorphic properties. In each case, an enantiotropic chiral nematic (N*) phase was observed. On cooling, a monotropic chiral smectic C (SmC*) phase was also observed for compound **Ia** and a monotropic blue phase (BP), which appears in a very narrow temperature range (2°C), was observed for compound **Ib**.

Replacement of the chiral alkoxy chain derived from chiral 2-octanol in compounds **Ia–Ic** by a chiral alkoxy chain derived from chiral ethyl lactate results in the disappearance of the enantiotropic N* phase in the compounds **IIa–IIb** and only the monotropic



Scheme 3. Synthetic route for chiral mesogens **Ia–Ic**, **IIa–IIc** and **IIIa–IIIc**.

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Table 1. Transition temperatures (°C) and enthalpies ($J\,g^{-1}$, in parentheses) of the chiral compounds **Ia–Ic**, **IIa–IIc** and **IIIa–IIIc** (Cr=crystal, SmC*=chiral smectic C, BP=blue phase, N*=chiral nematic, I=isotropic).

Compound	Transition temperatures (enthalpies)
Ia	Cr 38.4 (45.7) N* 43.4 (0.48) I
	I 42.2 (4.15) N* 33.5 (5.16) SmC* 13.6 (33.02) Cr
Ib	Cr 79.2 (49.5) N* 83.2 (0.36) I
	I 83.1[a] BP 81.1 (1.35) N* 72.9 (53.4) Cr
Ic	Cr 78.9 (78.4) N* 114.1 (1.32) I
	I 112.5 (1.53) N* 53.3 (65.7) Cr
IIa	Cr 57.1 (72.5) I
	I 53.8 (11.4) SmC* 21.8 (61.4) Cr
IIb	Cr 94.5 (52.6) I
	I 89.2 (7.15) SmC* 81.4 (55.8) Cr
IIc	Cr 104.6 (61.0) N* 202.7 (0.77) I
	I 201.1 (1.79) N* 82.1 (27.5) Cr
IIIa	Cr 51.9 (66.9) SmC* 56.7[a] N* 87.6 (1.94) I
	I 86.9[a] BP 85.7 (1.98) N* 54.6 (3.45) SmC* 28.1 (55.5) Cr
IIIb	Cr 106.9 (35.5) N* 125.8 (0.55) I
	I 124.6 (0.18) N* 98.9 (34.6) Cr
IIIc	Cr 80.6 (41.8) N* 160.6 (2.06) I
	I 159.2 (1.82) N* 67.9 (40.2) Cr

[a]Optical microscopy data.

SmC* phase present in compound **Ia** was maintained in compound **IIa**, and the monotropic BP phase present in compound **Ib** was replaced by a monotropic SmC* phase in compound **IIb**. In contrast, all compounds of the set **IIIa–IIIc**, which contain a chiral alkoxy chain derived from chiral isoleucine, display enantiotropic behaviour. An enantiotropic phase sequence is observed for compound **IIIa** (Cr–SmC*–N*–I), whereas compounds **IIIb** and **IIIc** are purely N* in character. Thus, the mesomorphic behaviour strongly depends of the nature of the chiral chain in the molecule.

These results show that the chiral chain derived from chiral isoleucine in compounds of set **IIIa–IIIc** favours the enantiotropic SmC* and N* phases in compounds **IIIa** and enantiotropic N* phase in compounds **IIIb** and **IIIc**, indicating that the lateral dipolar interactions associated with terminal chiral chain dipoles must be much more favoured in compounds **IIIa–IIIc**, containing a chiral alkoxy chain derived from chiral isoleucine, than compounds **Ia–Ic** and **IIa–IIc** with a chiral alkoxy chain derived from chiral 2-octanol and with a chiral alkoxy chain derived from chiral ethyl lactate, respectively.

On the other hand, in each set of compounds some significant differences between their rigid core can be noted. Compounds **Ia–IIIa** and **Ib–IIIb** contain a 1,3,4-oxadiazole ring, whereas compounds **Ic–IIIc** have a 1,2,4-oxadiazole heterocycle.

Although compounds **Ic, IIc** and **IIIc** have the same chiral alkoxy chain as compounds **Ia–Ib** (derived from chiral 2-octanol), **IIa–IIb** (derived from chiral ethyl lactate) and **IIIa–IIIb** (derived from chiral isoleucine), significant differences in their mesomorphic behaviour is observed. Compounds **Ic**, **IIc** and **IIIc** have broader mesomorphic temperature ranges (~35°C, 98°C and 80°C, respectively) than compounds **Ia** (5°C), **Ib** (4°C), **IIIa** (~36°C) and **IIIb** (~19°C).

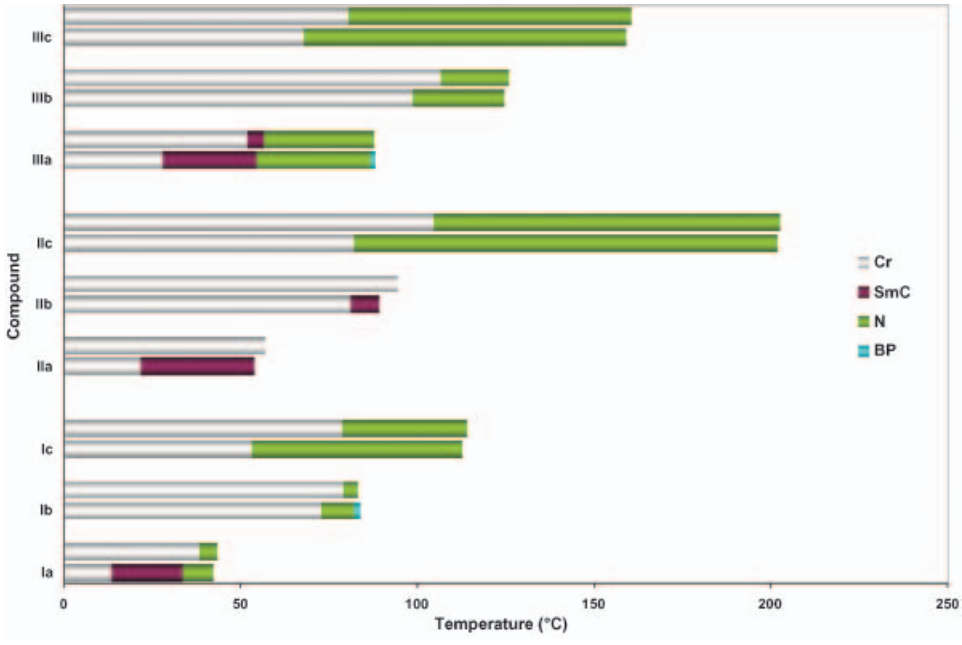

Figure 1. Plots of the mesomorphic behaviour of compounds **Ia–Ic**, **IIa–IIc** and **IIIa–IIIc**.

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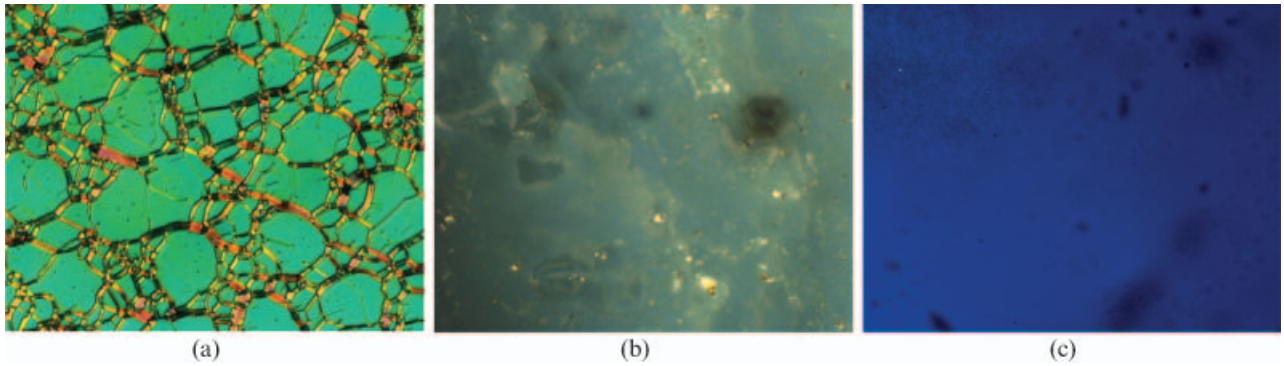

Figure 2. Mesophase textures obtained on cooling at $1^{\circ}C\,min^{-1}$: (a) Oily streaks texture (N*) at 40°C for compound **Ia**; (b) pseudo-homeotropic texture (SmC*) at 30°C for compound **Ia**; (c) blue phase at 82°C for compound **Ib**.

If we compare compounds **Ic–IIIc** with, for instance, their structural isomers **Ib–IIIb**, in each case the only structural difference relates with the heterocyclic ring, in one case 1,2,4-oxadiazole (**Ic–IIIc**) and the other case 1,3,4-oxadiazole (**Ib–IIIb**). Compounds **Ic–IIIc** have higher mesosomorphic thermal stability than their structural isomers, **Ib–IIIb**. Therefore, the mesomorphic thermal behaviour strongly depends on the nature of the heterocyclic ring in the molecule. This should mainly be due to the deviation of the molecular shape from linearity, which is much more significant for 1,3,4-oxadiazoles and is especially strong if the oxadiazole ring occupies a central position of the rigid aromatic core. It is known that 2,5-disubstituted 1,3,4-oxadiazole and 3,5-disubstituted 1,2,4-oxadiazole derivatives have an exocyclic bond angle of 134° and 140°, respectively (*37*), indicating that the 1,3,4-oxadiazole in the central rigid core produces a greater distortion of the linearity of the molecules when compared with the 1,2,4-oxadiazole derivatives. This deviation from the typical rod-like mesogen shape could explain the differences in the mesomorphic behaviour of these compounds reported here.

In summary, the mesomorphic properties of all the compounds were found to be strongly dependent on the molecular shape and on the type of chiral tail. The 1,2,4-oxadiazole derivatives exhibit stronger mesomorphic behaviour than the 1,3,4-oxadiazole derivatives and for compounds of set **IIIa–IIIc**, the alkoxy chiral tail derived from chiral isoleucine gives rise to the best mesomorphic properties.

In addition, we have prepared for the first time chiral LC compounds containing the 1,3,4- and 1,2,4-oxadiazole ring. The results are very promising and design and the synthesis of related mesomorphic optically active oxadiazoles is in progress and will be reported in due course.

Textures observed by polarizing optical microscopy

The mesophases observed for compounds **Ia–IIIc** were identified based on optical textures observed under optical microscope, using heating and cooling cycles. Figure 2 shows the typical optical textures of the mesophases exhibited by these compounds (*38, 39*).

The chiral nematic phase (N*) was characterized by the appearance of the oily-streaks texture characteristic of the cholesteric phase (see Figure 2(a)).

The SmC* phase present in compounds **Ia**, **IIa** and **IIIa** was identified by its characteristic pseudo-homeotropic texture (Figure 2(b)).

On the other hand, an amorphous texture similar to a blue fog was observed for the monotropic BP of compounds **Ib** and **IIIa**, which is consistent with a blue phase (see Figure 2(c)) (*40, 41*).

4. Experimental

Characterization

The structures of the compounds were confirmed by ^{1}H NMR and ^{13}C NMR (Bruker AC-250P) spectra and FTIR (Nicolet 550) spectra; the purity of the final products was evaluated by thin layer chromatography.

Transition temperatures and textures of mesophases were determined by optical microscopy using an Ortholux Pol BK-11 polarizing microscope equipped with a Mettler FP 800 hot stage.

The transition temperatures and enthalpies were investigated by DSC using a Rheometric DSC-V calorimeter. Samples were encapsulated in aluminium pans and studied at scanning rate of $5^{\circ}C\,min^{-1}$ during heating and cooling. The instrument was calibrated using an indium standard (156.6°C, $28.44\,J\,g^{-1}$).

Optical rotational measurements were obtained using a Polax-2L automatic polarimeter. The samples

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were prepared in spectroscopy grade chloroform, and results are quoted at 25°C with a monochromatic sodium light source.

Synthesis of intermediates and products

(*S*)-ethyl lactate, (*S*)-isoleucine and (*R*)-2-octanol were purchased from Merck. The organic solvents were of analytical grade quality and all were dried by traditional methods. Analytical thin layer chromatography (TLC) was conducted on Merck aluminum plates with 0.2 mm of silica gel 60 F-254.

The chiral alcohol (2*S*,3*S*)-2-chloro-3-methylpentanol was synthesized using (*S*)-isoleucine, according to the method described in the literature (*30–32*).

The chiral alcohol (*S*)-2-*n*-octyloxypropanol was synthesized by the method described in the literature (*33–35*).

*5-(4-hydroyphenyl)-2-n-dodecylthio-1,3,4-oxadiazole (**2**)*

This compound was synthesized from thione **1** by the method described elsewhere (*10, 24*). The product was obtained in solid form, and was purified by crystallization from ethanol/water (4/1). Yield 86%, m.p. 99°C. ^{1}H NMR (250 MHz, TMS, DMSO-d_6): δ 0.85 (t, 3H), 1.14–1.38 (m, 18H, aliph. chain), 1.73 (m, 2H), 3.25 (t, 2H, SCH_2), 6.92 (d, J=8.75 Hz, 2H, arom. H), 7.76 (d, J=8.75 Hz, 2H, arom. H), 10.33 (s, 1H, OH). ^{13}C NMR (62.9 MHz, TMS, DMSO-d_6): δ 13.9, 22.1, 27.7, 28.3, 29.0, 31.3, 32.0 (aliph. C), 116.1, 128.3 (arom. C), 113.7, 160.8, 162.6, 165.1 (quaternary arom. C). IR (KBr disk, cm^{-1}): 3435 (O–H), 2921 (Csp^3–H), 1599 (C=C).

*5-(4-hydroxyphenyl)-2-(4-n-dodecyloxyphenyl-1,3,4-oxadiazole (**4**)*

To a mixture of 1.95 mmol of **3**, 8 ml of cyclohexene and 16 ml of ethanol, was added in small portions and under a nitrogen atmosphere 0.1 g of $Pd(OH)_2$/C (20%). The mixture was heated at reflux for 24 h; it was then filtered through a pad of Celite and the solvent evaporated (*6*). The product was purified by crystallization in ethanol. Yield 85%, m.p. 134°C. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.80 (t, 3H, CH_3), 1.21–1.70 (m, 20H, aliph. chain), 4.03 (t, 2H, OCH_2), 6.05 (s, 1H, OH), 6.96 (d, J=7.84 Hz, 2H, arom. H), 7.11 (d, J=7.95 Hz, 2H, arom. H), 7.92 (d, J=7.79 Hz, 2H, arom. H), 7.98 (d, J=7.94 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 13.8, 22.0, 25.3, 28.4, 28.6, 28.9, 31.2 (aliph. C), 67.8 ($O\underline{C}H_2$), 115.2, 116.1, 128.2, 128.4 (arom. C), 114.2, 115.7, 160.7, 161.3, 163.2, 163.6 (quaternary arom. C). IR (KBr disk, cm^{-1}): 3109 (O–H), 2924 (Csp^3–H), 1606 (C=C), 1255 (C–O).

*3-(4-hydroxyphenyl)-5-(4-n-dodecyloxyphenyl)-1,2,4-oxadiazole (**6**)*

A mixture containing 0.78 mmol of compound **5**, 12 ml of glacial acetic acid and 6 ml of hydrochloride acid was heated under reflux for 6 h. The mixture was then poured into water/ice and was neutralized with aqueous NaOH. The solid was filtered and washed with water (*6*). The product was recrystallized from *n*-hexane. Yield 83%, m.p. 110–113°C. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.80 (t, J=6.20 Hz, 3H, CH_3), 1.25–1.73 (m, 20H, aliph. chain), 3.95 (t, 2H, OCH_2), 6.13 (s, 1H, O–H), 6.88 (d, J=8.75 Hz, 2H, arom. H), 6.94 (d, J=7.04 Hz, 2H, arom. H), 7.96 (d, J=8.76 Hz, 2H, arom. H), 8.05 (d, J=6.97 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 14.1, 22.7, 26.0, 29.3, 29.6, 31.9 (aliph. C), 70.1 ($O\underline{C}H_2$), 114.9, 115.8, 129.4, 130.0 (arom. C), 116.2, 119.5, 157.8, 163.5, 168.1, 175.8 (quaternary arom. C). IR (KBr disk, cm^{-1}): 3412 (O–H), 2922 (Csp^3–H), 1610 (C=C), 1251 (C–O).

*Optically active acids (**7–9**)*

To a mixture containing 6.30 mmol of methyl *4*-hydroxybenzoate and 9.45 mmol of triphenylphosphine (TPP) and 25 ml of dried THF, was added, under nitrogen atmosphere and at room temperature, 9.45 mmol of the appropriate chiral alcohol dissolved in 20 ml of dried THF. Then, a solution of 9.45 mmol of DIAD in 75 ml of dried THF was added dropwise to the solution (*36*). The reaction mixture was stirred for 23 h at room temperature. The solvent was later removed under reduced pressure and the residue was dissolved in a mixture of *n*-hexane/ethyl acetate 7/3 and stirred for 1 h. After this, a white solid of triphenylphosphine oxide was formed and filtered off. The filtered mixture was then concentrated under vacuum. The resulting chiral esters were obtained in liquid form, and were used in subsequent reactions without further purification.

The chiral benzoic acids (**7–9**) were obtained after saponification of the corresponding chiral esters with an excess of KOH in a mixture methanol/water 2/1 under reflux for 8 h. The mixture was poured into 100 ml of water and acidified with hydrochloric acid (*5*). The solid was filtered off, washed with water and recrystallized from ethanol.

For optically active 4-(1′-methylheptyloxy)benzoic acid (**7**), yield 56% of a white solid, m.p. 55°C. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.90 (t, 3H,

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CH_3), 1.11–1.75 (m, 13H, $5CH_2$, $C\underline{H}_3$–CH), 4.46 (m, 1H, CH_3–C<u>H</u>), 6.91 (d, J=8.86 Hz, 2H, arom. H), 8.05 (d, J=8.85 Hz, 2H, arom. H), 10.8 (1H, –COOH). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 14.1, 19.6, 22.6, 25.4, 29.2, 31.7, 36.3 (aliph. C), 74.5 (-O<u>C</u>H(CH_3)-), 115.1, 132.4 (arom C), 121.1, 162.9 (quaternary arom. C), 172.1 (C=O). IR (KBr disk, cm^{-1}): 3300–2500 (O–H), 2930 (Csp^3–H), 1680 (C=O), 1603 (C=C).

For optically active 4-(2′-octyloxypropyloxy)benzoic acid (**8**), yield 82% of a white solid, m.p. 45°C. ^{1}H NMR (250 MHz, TMS, DMSO-d_6): δ 0.93 (t, 3H, CH_3), 1.13 (d, 3H, CH-C<u>H</u>$_3$), 1.17–1.51 (m, 12H, aliph. chain), 3.48–3.58 (m, 2H, OCH_2), 3.80 (q, 1H, –C<u>H</u> of the chiral chain), 4.1 (m, 2H, ϕ-OC<u>H</u>$_2$–), 7.09 (d, J=8.65 Hz, 2H, arom. H), 7. 79 (d, J=8.70 Hz, 2H, arom. H), 13.7 (s, 1H, COO<u>H</u>). ^{13}C NMR (62.9 MHz, TMS, DMSO-d_6): δ 13.9, 16.8, 22.1, 25.6, 28.7, 28.8, 29.6, 31.2 (aliph. C), 68.3 (-O<u>C</u>H$_2$-CH$_2$-), 71.7 (-<u>C</u>H-), 72.9 (ϕ-O<u>C</u>H$_2$-), 114.3, 131.3 (arom C), 122.9, 162.2 (quaternary arom. C), 166.9 (C=O). IR (KBr disk, cm^{-1}): 3200–2500 (O–H), 2923 (Csp^3–H), 1721 (C=O), 1600 (C=C).

For optically active 4-(2′-chloro-3′-methylpentyloxy)benzoic acid (**9**), yield 56% of a white solid, m.p. 42°C. ^{1}H NMR (250 MHz, DMSO-d_6): δ 0.92 (t, 3H, CH_3), 1.09 (d, 3H, C<u>H</u>$_3$–CH–), 1.35–1.51 (m, 2H, –C<u>H</u>$_2$–CH$_3$), 1.96 (m, 1H, –C<u>H</u>–CH$_3$), 4.08 (m, 3H, OCH_2, CH–Cl), 6.95 (d, J=8.65 Hz, 2H, arom. H), 8.08 (d, J=8.70 Hz, 2H, arom. H), 11.6 (s, 1H, COO<u>H</u>). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ 11.3, 15.8 ($2CH_3$), 24.4 (CH_2), 37.9 (-<u>C</u>H-CH$_3$), 64.34 (-<u>C</u>H-Cl), 69.8 (-OCH_2-), 114.7, 131.8 (arom C), 130.2, 163.1 (quaternary arom. C), 190.5 (C=O). IR (KBr disk, cm^{-1}): 3300–2500 (O–H), 2926 (Csp^3–H), 1679 (C=O), 1605 (C=C).

*Optically active acid chlorides **Q1–Q3***

These compounds were obtained by reaction of the corresponding chiral acid (**7–9**) with oxalyl chloride in dried dichloromethane, at room temperature under stirring for 24 h. The chiral acid chlorides (**Q1–Q3**) were obtained in liquid form after evaporation of the excess of oxalyl chloride and dichloromethane and were used in subsequent reaction without further purification.

*Optically active esters **Ia–IIIc***

To a mixture of 1 mmol of the corresponding phenol (**2**, **4**, **6**), 0.032 g of DMAP, 1 ml of dry triethylamine and 35 ml of dry toluene, was added 1 mmol of the corresponding acid chloride (**Q1–Q3**). The mixture was stirred at room temperature for 24 h. The resulting mixture was diluted with ether (30 ml). The organic solution was washed twice with water (30 ml) and once with brine (20 ml). The organic phase was dried over Na_2SO_4, filtered off and the solvent was evaporated (*9, 10*). The residue was purified by column chromatography, circular chromatography and recrystallization from ethanol.

For optically active 4-(5-*n*-dodecylthio-1,3,4-oxadiazole-2-yl)phenyl 4′-(1″-methylheptyloxy)benzoate (**Ia**), the crude product was purified by column chromatography (silica-gel: *n*-hexane/ethyl acetate 4/1) and circular chromatography (Chromatotron: dichloromethane/ethyl acetate 10/2) and recrystallized from ethanol. Yield 71% of a white solid. $[\alpha]_D$ (ca. 0.0104 g ml^{-1})=+38.5°. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.88 (2t, 6H, $2CH_3$), 1.25–1.33 (m, 22H, aliph. chain), 1.35 (d, 3H, CH_3 of the chiral chain), 1.44–1.87 (m, 8H, aliph. chain), 3.30 (t, 2H, S–CH_2), 4.49 (m, 1H, OC<u>H</u>–CH_3), 6.96 (d, J=8.93 Hz, 2H, arom. H), 7.35 (d, J=8.76 Hz, 2H, arom. H), 8.07 (d, J=8.76 Hz, 2H, arom. H), 8.13 (d, J=8.91 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 14.1, 19.5, 22.6, 22.7, 25.4, 28.6, 29.0, 29.1, 29.3, 29.4, 29.5, 29.6, 31.7, 31.9, 32.7, 36.1 (aliph. C), 74.3 (O–<u>C</u>H–), 115.3, 122.6, 128.0, 132.4 (arom. C), 120.7, 121.2, 153.7, 163.1, 164.4, 164.6 (quaternary arom. C), 165.1 (C=O). IR (KBr disk, cm^{-1}): 2920 (Csp^3–H), 1731 (C=O), 1606 (C=C).

For optically active 4-[5-(4-*n*-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]phenyl 4′-(1″-methylheptyloxy)-benzoate (**Ib**), the crude product was purified by column chromatography (silica-gel: *n*-hexane/ethyl acetate 4/1) and circular chromatography (Chromatotron: dichloromethane/ethyl acetate 10/1) and recrystallized from ethanol. Yield 77% of a white solid. $[\alpha]_D$ (ca. 0.0107 g ml^{-1})= +32.7°. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.88 (2t, 6H, $2CH_3$), 1.26–1.34 (m, 22H, aliph. chain), 1.45 (d, 3H, CH_3 of the chiral chain), 1.46–1.82 (m, 8H, aliph. chain), 4.04 (t, 2H, O–CH_2), 4.49 (m, 1H, OC<u>H</u>–CH_3), 6.97 (d, J=8.95 Hz, 2H, arom. H), 7.02 (d, J=8.92 Hz, 2H, arom. H), 7.39 (d, J=8.76 Hz, 2H, arom. H), 8.06 (d, J=8.90 Hz, 2H, arom. H), 8.14 (d, J=8.91 Hz, 2H, arom. H), 8.19 (d, J=8.77 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 14.1, 19.5, 22.6, 22.7, 25.4, 25.9, 29.2, 29.3, 29.6, 31.7, 31.9, 36.3 (aliph. C), 68.3 (O–CH_2), 73.9 (O–CH–), 114.9, 115.3, 122.6, 128.2, 128.7, 132.4 (arom. C), 116.1, 120.6, 121.5, 153.6, 161.9, 162.9, 163.5, 164.4 (quaternary arom. C), 170.6 (C=O). IR (KBr disk, cm^{-1}): 2923 (Csp^3–H), 1734 (C=O), 1609(C=C).

For optically active 4-[5-(4-*n*-dodecyloxyphenyl)-1,2,4-oxadiazole-3-yl]phenyl 4′-(1″-methylheptyloxy)-benzoate (**Ic**), the crude product was purified by column chromatography (silica-gel: *n*-hexane/ethyl

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acetate 4/1) and circular chromatography (Chromatotron: dichloromethane/ethyl acetate 10/1) and recrystallized from ethanol. Yield 74% of a white solid. $[\alpha]_D$ (ca. 0.0105 g ml^{-1})= +38.1°. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.89 (2t, 6H, $2CH_3$), 1.27–1.31 (m, 22H, aliph. chain), 1.35 (d, 3H, CH_3 of chiral chain), 1.38–1.86 (m, 8H, aliph. chain), 4.05 (t, 2H, O–CH_2), 4.49 (m, 1H, OCH–CH_3), 6.96 (d, J=8.95 Hz, 2H, arom. H), 7.03 (d, J=8.93 Hz, 2H, arom. H), 7.36 (d, J=8.74 Hz, 2H, arom. H), 8.15 (d, J=8.87 Hz, 4H, arom. H), 8.23 (d, J=8.75 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 14.1, 19.6, 22.6, 22.7, 25.4, 25.9, 29.1, 29.2, 29.3, 29.6, 31.7, 31.9, 36.3 (aliph. C), 68.3 (O–CH_2), 74.1 (O–CH–), 114.9, 115.2, 122.3, 128.8, 130.0, 132.4 (arom C), 116.5, 120.8, 124.6, 153.2, 162.8, 163.0, 164.5, 165.7 (quaternary arom. C), 168.2 (C=O). IR (KBr disk, cm^{-1}): 2923 (Csp^3–H), 1735 (C=O), 1609 (C=C).

For optically active 4-(5-*n*-dodecylthio-1,3,4-oxadiazole-2-yl)phenyl 4′-(2″-octyloxypropyloxy)benzoate (**IIa**), the crude product was purified by column chromatography (silica-gel: *n*-hexane/ethyl acetate 7/3) and circular chromatography (Chromatotron: dichloromethane/ethyl acetate 10/2) and recrystallized from ethanol. Yield 47% of a white solid. $[\alpha]_D$ (ca. 0.0102 g ml^{-1})=−19.6°. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.88 (2t, 6H, $2CH_3$), 1.26–1.33 (m, 28H, aliph. chain), 1.35 (d, 3H, CH_3 of chiral chain), 1.43–1.87 (m, 4H, aliph. chain), 3.29 (t, 2H, S–CH_2), 3.56 (m, 2H, –CH_2–O), 3.82 (m, 1H, –C<u>H</u>–CH_3), 3.97 (m, 1H, –C<u>H</u>$_2$–O-ϕ), 4.07 (m, 1H, –C<u>H</u>$_2$–O-ϕ), 7.00 (d, J=8.96 Hz, 2H, arom. H), 7.36 (d, J=8.74 Hz, 2H, arom. H), 8.07 (d, J=8.69 Hz, 2H, arom. H), 8.14 (d, J=8.92 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 14.1, 17.2, 22.6, 26.1, 28.5, 29.0, 29.2, 29.4, 29.6, 30.0, 31.9 (aliph. C), 70.4 (O-CH_2-), 72.6 (-<u>C</u>H$_2$-O-ϕ), 74.2(O-CH-), 114.5, 122.6, 128.0, 132.3 (arom C), 115.8, 115.9, 154.3, 164.2, 165.0, 165.4 (quaternary arom. C), 165.8 (C=O). IR (KBr disk, cm^{-1}): 2922 (Csp^3–H), 1732 (C=O), 1606(C=C).

For optically active 4-[5-(4-*n*-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]phenyl 4′-(2″-octyloxypropyloxy]benzoate (**IIb**), the crude product was purified by column chromatography (silica-gel: *n*-hexane/ethyl acetate 4/1) and circular chromatography (Chromatotron: dichloromethane/ethyl acetate 10/2) and recrystallized from ethanol. Yield 64% of a white solid. $[\alpha]_D$ (ca. 0.0105 g ml^{-1})=−23.8°. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.87 (2t, 6H, $2CH_3$), 1.26–1.28 (m, 28H, aliph. chain), 1.31 (d, 3H, CH_3 of chiral chain), 1.44–1.87 (m, 4H, aliph. chain), 3.29 (m, 2H, CH_2–O–), 3.84 (m, 1H, –OC<u>H</u>–CH_3), 3.93–4.01 (m, 4H, $2CH_2$–O– of the chiral chain), 7.00 (d, J=8.94 Hz, 2H, arom. H), 7.03 (d, J=8.92 Hz, 2H, arom. H), 7.39 (d, J=8.61 Hz, 2H, arom. H), 8.06 (d, J=8.74 Hz, 2H, arom. H), 8.15 (d, J=8.95 Hz, 2H, arom. H), 8.21 (d, J=8.70 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 14.1, 17.2, 22.7, 25.9, 26.1, 29.1, 29.3, 29.6, 30.1, 31.8, 31.9 (aliph. C), 68.3, 69.7, 71.8 (O-CH_2-), 73.5 (O-CH-), 114.5, 114.9, 122.6, 128.2, 128.7, 132.4 (arom C), 115.8, 121.3, 121.6, 153.6, 161.9, 163.5, 164.6, 165.4 (quaternary arom. C), 170.1 (C=O). IR (KBr disk, cm^{-1}): 2923 (Csp^3–H), 1732 (C=O), 1606 (C=C).

For optically active 4-[5-(4-*n*-dodecyloxyphenyl)-1,2,4-oxadiazole-3-yl]phenyl 4′-(2″-octyloxypropyloxy)benzoate (**IIc**), the crude product was purified by column chromatography (silica-gel: *n*-hexane/ethyl acetate 4/1) and circular chromatography (Chromatotron: dichloromethane/ethyl acetate 10/2) and recrystallized from ethanol. Yield 51% of a white solid. $[\alpha]_D$ (ca. 0.0106 g ml^{-1})=−23.5°. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.88 (2t, 6H, $2CH_3$), 1.27–1.30 (m, 28H, aliph. chain), 1.44 (d, 3H, CH_3 of chiral chain), 1.50–1.85 (m, 4H, aliph. chain), 3.31 (m, 2H, CH_2O–), 3.85 (m, 1H, –C<u>H</u>–CH_3), 3.94–4.03 (m, 4H, $2CH_2$–O of the chiral chain), 7.01 (d, J=8.84 Hz, 2H, arom. H), 7.02 (d, J=8.92 Hz, 2H, arom. H), 7.41 (d, J=8.55 Hz, 2H, arom. H), 8.09 (d, J=8.82 Hz, 2H, arom. H), 8.17 (d, J=8.95 Hz, 2H, arom. H), 8.23 (d, J=8.60 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 14.1, 17.2, 22.7, 25.9, 26.1, 29.1, 29.3, 29.6, 30.1, 31.8, 31.9 (aliph. C), 68.6, 69.9, 71.9 (O–CH_2–), 74.7 (O–CH–), 114.5, 115.4, 122.6, 128.2, 128.7, 132.4 (arom C), 115.8, 121.3, 121.6, 153.6, 161.9, 163.5, 164.6, 165.4 (quaternary arom. C), 170.1 (C=O). IR (KBr disk, cm^{-1}): 2921 (Csp^3–H), 1736 (C=O), 1606(C=C).

For optically active 4-(5-*n*-dodecylthio-1,3,4-oxadiazole-2-yl)phenyl 4′-(2″-chloro-3″-methylpentyloxy]benzoate (**IIIa**), the crude product was purified by column chromatography (silica-gel: *n*-hexane/ethyl acetate 4/1) and circular chromatography (Chromatotron: dichloromethane) and recrystallized from ethanol. Yield 50% of a white solid. $[\alpha]_D$ (ca. 0.0101 g ml^{-1})= +24.7°. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.80 (t, 3H, CH_3), 0.93 (t, 3H, CH_3), 0.96 (d, 3H, CH_3 of the chiral chain), 1.19–1.80 (m, 22H, aliph. chain), 1.85 (m, 1H, C<u>H</u>–CH_3), 3.23 (t, 2H, S–CH_2), 4.1 (m, 3H, C<u>H</u>$_2$O, C<u>H</u>–Cl), 6.98 (d, J=8.92 Hz, 2H, arom. H), 7.35 (d, J=8.74 Hz, 2H, arom. H), 8.06 (d, J=8.75 Hz, 2H, arom. H), 8.14 (d, J=8.92 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 11.3, 14.1, 19.1, 22.7, 26.0, 29.1, 29.6, 31.4, 31.9, 35.6, 66.7, 70.3 (aliph. C), 115.0, 128.2, 128.7, 132.4 (arom. C), 116.7, 120.9, 121.6, 153.3, 161.9, 163.7 (quaternary arom. C), 164.4 (C=O). IR (KBr disk, cm^{-1}): 2921 (Csp^3–H), 1730 (C=O), 1610 (C=C).

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For optically active 4-[5-(4-*n*-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]phenyl 4′-(2″-chloro-3″-methylpentyloxy)benzoate (**IIIb**), the crude product was purified by column chromatography (silica-gel: *n*-hexane/ethyl acetate 4/1) and circular chromatography (Chromatotron: dichloromethane) and recrystallized from ethanol. Yield 30% of a white solid. $[\alpha]_D$ (ca. 0.0105 g ml^{-1})= +23.8°. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.86 (t, 3H, CH_3), 0.90 (t, 3H, CH_3), 0.94 (d, 3H, CH_3), 1.26–1.80 (m, 22H, aliph. chain), 1.90 (m, 1H, C<u>H</u>–CH_3), 4.04–4.14 (m, 5H, 2CH_2O, CH–Cl), 6.99 (d, J=8.95 Hz, 2H , arom. H), 7.02 (d, J=8.90 Hz, 2H , arom. H), 7.37 (d, J=8.78 Hz, 2H, arom. H), 8.16 (d, J=8.91 Hz, 2H, arom. H), 8.19 (d, J=8.89 Hz, 2H, arom. H), 8.24 (d, J=8.76 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 11.6, 14.5, 19.1, 22.7, 26.0, 29.1, 29.6, 31.4, 32.0, 35.6, 68.7, 70.3 (aliph. C), 114.4, 115.1, 122.6, 128.2, 128.7, 130.0 (arom. C), 116.7, 120.9, 121.6, 153.3, 161.9, 163.7, 164.4, 165.5 (quaternary arom. C), 170.2 (C=O). IR (KBr disk, cm^{-1}): 2921 (Csp^3–H), 1730 (C=O), 1605 (C=C).

For optically active 4-[5-(4-*n*-dodecyloxyphenyl)-1,2,4-oxadiazole-3-yl]phenyl 4′-(2″-chloro-3″-methylpentyloxy)benzoate (**IIIc**), the crude product was purified by column chromatography (silica-gel: *n*-hexane/ethyl acetate 7/3) and circular chromatography (Chromatotron: dichloromethane/n-hexane 1/1) and recrystallized from ethanol. Yield 30% of a white solid. $[\alpha]_D$ (ca. 0.0107 g ml^{-1})= +23.4°. ^{1}H NMR (250 MHz, TMS, $CDCl_3$): δ 0.88 (t, 3H, CH_3), 0.92 (t, 3H, CH_3), 0.96 (d, 3H, CH_3 of the chiral chain), 1.26–1.80 (m, 22H, aliph. chain), 1.89 (m, 1H, C<u>H</u>–CH_3), 4.04–4.14 (m, 5H, 2C<u>H</u>$_2$O, C<u>H</u>–Cl), 6.98 (d, J=8.95 Hz, 2H, arom. H), 7.02 (d, J=8.94 Hz, 2H, arom. H), 7.36 (d, J=8.76 Hz, 2H, arom. H), 8.14 (d, J=8.91 Hz, 2H, arom. H), 8.17 (d, J=8.92 Hz, 2H, arom. H), 8.23 (d, J=8.76 Hz, 2H, arom. H). ^{13}C NMR (62.9 MHz, TMS, $CDCl_3$): δ 11.5, 14.4, 19.0, 22.8, 26.0, 29.1, 29.4, 31.3, 31.9, 35.7, 66.7, 70.3 (aliph. C), 114.1, 115.3, 122.8, 128.0, 128.7, 130.0 (arom. C), 116.6, 121.0, 121.6, 153.4, 162.0, 163.7, 164.5, 165.5 (quaternary arom. C), 170.2 (C=O). IR (KBr disk, cm^{-1}): 2920 (Csp^3–H), 1729 (C=O), 1606 (C=C).

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