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FLCs with a five-membered ring in the mesogenic core

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A study has been undertaken of the structure–activity relationship of eight new chiral compounds having either a pyrazole (series **P**) or an isoxazole (series **I**) ring as a central bridge in the mesogenic core. The presence of dimers in the pyrazole compounds accounts for their lower P_s values in comparison with the isoxazole analogues. The corresponding four β-diketone precursors have also been studied and these, as expected given their bent molecular shape, show much worse mesomorphic and ferroelectric behaviour. In order to complete the study, the molecular dipoles of the three types of derivative have been determined using AM1 calculations. Two types of chiral tail have been incorporated into the compounds: alkoxy and alkanoyloxy. The latter tail gives rise to the best mesomorphic and ferroelectric properties. A study of the tail conformations by MM2 calculations provides an explanation of these results. The highest P_s value (137 nC cm^{-2}) has been obtained for the isoxazole derivative with the (2*S*)-2-butyloxypropanoyloxy chiral tail (compound **I4**). The potential of all twelve compounds as chiral dopants for FLC mixtures has been evaluated by a study of 10 mol% binary mixtures in a standard host system.

1. Introduction

Our interest in the relationship between molecular structure and mesomorphic and ferroelectric behaviour has led us to design new chiral molecules which incorporate a five-membered heterocycle as a central bridge in the mesogenic core. Only a few examples of this type of structure in FLCs have been reported in the literature, and these include chiral thiadiazole derivatives which show broad S$_C^*$ ranges with high spontaneous polarization values [1]. Other five-membered heterocyclic compounds, such as pyrazoles and isoxazoles, have also proved highly efficient in promoting mesomorphic properties when acting as central bridges in 1,3-diphenylpyrazole and 1,3-diphenylisoxazole derivatives [2, 3]. These heterocyclic derivatives show a marked tendency to display smectic mesomorphism (both smectic A and smectic C). In addition, pyrazole and isoxazole rings can contribute significantly to the molecular dipole by virtue of the high dipole moment contained in the plane of the heterocycle. Both of the above aspects are relevant in the design of new compounds as ferroelectric liquid crystals.

On the basis of the points discussed above, we have synthesized and investigated the mesomorphic and ferroelectric properties of three novel series of compounds. The first series consists of four 1,3-diphenylpropane-1,3-diones (**dK**) substituted with a tail group in the *para*-position of each phenyl ring. The mesomorphic behaviour of previously reported β-diketones is rather poor [4]. Indeed, the most important role of β-diketones within the field of liquid crystals has been as precursors of mesogenic compounds such as metal-containing liquid crystal materials [5] and heterocyclic derivatives [2, 3]. The two other series of compounds described here are 1,3-diphenylpyrazoles (**P**) and 1,3-diphenylisoxazoles (**I**). These compounds are obtained from the corresponding β-diketones by reaction with hydrazine monohydrate or hydroxylamine hydrochloride, respectively. In order to achieve the non-centrosymmetry in the S$_C$ phase necessary for ferroelectric behaviour, one of the tail groups is chiral. The following alcohols and acids were chosen as chiral precursors: (1*S*)-1-butyloxycarbonylethanol (**1**), (2*S*)-2-octanol (**2**), (2*S*,3*S*)-2-chloro-3-methylpentanoic acid (**3**) and (2*S*)-2-butyloxypropanoic acid (**4**) (see structures over).

Computational techniques such as molecular mechanics calculations (MM2) [6] and semi-empirical calculations (MOPAC-AM1) [7] have been used to examine the conformational characteristics of these structures, as well as to estimate their dipole moments. The correlation of the results from these calculations and the experimental studies has provided interesting data concerning the relationship between molecular structure and mesomorphic and ferroelectric properties.

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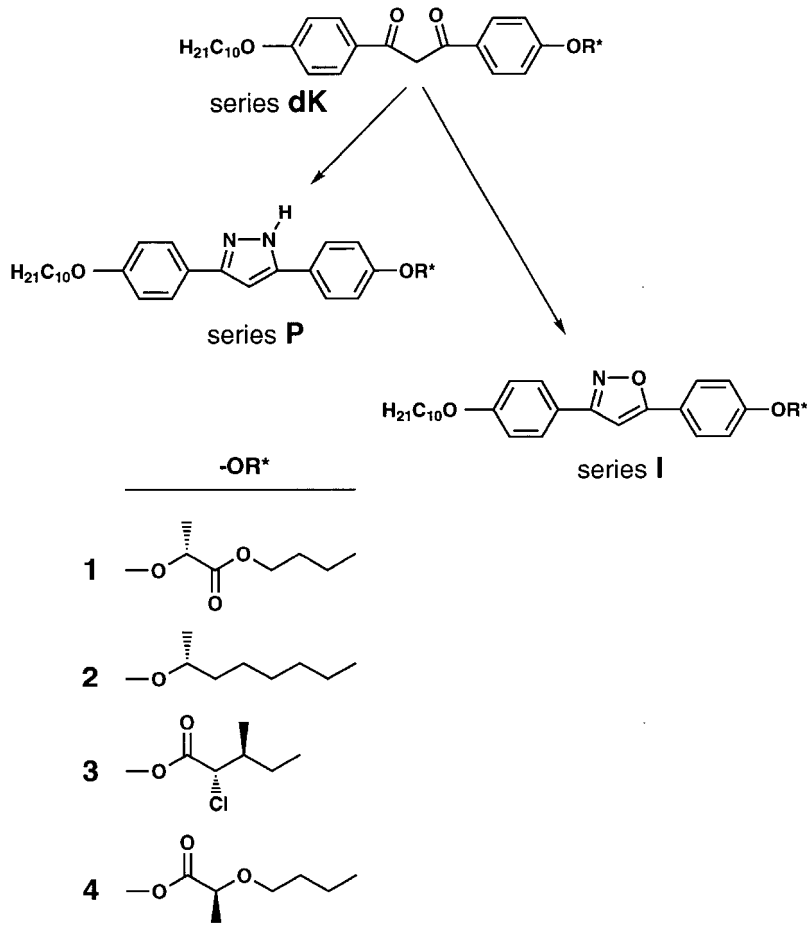


2. Results and discussion

2.1. *Synthesis*

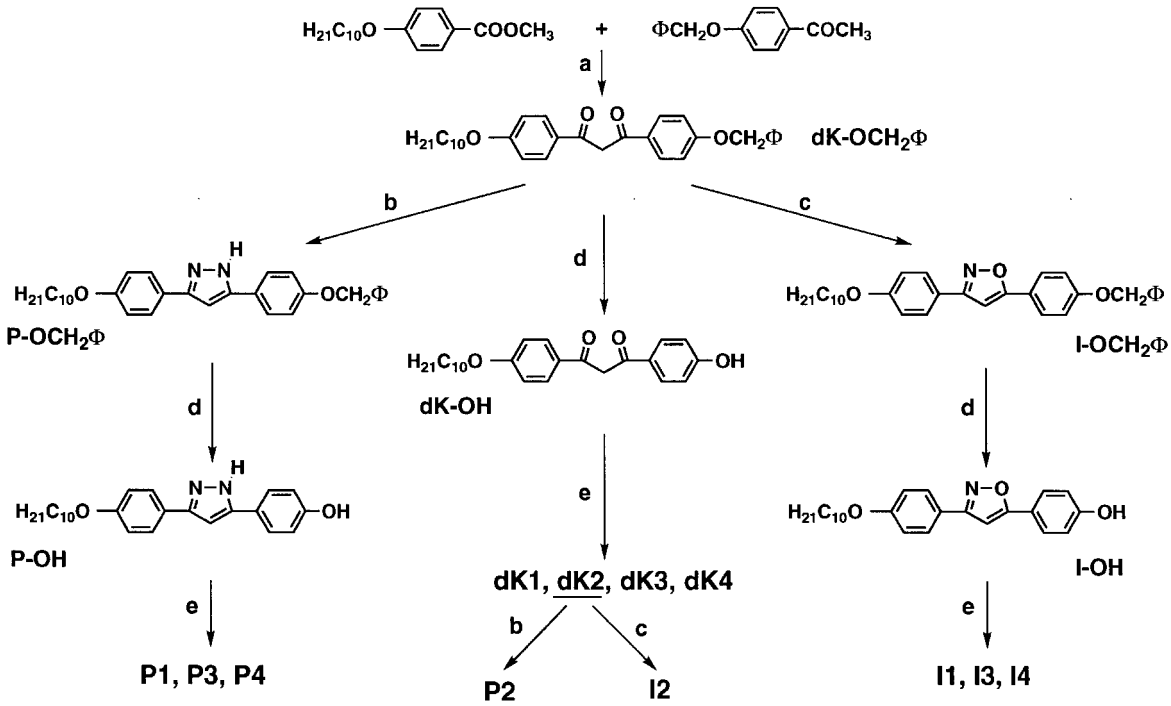
The synthesis of all the twelve compounds is outlined in the scheme. Only the heterocyclic derivatives bearing the (1*R*)-1-methylheptyloxy chiral tail (**P2** and **I2**) could be obtained directly from the corresponding β-diketone (**dk2**) by reaction with hydrazine monohydrate and hydroxylamine hydrochloride, respectively. Compounds in which the chiral tail incorporates an ester group, i.e. (1*R*)-1-butyloxycarbonylethoxy (**P1** and **I1**), (2*S*,3*S*)-2-chloro-3-methylpentanoyloxy (**P3** and **I3**) and (2*S*)-2-butyloxypropanoyloxy (**P4** and **I4**), could not be obtained directly from their β-diketone precursors **dK1**, **dK3** and **dK4**. In each case, the ester group underwent hydrolysis in the presence of the reagents hydrazine hydrate and hydroxylamine hydrochloride. As a consequence, it was necessary to obtain the heterocycle before incorporating the chiral tail, and hence the protected pyrazole and isoxazole derivatives (**P-OCH$_2\Psi$**, **I-OCH$_2\Psi$**) were prepared first.

2.2. *Mesomorphic properties*

Thermal and thermodynamic data corresponding to all the twelve compounds are gathered in table 1.

The β-diketone derivatives do not show liquid crystalline properties. However, cyclysation of the diketone unit to give the five-membered ring pyrazoles and isoxazoles, generally leads to the appearance of mesophases on melting. These results are in accordance with our previous findings on the analogous achiral systems [3]. In that study, the degree of deviation from linearity of the molecular structures clearly influenced the appearance of mesophases. The molecular shape of each system was assessed by means of both experimental and theoretical techniques (X-ray diffraction and semi-empirical calculations) as represented in figure 1.

The 1,3-diphenylpropane-1,3-dione core deviates from linearity by between 27·1° and 26·65°. In contrast, the corresponding pyrazole and isoxazole derivatives have a more linear shape with angles of only 14·7° and 10·7°, respectively. It was concluded that the more linear geometry of the heterocyclic derivatives led to the appearance of the smectic mesomorphism. In contrast, the more pronounced bent shape of the β-diketone precursors proved detrimental to the appearance of liquid crystalline phases. However, this reasoning cannot be independently applied to the compounds investigated here. The *n*-alkoxy tails used in the previous study [3]



a) NaH/dimethoxyethane; b) $N_2H_4.H_2O$/ethanol; c) $NH_2OH.HCl/Et_3N$/ethanol; d) $Pd(OH)_2$-C/cyclohexane/ethanol; e) R*-OH, reaction conditions depend on R* (see experimental section).

Scheme 1.

Table 1. Thermal and thermodynamic data for the twelve chiral compounds; temperatures in °C. (...): ΔH (KJ mol) for the corresponding transition. (...) : the enthalpy corresponds to the sum of two phase transitions. [...]: monotropic transition. Cr and Cr′ denote two polymorphic crystalline phases.

Compound	Cr		Cr′		S_C^*		S_A		Ch		I
dK1	•	0·4 (14·9)	•	19·4 (8·5)							•
dK2			•	55·8 (25·2)							•
dK3	•	59·9 (11·5)	•	75·5 (36·1)							•
dK4			•	56·3 (26·6)							•
P1			•	54·6 (25·7)							•
P2			•	102·8 (15·9)							•
P3	•	108·4 (6·7)	•	125·2 (16·2)	•	134·8	•	156·0 (3·3)			•
P4			•	123·6 (15·9)	•	127·6	•	133·6 (3·0)			•
I1			•	66·4 (35·0)							•
I2			•	70·7 (40·1)	[•	65·5]	•	70·7	• (1·8)	75·3	•
I3			•	88·7 (49·5)	•	103·3	•	115·4	• (4·3)	116·6	•
I4			•	86·0 (29·1)	•	102·2	•	104·3 (3·0)			•

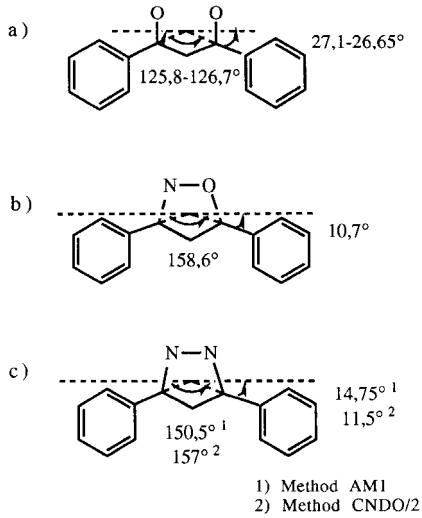


Figure 1. (*a*), (*b*) Diffraction data for β-diketones [8,9] and isoxazoles [10] taken from the literature; (*c*) AM1 and CNDO/2 calculations carried out on pyrazole compounds, for which diffraction data have not been found in the literature.

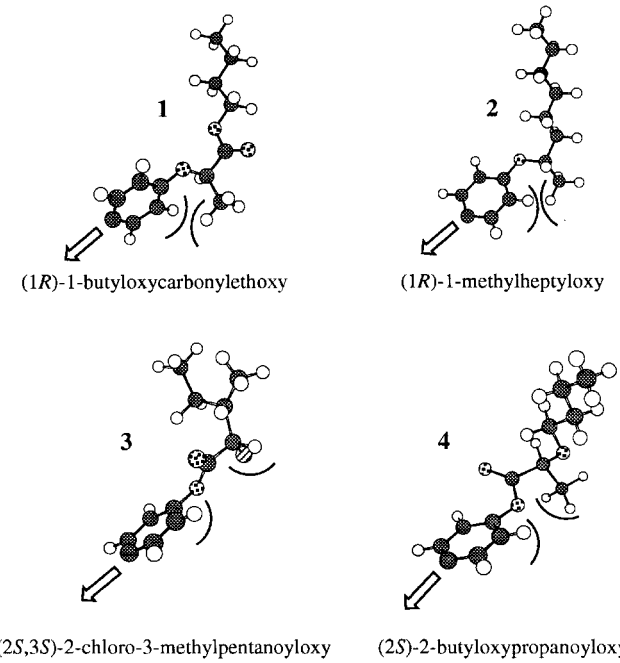


Figure 2. Most abundant conformation calculated by MM2 for each chiral tail.

have been replaced by either alkoxy or alkanoyloxy tails which bear a stereogenic centre. As a result, the mesomorphic behaviour strongly depends on the nature of the chiral tail in the molecule. Mesophase ranges of between 10 and 30°C appear for the compounds bearing chiral alkanoyloxy tails (**3** and **4**). Enantiotropic phase sequences are observed (Cr–S_C*–S_A–I for compounds **P3**, **P4** and **I4**, and Cr–S_C*–S_A–Ch–I for compound **I3**). The chiral alkoxy derivatives show much worse mesomorphic properties. Only compound **I2** shows liquid crystalline behaviour (Cr–(S_C*)–S_A–Ch–I) and this is over a short temperature range (c. 5°C).

Modelling of these structures by means of molecular mechanics and semi-empirical (MOPAC-AM1) calculations allows certain interesting conclusions to be drawn concerning their mesomorphic behaviour. The most stable conformation of each tail is represented in figure 2. It is noticeable that the effect of the branch in the stereogenic centre is quite different for alkoxy tails than for alkanoyloxy tails. Lateral interactions between the polarizable nuclei must be much more hindered in the alkoxy derivatives in which the stereogenic centre bearing a methyl group is close to the rigid core. In contrast, chain branching appears to be less harmful to the lateral interactions of molecules within the mesophase in derivatives with an alkanoyloxy tail. It is also worth noting that a short range chiral nematic phase appears in the isoxazole derivatives **I2** and **I3**.

2.3. *Ferroelectric properties*

The ferroelectric properties were studied for all compounds showing the S_C* phase. Compounds **P3** and **I3** decomposed on application of electric fields, probably due to the presence of both the –CO–CCl– unit and the basic nitrogen atom in the heterocycle. The dependence of the spontaneous polarization of compounds **I2**, **P4** and **I4** on temperature is shown in figure 3, along with the P_s max values and response times.

Unfortunately, a direct comparison between the ferroelectric behaviour of isoxazole and pyrazole derivatives can only be made in terms of the P_s values of two compounds, **P4** and **I4**. However, there is a clear difference between the P_s values of these compounds and this may arise due to a number of factors. Firstly, the presence of dimers has been previously demonstrated [3] in the mesophase of pyrazole derivatives. Although the dimers do not seem to have a noticeable influence on the mesomorphic properties, formation of the dimer may give rise to some cancellation of molecular dipoles, leading to lower P_s values. Secondly, the molecular dipole of both compounds has been assessed by MOPAC-AM1 calculations for the most stable molecular conformation in each case. Both the molecules and their corresponding dipoles are represented in figure 4. The difference in dipole moduli between the compounds is clear, with that of the isoxazole derivative being smaller. It appears reasonable that partial cancellation of molecular dipoles in the pyrazole compound occurs. As a consequence, probably due to the presence of dimers, the greater dipoles of single molecules compound **P4** must be collectively less effective in contributing

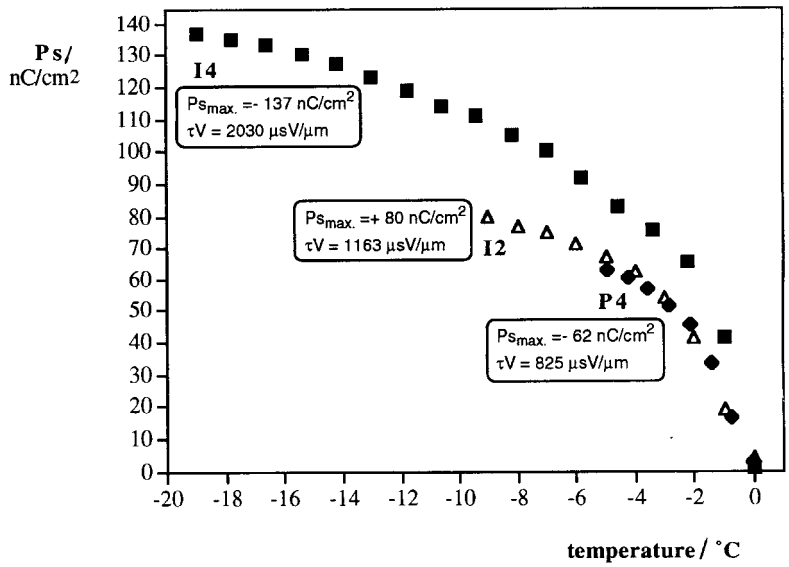


Figure 3. Plot of P_s versus temperature for the compounds which could be evaluated in their pure state. P_s max values and response times are also given.

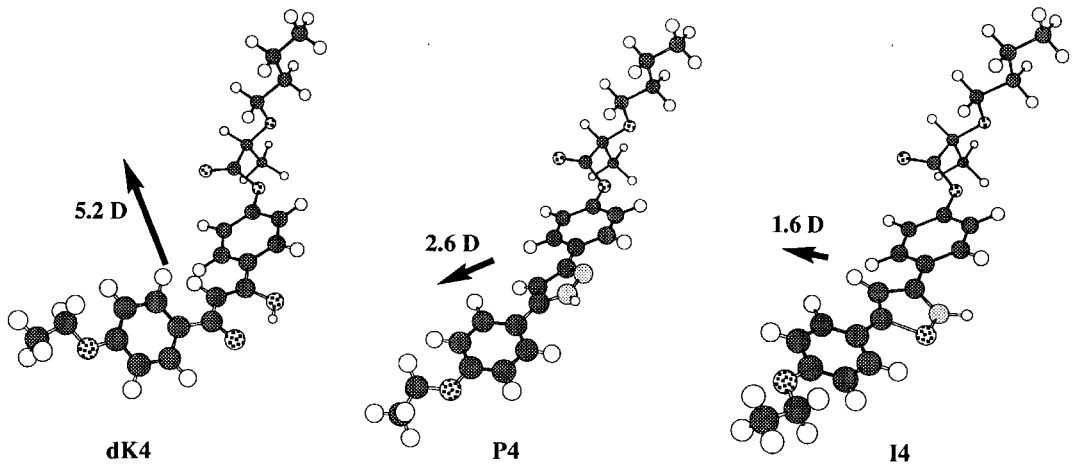


Figure 4. Molecular conformation and dipole moment calculated by MM2 and AM1 for the three compounds derived from the (2*S*)-2-butyloxypropanoic acid, i.e. **dK4**, **P4** and **I4**.

to the overall P_s value than the smaller dipole of compound **I4**.

The potential of all twelve compounds as chiral dopants for FLC materials has been studied using 10 mol % binary mixtures with 4-hexyloxyphenyl 4-decyloxybenzoate [11]. (I–Ch–S_A–S_C –S_{Bhex}–Cr) as achiral host. Values of maximum polarization ($P_s$max), normalised polarization (P_o), polarization at 10°C below the formation of the S_C phase [$P_s(-10°)$] and tilt angles at the P_s max value (θmax) are gathered in table 2.

In general, heterocyclic dopants (series **P** and **I**) give rise to higher polarization values that the corresponding β-diketone (series **dK**) precursors. Comparison of P_s and P_o values of separate mixtures containing each of the two types of heterocyclic dopant shows that pyrazole derivatives tend to exhibit the higher values. This trend is opposite to that observed for the pure compounds (**P4** and **I4**), and this could be accounted for by the absence of dimers in the mixtures due to the dilution of the chiral component. However no experimental verification for this could be achieved. By far the smallest P_s values are those corresponding to the β-diketone dopants. In two cases (**dK1** and **dK2**), the P_s values could not be adequately determined because they were smaller than the margins of error inherent in the method of evaluation (0·1 nC cm^{-2}). P_o values are also rather low, although the tilt angles are clearly smaller than those of the heterocyclic analogues. When we look at the calculated molecular dipole moments represented in figure 4, it is surprising that the highest modulus corresponds to the β-diketone derivative, and moreover, its disposition transverse to an average longitudinal

Table 2. Mesomorphic and ferroelectric properties [spontaneous polarization (P_s max and P_s (-10°C)), reduced polarization (P_o max) and tilt angle (θ max)] for binary mixtures of the chiral compounds with the host (see text). All the binary mixtures contained 10 mol % of the chiral dopant.

Chiral dopant	Mesomorphic properties												P_s max /nC cm^{-2}	θ max /°	P_o /nC cm^{-2}	$P_s(-10^\circ C)$ /nC cm^{-2}
	I		Ch		S_A		S_C^*		S_Bh		Cr					
dK1	•	79	•	73	•	56	•	32	•	26	•		$<-0{\cdot}1$	18	—	—
dK2	•	78	•	74	•	54	•	31			•		$<+0{\cdot}1$	16	—	—
dK3	•	80	•	76	•	52	•	31	•	26	•		$-1{\cdot}0$	15	4·0	0·8
dK4	•	79	•	76	•	52	•	25			•		$+1{\cdot}6$	15	6·9	—
P1	•	86	•	82	•	71	•	36			•		$+6{\cdot}9$	23	17·6	4·9
P2	•	90	•	87	•	75	•	36			•		$+3{\cdot}0$	24	7·5	2·9
P3	•	93	•	90	•	75	•	38			•		$-7{\cdot}2$	22	18·9	5·7
P4	•	91	•	89	•	72	•	37			•		$+4{\cdot}3$	24	11·8	3·6
I1	•	85	•	78	•	67	•	35			•		$+3{\cdot}4$	25	8·2	3·2
I2	•	88	•	83	•	72	•	35			•		$+2{\cdot}2$	23	5·7	2·1
I3	•	91	•	86	•	75	•	36			•		$-5{\cdot}2$	24	12·9	3·8
I4	•	89	•	85	•	70	•	36			•		$+4{\cdot}4$	29	9·8	4·1

molecular axis should be favourable for higher P_s values. It is well established that molecular ordering within the ferroelectric phase strongly influenced P_s values [12]. In the case of the β-diketones, the bent molecular shape seems to lead to less efficient lateral interactions, thus preventing favourable dipole coupling. In contrast, the more linear molecular structure of the heterocyclic dopants should allow stronger dipole coupling in the chiral phase, due to the less hindered packing interactions between molecules, thus leading to higher polarization values.

3. Conclusions

Three new series of chiral compounds have been synthesized. One series contains a β-diketone group (series **dK**) and the other two series contain a five-membered heterocycle as the central bridge in the mesogenic core (series **P** and series **I**).

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 heterocyclic derivatives show much stronger mesomorphic behaviour than their β-diketone precursors, thus supporting previous conclusions [3]. In addition, for systems containing the same heterocyclic unit in the core, the alkanoyloxy chiral tails give rise to the best mesomorphic properties.

P_s values were measured for all the pure compounds displaying the S$_C^*$ mesophase. The highest P_s value (137 nC cm^{-2}) corresponds to the isoxazole derivative with the (2*S*)-2-butyloxypropanoyloxy chiral tail (**I4**). The smaller P_s values of the pyrazole derivative **P4**, in comparison with the isoxazole derivative **I4**, must be due to the presence of dimers in the pyrazole case. A marked influence of molecular shape on the effective coupling of dipoles in induced S$_C^*$ phases is observed from the experimental P_s values (P_s **dK** $< P_s$ **P** $\approx P_s$ **I**) obtained for binary mixtures consisting of 10 mol % of the chiral dopant.

4. Experimental

4.1. *Techniques*

Elemental microanalysis was performed using a Perkin-Elmer 240-B microanalyser. Infrared spectra for all the compounds were obtained using a Perkin-Elmer 1600 (FTIR) spectrophotometer in the 400–4000 cm^{-1} spectral range. ^{1}H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer in deuteriochloroform as solvent.

The textures of the mesophases were studied using an optical microscope (Nikon) with crossed polarizers, in conjunction with a Mettler FP82 hot stage and Mettler central processor. Measurements of the transition temperatures were made using a TA2910 differential calorimeter with a heating or cooling rate of 10°C min^{-1}. The apparatus was calibrated with indium (156·6°C, 28·44 J g^{-1}) and tin (232·1°C, 60·5 J g^{-1}).

The spontaneous polarizations and the response times were obtained simultaneously using the triangular wave form method [13 (*a*)]. In the experimental set-up, the triangular wave voltage was supplied by an HP3245A Function Generator. The current–voltage cycles were recorded by a digital acquisition system (*tech* ADC488/16A). All the equipment was interfaced to a microcomputer. The cells used for the measurements were coated with polyimide and carried indium tin oxide (ITO) electrodes.

The values of the spontaneous polarization (P_s) were determined by integrating the displacement current peak which appears due to the reversal of the P_s, in response to an applied triangular voltage [10(*b*)]. The maximum amplitudes and frequencies used for both the pure compounds and the mixtures, were 20 Vpp, 50 Hz and 4 μm, respectively. Good alignment was obtained by slow cooling (0·5 or 1°C min^{-1}) of the cell filled from the isotropic liquid. The rotational viscosity, γ_c, was obtained from the parameters of the current peak calculated from the P_s measurement. Using both values, the response time was calculated using the equation $\tau = 1{\cdot}75\ \gamma_c/P_s\ E$ [11]. The sign of P_s was determined by the field reversal method by optical observation of the extinction direction on rotating the stage according to Lagerwall's convention [15]. The tilt angles were measured as a function of temperature for samples mounted between crossed polarizers; they were recorded as half the rotation angle between the two extinction positions associated with the oppositely directed polarizations. The extinction positions were determined using a photomultiplier tube; the applied electrical d.c. field was 5 V μm^{-1}.

4.2. *Synthesis*

Chiral starting alcohols L-butyl lactate and (*S*)-2-octanol were purchased from Fluka and Aldrich, respectively. The synthesis of (2*S*,3*S*)-2-chloro-3-methylpentanoic acid (**3**) and (2*S*)-2-butyloxypropanoic acid (**4**) required for the chiral tail groups was carried out following methods described in the literature [9(*a*), 16].

4.2.1. *Synthesis and analytical data for the β-diketones (series* **dK***)*

*4.2.1.1. 1-(4-benzyloxyphenyl)-3-(4-decyloxyphenyl)-propan-1,3-dione (**dK–OCH$_2$Φ**).* A mixture of 5·84 g (0·02 mol) of methyl 4-decyloxybenzoate and 4·52 g (0·02 mol) of 4-benzyloxyacetophenone in 200 ml of dimethoxyethane was heated at reflux for 2 h in the presence of 0·99 g of 97% sodium hydride (0·04 mol) and then stirred overnight. A small amount of water was added very carefully to the reaction mixture. After acidifying with dilute hydrochloric acid, the product was extracted into diethyl ether. The solvent was removed under vacuum and the crude product was twice recrystallized from ethanol and hexane, respectively. Yield: 57%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·87 (t, J=6·7 Hz, 3H), 1·26 (m, 12H), 1·45 (m, 2H), 1·79 (m, 2H), 4·00 (t, J=6·5 Hz, 2H), 5·13 (s, 2H), 6·71 (s, 1H), 6·94 (d, J=9·0 Hz, 2H), 7·03 (d, J=9·0 Hz, 2H), 7·42 (m, 5H), 7·92 (d, J=9·0 Hz, 2H), 7·94 (d, J=9·0 Hz, 2H), 17·12 (s, 1H). IR (Nujol): 1604, 1514, 1454, 1255, 846, 783 cm^{-1}.

*4.2.1.2. 1-(4-hydroxyphenyl)-3-(4-decyloxyphenyl)propan-1,3-dione (**dK–OH**).* 3 g of the protected β-diketone (**dK–OCH$_2$Ψ**) were dissolved in ethanol (48 ml) and cyclohexane (24 ml). 0·3 g of 20% palladium hydroxide on carbon (1:10 catalyst/substrate by weight) was added, and the suspension stirred under reflux for 2 h. The catalyst was removed by filtration through celite and the solvent removed under vacuum. The crude product was recrystallized from acetonitrile. Yield: 91%. M.p. 94°. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·89 (t, J=6·7 Hz, 3H), 1·28 (m, 12H), 1·47 (m, 2H), 1·82 (m, 2H), 4·03 (t, J=6·5 Hz, 2H), 5·6 (s, 1H), 6·73 (s, 1H), 6·92 (d, J=8·8 Hz, 2H), 6·97 (d, J=9·0 Hz, 2H), 7·92 (d, J=8·6 Hz, 2H), 7·95 (d, J=8·6 Hz, 2H), 17·10 (s, 1H). IR (Nujol): 3418, 3288, 1592, 1504, 1462, 1258, 845, 784 cm^{-1}.

*4.2.1.3. 1-{4-[(1R)-1-Butyloxycarbonylethoxy]phenyl}-3-(4-decyloxyphenyl)propan-1,3-dione (**dK1**).* To a stirred solution of 1 g (2·53 mmol) of 1-(4-hydroxyphenyl)-3-(4-decyloxyphenyl)propan-1,3-dione and 1·66 g (6·04 mmol) of triphenylphosphine in 30 ml of diethyl ether, under an argon atmosphere, 0·37 g (2·53 mmol) of butyl L-lactate in 5·8 ml of diethyl ether was added via a syringe. 0·53 g (3·03 mmol) of DEAD in 28 ml of dry diethyl ether was added dropwise and the mixture stirred for 24 h at room temperature. The precipitate was filtered off and the solvent removed under vacuum. The product was purified by flash chromatography using 19:1 hexane/ethyl acetate as eluent. Yield: 42%. R_F 0·585 (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·86 (t, J=6·5 Hz, 3H), 0·87 (t, J=7·5 Hz, 3H), 1·26 (m, 14H), 1·45 (m, 2H), 1·56 (m, 2H), 1·64 (d, J=5·8 Hz, 3H), 1·79 (m, 2H), 3·99 (t, J=6·6 Hz, 2H), 4·15 (dt, J=6·6 Hz, 2H), 4·82 (c, J=5·8 Hz, 1H), 6·70 (s, 1H), 6·92 (d, J=9·0 Hz, 2H), 6·94 (d, J=9·0 Hz, 2H), 7·91 (d, J=9·0 Hz, 2H), 7·92 (d, J=9·0 Hz, 2H), 17·10 (s, 1H). IR (Nujol): 1753, 1602, 1503, 1258, 1228, 1174, 844, 787 cm^{-1}. Anal: calc. for $C_{32}H_{44}O_6$ C 73·28, H 8·40%; found C 72·90, H 7·99%.

*4.2.1.4. 1-{4-[(1R)-1-Methylheptyloxy]phenyl}-3-(4-decyloxyphenyl)propan-1,3-dione (**dK2**).* This compound was synthesized using the procedure described for **dK1**. Yield: 42%. R_F 0·86 (60:40 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·87 (t, J=6·6 Hz, 6H), 1·27 (m, 20H), 1·32 (d, J=6·0 Hz, 3H), 1·46 (m, 2H), 1·60 (m, 1H), 1·75 (m, 1H), 1·79 (m, 2H), 4·02 (t, J=6·6 Hz, 2H), 4·45 (c, J=6·1 Hz, 1H), 6·72 (s, 1H), 6·92 (d, J=9·0 Hz, 2H), 6·95 (d, J=9·0 Hz, 2H), 7·92 (d, J=9·0 Hz, 2H), 7·92 (d, J=9·0 Hz, 2H), 17·15 (s, 1H). IR (Nujol): 1604, 1506, 1465, 1259, 842, 785 cm^{-1}. Anal: Calc. for $C_{33}H_{48}O_4$ C 77·95, H 9·45%; found C 77·66, H 9·15%.

*4.2.1.5. 1-{4-[(2S,3S)-2-Chloro-3-methylpentanoyloxy]-phenyl}-3-(4-decyloxyphenyl)propan-1,3-dione (**dK3**).* 1 g (2·53 mmol) of the phenol **dK–OH** was dissolved in 45 ml of CH_2Cl_2, and 0·31 g (3·03 mmol) of dry triethylamine was added under an argon atmosphere. 0·43 g (2·53 mmol) of (2*S*,3*S*)-2-chloro-3-methylpentanoyl chloride dissolved in 5 ml of CH_2Cl_2 was added dropwise. The mixture was stirred for 15 h at room temperature. The solvent was removed under vacuum and the crude product purified by flash chromatography using 4:1 hexane/ethyl acetate as eluent. The product was recrystallized from acetonitrile. Yield: 46%. R_F 0·64 (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·86 (t, J=6·6 Hz, 3H), 0·97 (t, J=7·4 Hz, 3H), 1·12 (d, J=6·78 Hz, 3H), 1·25 (m, 12H), 1·43 (m, 3H), 1·79 (m, 3H), 2·21 (m, 1H), 4·01 (t, J=6·41 Hz, 2H), 4·37 (d, J=7·14 Hz, 1H), 6·74 (s, 1H), 6·95 (d, J=8·8 Hz, 2H), 7·23 (d, J=8·2 Hz, 2H), 7·94 (d, J=8·6 Hz, 2H), 8·00 (d, J=8·8 Hz, 2H), 17·00 (s, 1H). IR (Nujol): 3518, 1759, 1606, 1501, 1466, 1262, 858, 787 cm^{-1}. Anal: calc. for $C_{31}H_{41}O_5Cl$ C 70·39, H 7·76%; found C 70·40, H 7·65%.

*4.2.1.6. 1-{4-[(2S)-2-Butyloxypropanoyloxy]phenyl}-3-(4-decyloxyphenyl)propan-1,3-dione (**dK4**).* 0·48 g (1·21 mmol) of **dK–OH** and 0·19 g (1·33 mmol) of (2*S*)-2-butyloxypropanoic acid were dissolved in dichloromethane. *N*,*N*′-dicyclohexylcarbodiimide and 0·02 g (0·2 mmol) of 4-dimethylaminopyridine were added to the solution. The mixture was stirred under atmosphere for 20 h. The mixture was filtered and the solvent removed under vacuum. The product was recrystallized from ethanol and hexane. Yield: 27%. R_F 0·73 (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·88 (t, J=7·0 Hz, 3H), 0·94 (t, J=7·3 Hz, 3H), 1·28 (s, 12H), 1·41 (m, 4H), 1·58 (d, J=7·0 Hz, 3H), 1·62 (m, 2H), 1·81 (m, 2H), 3·51 (dt, J=9·0, 6·6 Hz, 1H), 3·69 (dt, J=9·0, 6·6 Hz, 1H), 4·02 (t, J=6·6 Hz, 2H), 4·20 (c, J=6·8 Hz, 1H), 6·76 (s, 1H), 6·96 (d, J=8·8 Hz, 2H), 7·22 (d, J=8·6 Hz, 2H), 7·95 (d, J=8·8 Hz, 2H), 8·00 (d, J=8·6 Hz, 2H), 17·01 (s, 1H). IR (Nujol): 1765·0, 1605·4, 1501·5, 1473·9, 1258·1, 839·6, 782·4 cm^{-1}. Anal: calc. for $C_{32}H_{44}O_6$ C 73·28, H 8·40%; found C 72·96, H 8·15%.

4.2.2. *Synthesis and analytical data for the pyrazoles (series* **P***)*

*4.2.2.1. 3-(4-Benzyloxyphenyl)-5-(4-decyloxyphenyl)-pyrazole (**P–OCH$_2\Phi$**).* 2 g (0·004 mol) of the protected β-diketone (**dK–OCH$_2\Psi$**) and 2·56 ml of $N_2H_4{\cdot}H_2O$ were heated at reflux in 88 ml of ethanol for 2 h, and then stirred overnight at room temperature. The product was filtered off and purified by recrystallization from ethanol. Yield: 85%. Cr 126·5°C Cr 153°C S_A 201·3°C N 207·6°C I. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·87 (t, J=5·8 Hz, 3H), 1·26 (m, 12H), 1·43 (m, 2H), 1·76 (m, 2H), 3·92 (t, J=6·4 Hz, 2H), 5·03 (s, 2H), 6·61 (s, 1H), 6·85 (d, J=8·4 Hz, 2H), 6·93 (d, J=8·4 Hz, 2H), 7·40 (m, 5H), 7·57 (d, J=8·1 Hz, 2H), 7·59 (d, J=8·0 Hz, 2H). IR (Nujol): 3235, 1618, 1508, 1467, 1256, 827, 786 cm^{-1}.

*4.2.2.2. 3-(4-Hydroxyphenyl)-5-(4-decyloxyphenyl)-pyrazole (**P–OH**).* This compound was obtained from **P–OCH$_2\Psi$** according to the procedure described for **dK–OH**. Yield: 77%. M.p. 171°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0·84 (t, J=6·4 Hz, 3H), 1·24 (m, 12H) < 1·39 (m, 2H), 1·70 (m, 2H), 3·97 (t, J=6·4 Hz, 2H), 6·80 (d, J=8·3 Hz, 2H), 6·86 (s, 1H), 6·90 (d, J=8·1 Hz, 2H), 7·60 (d, J=6·8 Hz, 2H), 7·70 (d, J=7·2 Hz, 2H), 9·50 (s, 1H), 12·96 (s, 1H). IR (Nujol): 3241·6, 1617, 1509, 1465, 1264, 833, 789 cm^{-1}.

*4.2.2.3. 3-{4-[(1R)-1-Butyloxycarbonylethoxy]phenyl}-5-(4-decyloxyphenyl)pyrazole (**P1**).* This compound was obtained from **P–OH** according to the procedure described for **dK1**. Yield: 31%. R_F 0·5 (60:40 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·87 (t, J=7·4 Hz, 6H), 1·26 (m, 14H), 1·45 (m, 2H), 1·58 (m, 2H), 1·63 (d, J=6·8 Hz, 3H), 1·78 (m, 2H), 3·97 (t, J=6·6 Hz, 2H), 4·15 (dt, 2H), 4·78 (c, J=7·0 Hz, 1H), 6·66 (s, 1H), 6·90 (d, J=8·6 Hz, 2H), 6·93 (d, J=8·6 Hz, 2H), 7·30 (d, J=8·6 Hz, 2H), 7·50 (d, J=8·6 Hz, 2H), 10·20 (s, 1H). IR (Nujol): 3253, 1752, 1616, 1508, 1464, 1243, 838, 782 cm^{-1}. Anal: calc. for $C_{32}H_{44}O_4N_2$ C 73·85, H 8·46, N 5·38%; found C 73·66, H 8·12, N 5·36%.

*4.2.2.4. 3-{4-[(1R)-1-Methylheptyloxy]phenyl}-5(4-decyloxyphenyl)pyrazole (**P2**).* This compound was obtained from compound **dK2** according to the procedure described for **P–OCH$_2\Psi$**. Yield: 46%. R_F 0·7 (60:40 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·87 (t, J=6·5 Hz, 6H), 1·26 (d, 3H), 1·27 (m, 20H), 1·42 (m, 2H), 1·55 (m, 1H), 1·72 (m, 1H), 1·73 (m, 2H), 3·88 (t, J=6·5 Hz, 2H), 4·30 (c, J=5·8 Hz, 1H), 6·53 (s, 1H), 6·75 (d, J=8·4 Hz, 2H), 6·77 (d, J=8·4 Hz, 2H), 7·53 (d, J=8·4 Hz, 2H), 7·55 (d, J=8·4 Hz, 2H), 12·51 (s, 1H). IR (Nujol): 3227, 1616, 1506, 1463, 1264, 830, 790 cm^{-1}. Anal: calc. for $C_{33}H_{48}O_2N_2$ C 78·57, H 9·52, N 5·56%; found C 78·23, H 9·33, N 5·51%.

*4.2.2.5. 3-{4-[(2S,3S)-2-Chloro-3-methylpentanoyloxy]-phenyl}-5-(4-decyloxyphenyl)pyrazole (**P3**).* This compound was obtained from 3-(4-hydroxyphenyl)-5-(4-decyloxyphenyl)pyrazole according to the procedure described for **dK3**. Yield: 27%. R_F 0·58 (60:40 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·86 (t, J=6·8 Hz, 3H), 0·97 (t, J=7·4 Hz, 3H), 1·10 (d, J=6·6 Hz, 3H), 1·25 (m, 12H), 1·42 (m, 3H), 1·76 (m, 3H), 2·22 (m, 1H), 3·95 (t, J=6·6 Hz, 2H), 4·37 (d, J=

7·1 Hz, 1H), 6·70 (s, 1H), 6·90 (d, J=9·0 Hz, 2H), 7·13 (d, J=8·6 Hz, 2H), 7·55 (d, J=8·2 Hz, 2H), 7·75 (d, J=8·1 Hz, 2H), 10·80 (s, 1H). IR (Nujol): 3243, 1757, 1616, 1505, 1465, 1450, 1254, 830, 783 cm^{-1}. Anal: calc. for $C_{31}H_{41}O_3ClN_2$ C 70·92, H 7·82, N 5·34%; found C 69·87, H 7·78, N 5·36%.

*4.2.2.6. 3-{4-[(2S)-2-Butyloxypropanoyloxy]phenyl}-5-(4-decyloxyphenyl)pyrazole (**P4**).* This compound was obtained from 3-(4-hydroxyphenyl)-5-(4-decyloxyphenyl)pyrazole according to the procedure described for **dK4**. Yield: 37%. R_F 0·54 (60:40 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·86 (t, J=6·4 Hz, 3H), 0·92 (t, J=7·4 Hz, 3H), 1·26 (s, 14H), 1·43 (m, 2H), 1·56 (d, J=6·9 Hz, 3H), 1·60 (m, 2H), 1·78 (m, 2H), 3·50 (dt, J=8·8, 6·6 Hz, 1H), 3·68 (dt, J=8·8, 6·6 Hz, 1H), 3·96 (t, J=6·6 Hz, 2H), 4·18 (c, J=6·9 Hz, 1H), 6·70 (s, 1H), 6·91 (d, J=8·8 Hz, 2H), 7·13 (d, J=8·4 Hz, 2H), 7·57 (d, J=8·2 Hz, 2H), 7·74 (d, J=8·2 Hz, 2H). IR (Nujol): 3241·5, 1766·1, 1620·3, 1504·3, 1469·3, 1127·6, 835·88, 781·5 cm^{-1}. Anal: calc. for $C_{32}H_{44}O_4N_2$ C 73·85, H 8·46, N 5·38%; found C 73·73, H 8·22, N 5·29%.

4.2.3. *Synthesis and analytical data of the isoxazoles (series* **I***)*

*4.2.3.1. 3-(4-Benzyloxyphenyl)-5-(4-decyloxyphenyl)-isoxazole (**I–OCH$_2\Phi$**).* A mixture of 2 g (4·12 mmol) of protected β-diketone, 0·42 g (4·12 mmol) of triethylamine and 0·29 g (4·12 mmol) of hydroxylamine hydrochloride in 82 ml of ethanol was heated at reflux for 24 h. An additional 0·29 g of $NH_2OH{\cdot}HCl$ was then added and the mixture was boiled for 6 h, and stirred overnight at room temperture. The precipitated product was filtered off and recrystallized from toluene. Yield: 72%. Cr 125°C S_C 134°C S_A 165°C N 168·8°C I. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·87 (t, J=6·9 Hz, 3H), 1·26 (m, 12H), 1·30 (m, 2H), 1·79 (m, 2H), 3·99 (t, J=6·6 Hz, 2H), 5·11 (s, 2H), 6·62 (s), 6·63 (s), 6·96 (d, J=9·0 Hz, 2H), 7·05 (d, J=8·8 Hz, 2H), 7·42 (m, 5H), 7·73 (d, J=8·8 Hz), 7·74 (d, J=9·0 Hz), 7·76 (d, J=8·6 Hz), 7·77 (d, J=9·0 Hz). IR (Nujol): 3117, 1617, 1508, 1463, 1454, 1253, 808, 744 cm^{-1}.

*4.2.3.2. 3-(4-Hydroxyphenyl)-5-(4-decyloxyphenyl)-isoxazole (**I–OH**).* This compound was obtained from **I–OCH$_2\Psi$** according to the procedure described for **dK–OH**. Yield: 60%. M.p. 147°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0·82 (t, J=6·4 Hz, 3H), 1·21 (m, 12H), 1·30 (m, 2H), 1·69 (m, 2H), 3·99 (dt, J=6·2 Hz), 6·86 (d, J=8·1 Hz), 6·88 (d, J=8·2 Hz), 7·03 (d, J=8·4 Hz), 7·06 (d, J=8·4 Hz), 7·26 (s), 7·29 (s), 7·69 (d, J=8·6 Hz, 2H), 7·76 (d, J=8·7 Hz, 2H), 9·9 (s), 10·07 (s). IR (Nujol): 3399, 3121, 1613, 1506, 1460, 1443, 1252, 840 cm^{-1}.

*4.2.3.3. 3-{4-[(1R)-1-Butyloxycarbonylethloxy]-phenyl}-5-(4-decyloxyphenyl)isoxazole (**I1**).* This compound was obtained from 3-(4-hydroxyphenyl)-5-(4-decyloxyphenyl)isoxazole according to the procedure described for **dK1**. Yield: 35%. R_F 0·53 (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·88 (t, J=6·5 Hz, 3H), 0·89 (t, J=7·3 Hz, 3H), 1·25 (m, 14H), 1·45 (m, 2H), 1·58 (m, 2H), 1·63 (d, J=7·2 Hz, 3H), 1·78 (m, 2H), 3·99 (t, J=6·4 Hz, 2H), 4·15 (m, 2H), 4·8 (c, J=6·8 Hz, 1H), 6·61 (s), 6·64 (s), 6·94 (d, J=9·0 Hz, 2H), 6·95 (d, J=8·6 Hz, 2H), 7·74 (d, J=8·8 Hz, 2H), 7·77 (d, J=8·0 Hz, 2H). IR (Nujol): 3122, 1744, 1617, 1508, 1457, 1436, 1253, 835, 804 cm^{-1}. Anal. calc. for $C_{32}H_{43}O_5N$ C 73·70, H 8·25, N 2·69%; found C 73·76, H 8·15, N 2·70%.

*4.2.3.4. 3-{4-[(1R)-1-Methylheptyloxy]phenyl}-5-(4-decyloxyphenyl)isoxazole (**I2**).* To a solution of 0·5 g (1·029 mmol) of **dK2** and 0·10 g (1·03 mmol) of dry triethylamine in 20 ml of ethanol, 0·07 g (1·03 mmol) of hydroxylamine hydrochloride was added. The mixture was heated at reflux for 20 h, and then stirred overnight at room temperature. The precipitate was collected by filtration and recrystallized from hexane. Yield: 40%. R_F 0·7 (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·87 (t, J=6·6 Hz, 6H), 1·27 (m, 20H), 1·31 (d, J=5·8 Hz, 3H), 1·45 (m, 2H), 1·57 (m, 1H), 1·74 (m, 1H), 1·79 (m, 2H), 3·99 (t, J=6·5 Hz, 2H), 4·4 (c, J=5·8 Hz, 1H), 6·6 (s, 1H), 6·94 (d, J=8·5 Hz, 2H), 6·96 (d, J=8·5 Hz, 2H), 7·72 (d, J=8·5 Hz), 7·73 (d, J=8·9 Hz), 7·75 (d, J=8·6 Hz), 7·76 (d, J=8·8 Hz). IR (Nujol): 3135, 1615, 1507, 1464, 1248, 835, 798 cm^{-1}. Anal: calc. for $C_{33}H_{47}O_3N$ C 78·42, H 9·31, N 2·77%; found C 77·99, H 9·23, N 2·74%.

*4.2.3.5. 3-{4′-[(2S,3S)-2-Chloro-3-methylpentanoyloxy]-phenyl}-5-(4-decyloxyphenyl)isoxazole (**I3**).* This compound was obtained from 3-(4-hydroxyphenyl)-5-(4-decyloxyphenyl)isoxazole according to the procedure described for **dK3**. Yield: 56%. R_F 0·76 (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·86 (t, J=6·6 Hz, 3H), 0·98 (t, J=7·4 Hz, 3H), 1·12 (d, J=6·8 Hz, 3H), 1·26 (m, 12H), 1·33 (m, 2H), 1·43 (m, 3H), 1·79 (m, 3H), 2·22 (m, 1H), 3·99 (t, J=6·5 Hz, 2H), 4·37 (d, J=6·0 Hz, 1H), 6·66 (s), 6·75 (s), 6·96 (d, J=8·7 Hz, 2H), 7·21 (d, J=8·7 Hz), 7·23 (d, J=8·7 Hz), 7·74 (d, J=7·9 Hz, 2H), 7·75 (d, J=8·7 Hz, 2H), 7·76 (d, J=8·7 Hz, 2H), 7·77 (d, J=8·7 Hz, 2H). IR (Nujol): 3132, 1769, 1615, 1506, 1467, 1269, 1210, 832, 801 cm^{-1}. Anal: calc. for $C_{31}H_{40}O_4ClN$ C 70·79, H 7·61, N 2·66%; found C 70·55, H 7·12, N 2·63%.

*4.2.3.6. 3-{4-[(2S)-2-Butyloxypropanoloxy]phenyl}-5-(4-decyloxyphenyl)isoxazole (**I4**).* This compound was

obtained from 3-(4-hydroxyphenyl)-5-(4-decyloxyphenyl)isoxazole according to the procedure described for **dK4**. Yield: 27%. R_F 0·56 (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0·86 (t, J=6·8 Hz, 3H), 0·93 (t, J=7·4 Hz, 3H), 1·26 (m, 14H), 1·43 (m, 2H), 1·57 (d, J=7·4 Hz, 3H), 1·60 (m, 2H), 1·79 (m, 2H), 3·49 (dt, J=6·6, 8·8 Hz, 1H), 3·68 (dt, J=6·6, 8·8 Hz, 1H), 3·99 (t, J=6·5 Hz, 2H), 4·19 (c, J=6·8 Hz, 1H), 6·66 (s), 6·74 (s), 6·96 (d, J=8·5 Hz, 2H), 7·20 (d, 8·5H), 7·22 (d, 8·2H), 7·75 (t, J=8·2 Hz, 2H), 7·85 (t, J=8·5 Hz, 2H). IR (Nujol): 3131·8, 1763·7, 1617·0, 1506·1, 1465·8, 1213·7, 1168·1, 1127·4, 838·0, 798·3 cm^{-1}. Anal: calc. for $C_{32}H_{43}O_5N$ C 73·70, H 8·25, N 2·69%; found C 73·66, H 8·16, N 2·63%.

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