Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Parra, M. L. , Saavedra, C. G. , Hidalgo, P. I. and Elgueta, E. Y.(2008) 'Novel chiral liquid crystals based on amides and azo compounds derived from 2-amino-1,3,4-thiadiazoles: synthesis and mesomorphic properties', Liquid Crystals, 35: 1, 55 — 64
To link to this Article: DOI: 10.1080/02678290701751434
URL: http://dx.doi.org/10.1080/02678290701751434

Liquid Crystals, Vol. 35, No. 1, January 2008, 55–64

Novel chiral liquid crystals based on amides and azo compounds derived from 2-amino-1,3,4-thiadiazoles: synthesis and mesomorphic properties

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(*Received 21 August 2007; accepted 10 October 2007*)

Novel chiral amides (**Ia**–**Ie**, **II**) and azo compounds (**III**, **IV**) with a 1,3,4-thiadiazole unit in the rigid core were synthesized and their liquid crystalline properties investigated by polarizing optical microscopy and differential scanning calorimetry. The amides **Ia**–**Ie** contain a chiral alkoxy chain derived from (*R*)-2-octanol and an achiral chain varying from 6 to 10 carbon atoms at the end of the rigid core. In amide **II** one of the terminal group is a chiral alkoxy chain derived from (*S*)-isoleucine and the other terminal substituent is an achiral *n*-decyloxy chain. Azo compounds **III** and **IV** contain an achiral *n*-decyloxy chain and a chiral alkoxy chain derived from (*R*)-2-octanol and (*S*)-isoleucine, respectively, at the end of the rigid core. The first homologue in the series of amides (**Ia**) exhibits enantiotropic smectic X (SmX)–chiral nematic (N*) dimorphism and the homologues **Ib**–**Ie** display enantiotropic SmX–chiral smectic C (SmC*)–N* mesomorphism. Amide **II** displays an enantiotropic smectic A phase. The azo compounds **III** and **IV** do not show smectic order and only an enantiotropic N* phase was observed. Thus, the mesomorphic behaviour depends on the nature of the central linkage and on the nature of the chiral alkoxy chain.

1. Introduction

The synthesis of chiral liquid crystal materials possessing smectic phases of C_2 symmetry, such as the chiral smectic C (SmC*) phase, has gained considerable interest due to their expected ferroelectric properties. The interest in ferroelectric liquid crystalline materials (FLCs) has recently increased because of their potential application in high-resolution microdisplays due to their fast response time, bistability and wide viewing angle. They are also potential candidates for nonlinear and photonic applications [1–3]. Hence, the synthesis of new materials and the characterization of their physical properties are important activities in the development of new liquid crystalline materials.

The 2-amino-1,3,4-thiadiazoles are interesting systems for the design and synthesis of liquid crystalline compounds with a classical rod-like structure. We have previously reported the synthesis and mesomorphic properties of achiral 1,3,4-thiadiazoles with nitrogen-based linkers (Schiff bases, azo compounds or amides) at the 2-position exhibiting, amongst other phases, the SmC phase [4–6]. More recently, we have reported the mesomorphic and ferroelectric properties of chiral Schiff bases containing the 1,3,4-thiadiazole ring in their rigid core, in which one terminal group is a chiral ester chain derived from (*S*)-ethyl lactate [7] or a chiral alkoxy chain derived from (*R*)-2-octanol and (*S*)-isoleucine [8].

Our interest in ferroelectric (SmC*) and cholesteric (N*) phases, has led us to design new chiral molecules that incorporate 1,3,4-thiadiazole in the mesogenic core. Only a few examples of FLCs derived from 1,3,4-thiadiazole have reported in the literature [7–11]. However, to the best of our knowledge, there are no reports of chiral amides and chiral azo compounds incorporating this five-membered ring in chiral liquid crystals.

Continuing our work on the liquid crystal possibilities of thiadiazole systems, in this paper we report the design, synthesis and phase behaviour of novel chiral amides (**Ia**–**Ie**, **II**) and azo compounds (**III**, **IV**) incorporating the 1,3,4-thiadiazole moiety.

In order to achieve the non-centrosymmetry in the SmC and nematic (N) phases neccesary for ferroelectric and cholesteric behaviour, respectively, one of the terminal groups is a chiral alkoxy chain derived from (*R*)-2-octanol and (*S*)-isoleucine. The other terminal

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2008 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701751434

substituent is an achiral alkoxy chain varying from 6 to 10 carbon atoms in amides **Ia**–**Ie**. For comparative purposes, we have synthesized an analogous amide (**II**) incorporating a chiral chain derived from (*S*)-isoleucine and azo compounds **III** and **IV** incorporating a chiral chain derived from (*R*)-octanol and (*S*)-isoleucine, respectively. In these compounds the number of carbon atoms of the achiral alkoxy chain was kept constant at $n=10$. The structures of the amides (**Ia**–**Ie**, **II**) and azo compounds (**III**, **IV**) studied are shown in figure 1.

The main aim of this work was to study the effect of the nature of the central linkage and the effect of the chiral chain on the mesomorphic properties of the amides and azo compounds. The imine group used in the previous study [8] has been replaced by either an amide or an azo group. As a result, the mesomorphic behaviour strongly depends on the nature of the central linkage and on the nature of the chiral chain in the molecule.

2. Synthesis

This study involved the synthesis and characterization of new chiral amides and new chiral azo compounds incorporating the thiadiazole heterocycle in the rigid core (see figure 1). Amides **Ia**–**Ie** were obtained by reaction of the 5-(4-*n*-alkoxy)phenyl-2-amino-1,3,4-thiadiazole ($n=6$–10) with the corresponding chiral benzoic acid chloride. The homologue 5-(4-*n*-decyloxy) phenyl-2-amino-1,3,4-thiadiazole was used in the synthesis of amide **II**. The azo compounds were synthesized by reaction of the 5-(4-*n*-decyloxy)phenyl-2-amino-1,3,4-thiadiazole with the corresponding chiral alkoxybenzene. The alcohols chosen as chiral precursors were (2*S*,3*S*)-2-chloro-3-methylpentanol and (*R*)-2-octanol. The latter was purchased from Merck, whereas the former was prepared using (*S*)-isoleucine as chiral precursor. The synthesis of all compounds is outlined in schemes 1 and 2.

The chiral alcohol (2*S*,3*S*)-2-chloro-3-methylpentanol was obtained by diazotization of (*S*)-isoleucine with sodium nitrite and HCl followed by reduction of the acid group with $LiAlH_4$ [12–14].

The synthesis of the chiral 4-alkoxybenzoic acid chlorides (**3** and **4**) was achieved by the Mitsunobu reaction [8, 15] starting from methyl 4-hydroxybenzoate and the corresponding chiral alcohol, (*R*)-2-octanol or (2*S*,3*S*)-2-chloro-3-methylpentanol. The resulting esters (**1** and **2**) were saponified, followed by reaction with thionyl chloride. The Mitsunobu reaction between phenol and (*R*)-2-octanol or (2*S*,3*S*)-2-chloro-3-methylpentanol yielded the chiral ethers **5** and **6**, respectively.

The homologue series of aminothiadiazole derivatives and amides (**Ia**–**Ie** and **II**) and azo compounds **III** and **IV** were synthesized according to methods previously described [4–6].

3. Results and discussion

3.1. *Mesomorphic properties*

The transition temperatures and phase behaviour of the new materials are listed in table 1; a graphical representation of the mesomorphic behaviour is presented in figure 2.

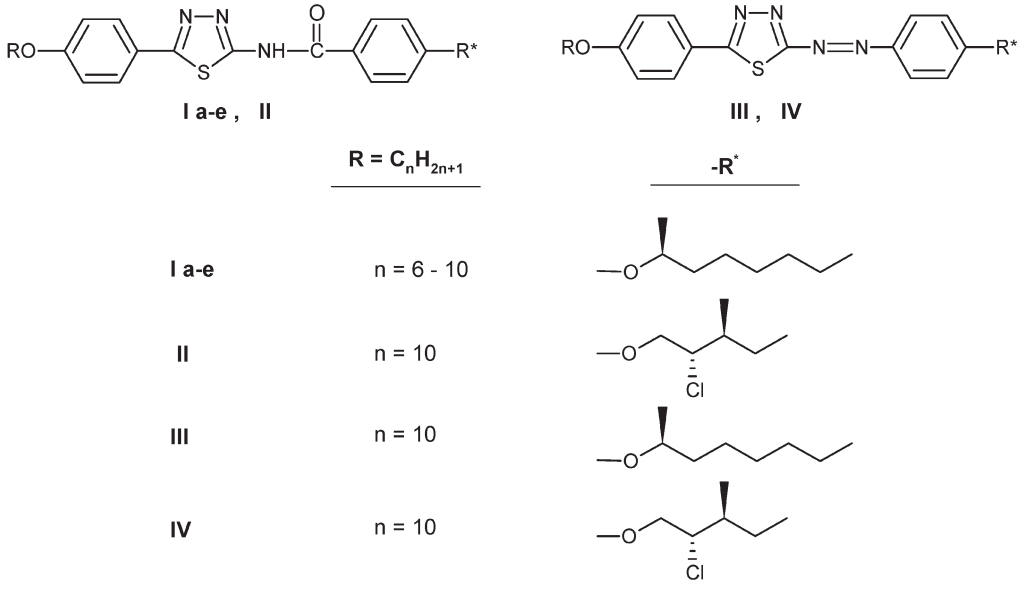
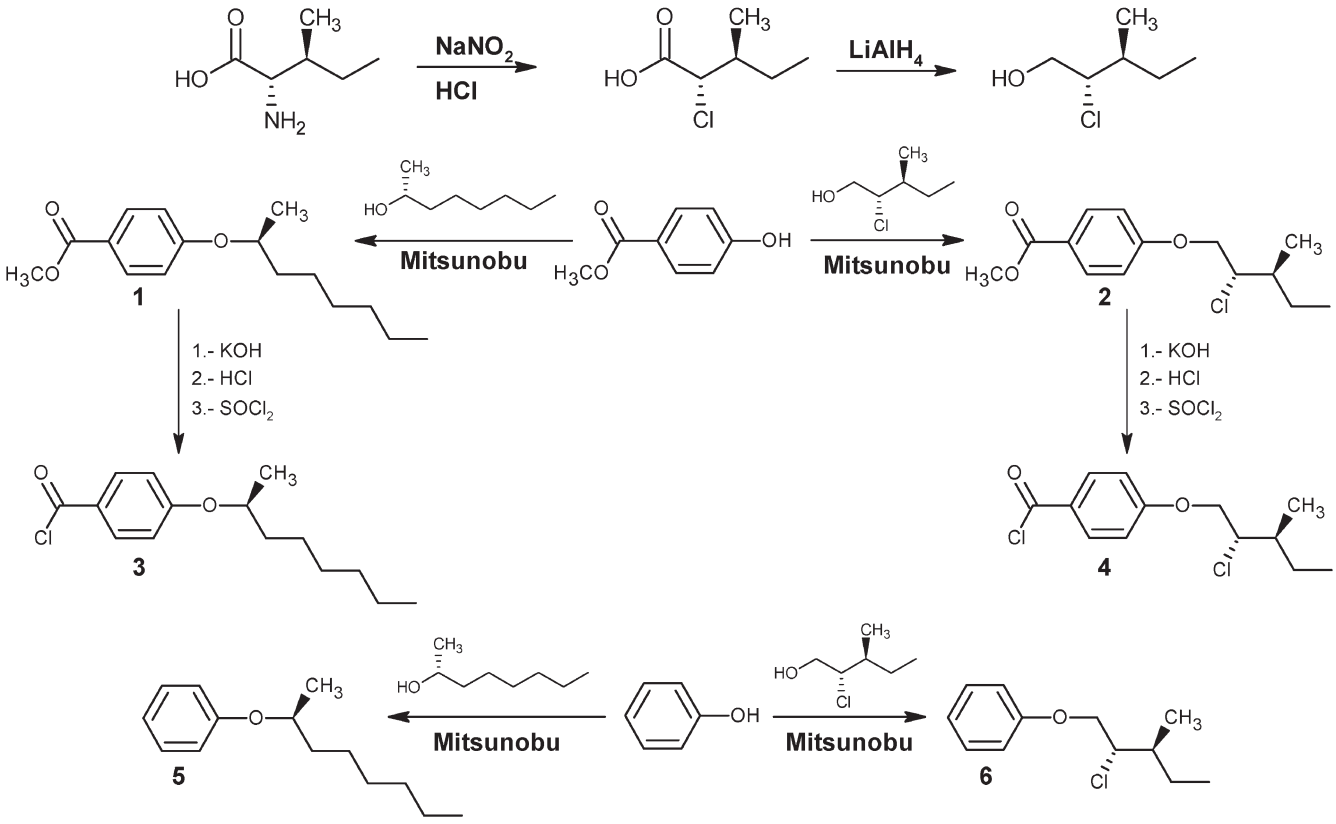
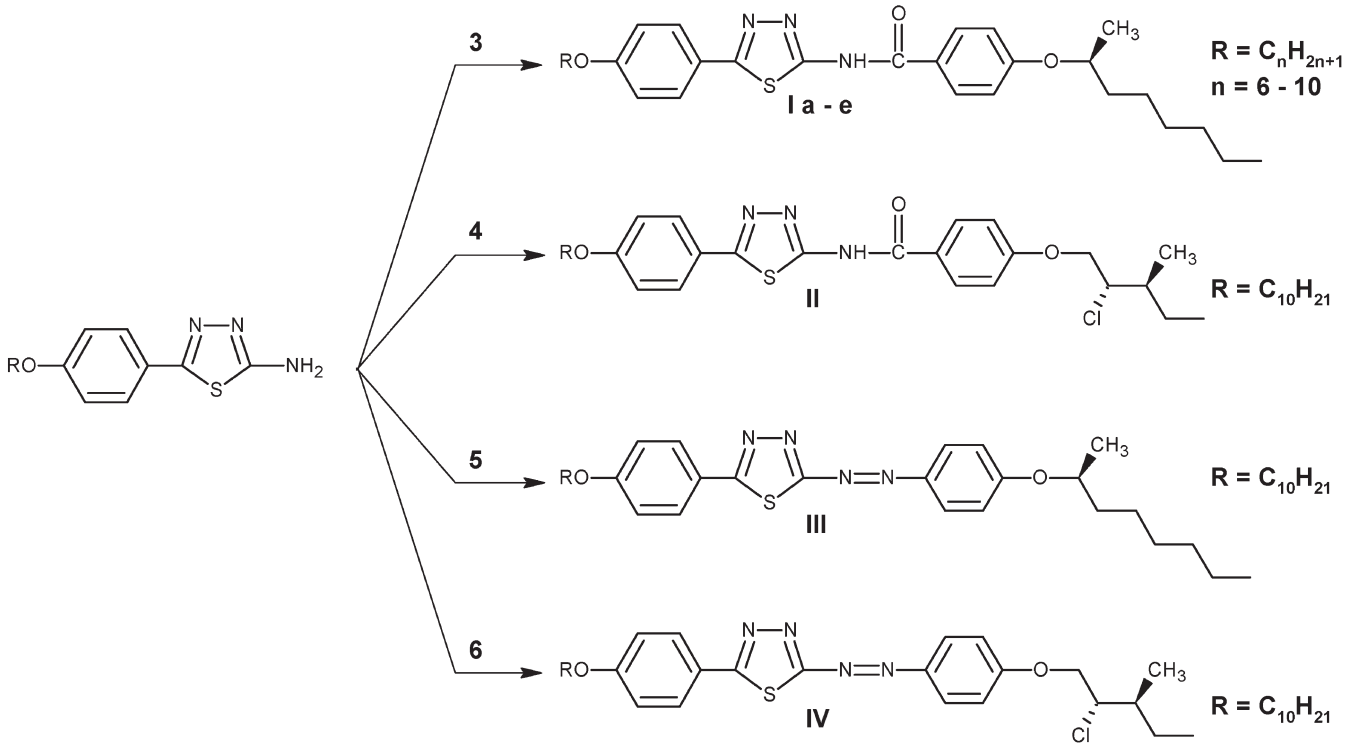


Figure 1. Structures of the chiral compounds **Ia**–**Ie** and **II**–**IV**.



Scheme 1. Synthetic route for chiral precursors **1**–**6**.



Scheme 2. Synthetic route for chiral amides **Ia**–**Ie** and **II** and azo compounds **III** and **IV**.

Table 1. Transition temperatures and enthalpies of the chiral compounds **Ia**–**Ie**, **II**, **III** and **IV** (Cr=crystal, SmX=smectic X, SmC*=chiral smectic C, SmA=smectic A, N*=chiral nematic, I=isotropic).

Compound	Transition	T/°C	ΔH/J g^{-1}
Ia (n=6)	Cr–SmX	153.8	37.9
	SmX–N*	157[a]	–
	N*–I	162.3	0.65
Ib (n=7)	Cr–SmX	155.6	38.9
	SmX–SmC*	158[a]	–
	SmC*–N*	161.1	1.1
	N*–I	165.2	0.63
Ic (n=8)	Cr–SmX	154.7	38.5
	SmX–SmC*	157[a]	–
	SmC*–N*	160.9	6.44
	N*–I	164.2	1.1
Id (n=9)	Cr–SmX	156.8	39.1
	SmX–SmC*	159.3	4.1
	SmC*–N*	161.5	1.5
	N*–I	163.2	1.4
Ie (n=10)	Cr–SmX	145.9	40.2
	SmX–SmC*	150[a]	–
	SmC*–N*	162.7	6.8
	N*–I	170.2	1.1
II (n=10)	Cr–SmA	142.4	47.2
	SmA–I	163.0	1.0
III (n=10)	Cr–N*	81.7	50.9
	N*–I	92.8	0.7
IV (n=10)	Cr–N*	113.1	52.1
	N*–I	118.3	0.6

[a]Optical microscopy data.

All the compounds in the series **Ia**–**Ie** show mesomorphic properties. In each case a phase of high order, denoted as a SmX phase, is observed.

Enantiotropic phase sequences are observed for compounds **Ib**–**Ie** (Cr–SmX–SmC*–N*–I). Compound **Ia** does not exhibit a SmC* phase, instead exhibiting an enantiotropic SmX–N* dimorphism.

Compound **Ie** has a lower melting point and higher clearing temperatures than the corresponding **Ia**–**Id** compounds. In addition, compound **Ie** exhibits broader SmC* (12.7°C) and N* (7.5°C) temperature ranges than compounds **Ia**–**Id**, which have a lower clearing temperature, reduced SmC* and N* temperature ranges and decreased mesomorphic stability.

On the other hand, replacement of the chiral alkoxy chain derived from (*R*)-2-octanol in compound **Ie** (n=10) by a chiral alkoxy chain derived from (*S*)-isoleucine results in the disappearance of the SmX–SmC*–N* mesomorphism in compound **II**, which is purely smectic A (SmA) in character. Thus, the mesomorphic behaviour strongly depends of the nature of the chiral chain in the molecule.

These results show that the chiral alkoxy chain derived from (*R*)-2-octanol (series **Ia**–**Ie**) favours polymorphism, in particular the SmC* phase, indicating that the lateral dipolar interactions associated with terminal chiral chain dipoles must be much more favoured in **Ia**–**Ie** amides (which contain a chiral alkoxy chain derived from (*R*)-2-octanol) than amide **II** with a chiral alkoxy chain derived from (*S*)-isoleucine [8].

Compounds **III** and **IV** show enantiotropic mesomorphic properties. In each case a chiral nematic (N*) mesophase is observed. Azo compound **III** has a broader mesomorphic range than azo compound **IV**.

It is also interesting to compare the mesogenic properties of the amides **Ie** and **II** with the azo compounds **III** and **IV**. The azo compounds show a different mesomorphic behaviour from the corresponding amides. The amides (**Ie** and **II**) and the azo compounds (**III** and **IV**) have the same central core and the same achiral alkoxy chain (*n*-decyloxy). Although **Ie** and **III** have the same chiral alkoxy chain derived from (*R*)-2-octanol and **II** and **IV** have one derived from (*S*)-isoleucine, some significant differences between their central linkages can be noted. The amide **Ie** displays enantiotropic smectic phases (SmX, SmC*) and enantiotropic chiral nematic phase (N*) and amide **II** shows an enantiotropic SmA phase; in contrast, the azo compounds (**III** and **IV**) do not show smectic order, and only display a chiral nematic phase (N*). This can be explained by taking into account the formation of hydrogen bonding between the amide molecules. This parallel molecular arragement would encourage smectic mesomorphism by providing additional lateral intermolecular attraction and by lining up molecules in a layered order [5, 16]. For amides the layered smectic order is more favoured than for azo compounds; this is fully compatible with a molecular arrangement resulting from intermolecular hydrogen bonding, which is a powerful tool for stabilizing and inducing mesophases, even in compounds in which the structure largely deviates from that of the classical calamitic liquid crystals. It has long been known that in several liquid crystals intermolecular hydrogen bonding is responsible for the existence of the mesophases [17]. However, the amide group is not frequently encountered in liquid crystalline materials because, in general, it gives rise to significantly higher intermolecular interactions that often preclude mesomorphic behaviour. For example, Baeyens-Volant *et al.* previously reported a number of calamitic benzamide derivatives, but only one of these compounds showed mesomorphic behaviour [16]. In contrast, all the amides reported here (**Ia**–**Ie**, **II**) displayed liquid crystalline behaviour in a reasonable temperature ranges. We think that the molecules must be associated in such a way that the layers containing the rigid moieties are connected through hydrogen bonds. In addition, the introduction

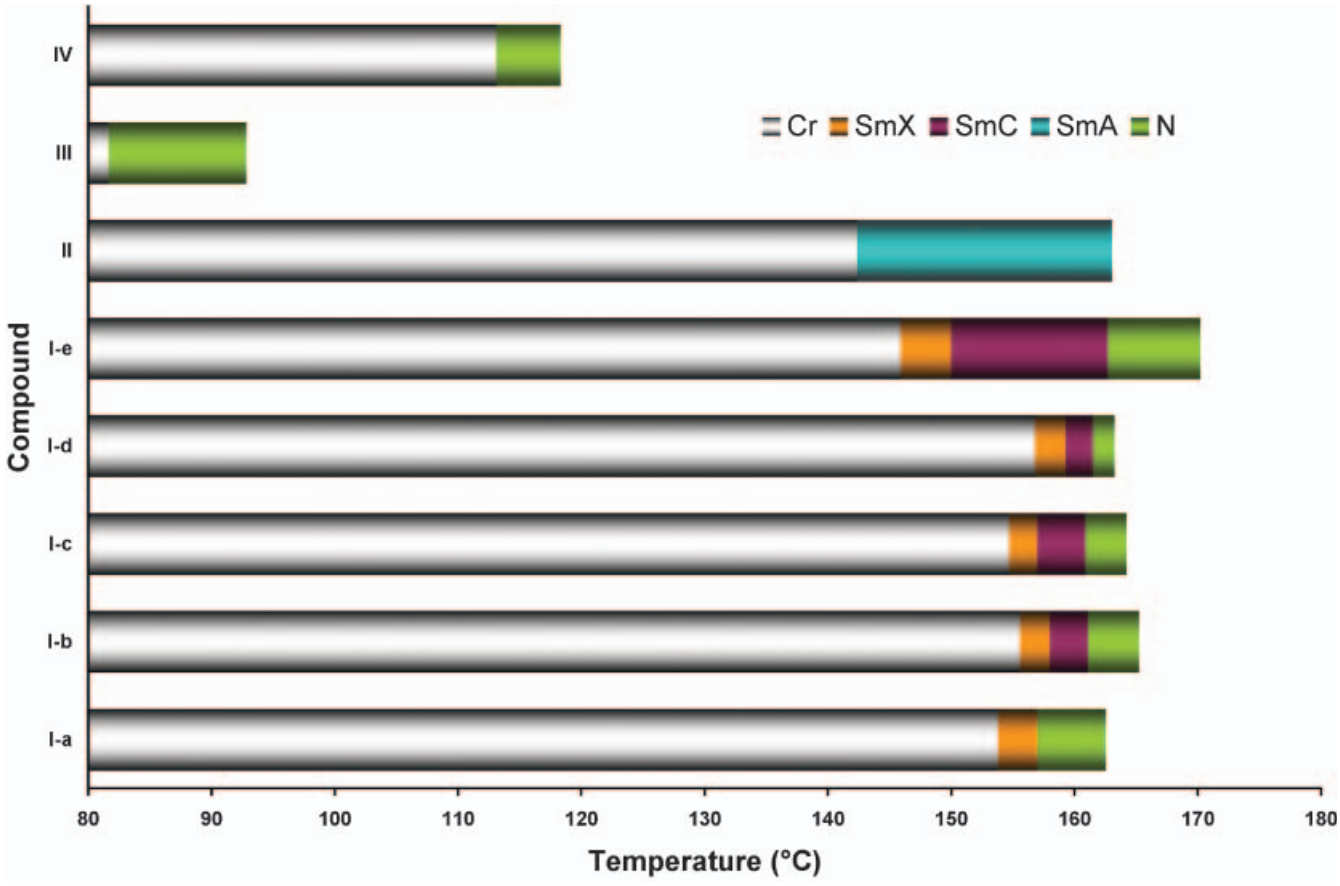


Figure 2. Plots of the mesomorphic behaviour of compounds **Ia**–**Ie** and **II**–**IV**.

of a thiadiazole ring within the central core of calamitic molecules strongly influences their mesomorphic behaviour due (though not only) to the permanent dipolar moment associated with the heterocyclic ring. These factors could explain the mesomorphic properties of the amides reported here.

As mentioned above, previously we have reported FLCs with a thiadiazole ring in the mesogenic core [8], which had the same central rigid core and same achiral alkoxy chain (*n*-decyloxy) and the same chiral alkoxy chain at the end of the rigid core as those compounds **Ie**, **II**–**IV**. The main difference is in their central linkages. The former have an imine group, whereas the latter have an amide group (**Ie** and **II**) and azo group (**III** and **IV**). The compounds reported previously [8] display SmC* (ferroelectric) and N* (cholesteric) phases as well as the analogous amide **Ib**–**Ie** reported here. In contrast, the azo compounds **III** and **IV** do not show smectic mesophase, and only display an enantiotropic N* (cholesteric) phase. These results are in accordance with our previous findings on analogous achiral systems [5, 18]. Based on semiempirical calculations (AM1) we found that the most stable conformation in these achiral systems (amides, Schiff bases and azo compounds) is that with a coplanar arrangement between the thiadiazole unit and the central bridge. The only significant difference is the different stabilization obtained between the extreme values of the conformers. Both the amides and Schiff bases had a major rotational barrier and also showed a hindered rotation around C(thiadiazole)–C(central bridge), and consequently a major rigid core linearity than azo compounds. From these results we assume that the chiral Schiff bases previously reported [8] and the chiral amides reported here have a more rigid core linearity than the chiral azo compounds, which in turn favours smectic order.

3.2. *Textures observed by polarizing optical microscopy*

The existence of SmC*, N* and SmA phases was determined from textural observations using polarizing optical microscopy (POM) under both heating and cooling conditions. Phase transition temperatures observed by POM were found to be in reasonable agreement with the corresponding differential scanning calorimetry (DSC) thermograms. Representative photomicrographs

of the textures observed for N*, SmC* and SmX phases are shown in figure 3.

The SmA phase of compound **II** was characterized by the formation of the typical focal-conic fan texture. When SmA phases consist of chiral molecules they can adopt helical ordering, thus forming a TGBA frustrated structure [19, 20]. However, the texture observed by POM for compound **II** is orthogonal SmA, typical of where the molecules are arranged in layers so that their long axes are on average perpendicular to the diffuse layer planes.

The N* phase of the homologues of series **Ia**–**Ie** and azo compounds **III** and **IV** was characterized by the formation of the oily-streaks texture characteristic of the cholesteric phase [21]. In figures 3 a and 3 b, typical optical photomicrographs for the N* phase of amide **Ie** and azo compound **III** are displayed.

For the high-order phase (SmX), a mosaic texture was observed for each homologue of series **Ia**–**Ie** compounds (see figure 3 c).

The SmC* phase was identified by its characteristic iridescent petal (figure 3 d) and broken focal conic (figure 3 e) textures [22, 23]. In figure 3 f, an electro-optical photomicrograph for the SmC* phase for compound **Ie** is shown. The texture was achieved applying 1 Vpp with a 1 Hz triangular wave; in this situation an electro-optical response was observed. The same SmC* region with no voltage treatment can be seen in figure 3 e.

Some chiral liquid crystalline 1,3,4-thiadiazole derivatives incorporating differently substituted allenic moieties exhibit a complex SmC* polymorphism [11]. In addition to a ferroelectric phase, the ocurrence of an antiferroelectric and ferrielectric phases was proposed [24]. In compounds **Ib**–**Ie** reported here no additional phase transitions have been detected within the SmC* phase region by DSC, and the optical textures show no significant changes in the SmC* phase range. Therefore, the amides **Ib**–**Ie** are FLCs. The physical properties of the ferroelectric SmC* liquid crystal phase, e.g. switching behaviour, spontaneous polarization and pyroelectric properties, are being investigated and will be reported in a future publication.

4. Experimental

4.1. *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 POM 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°C min^{-1} during heating and cooling. The instrument was calibrated using an indium standard (156.6°C, 28.44 J g^{-1}).

4.2. *Synthesis of intermediates and products*

(*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. Analitycal 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 [12–14].

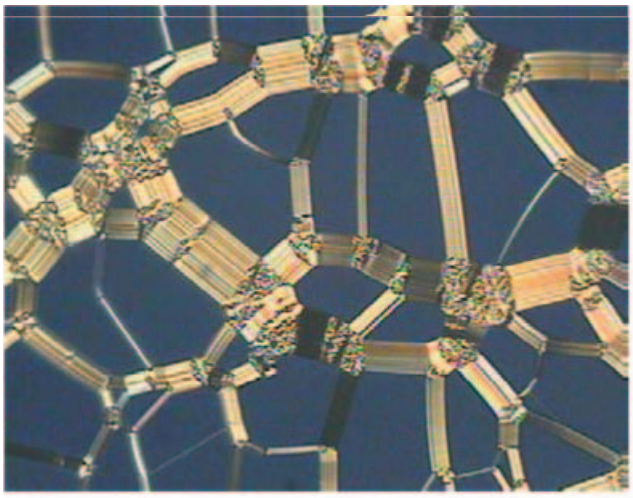
The 5-(*4-n*-decyloxy)phenyl-2-amino-1,3,4-thiadiazole was synthesized according to methods described elsewhere [4–6].

4.2.1. Methyl 4-(1-methyl)heptyloxybenzoate (1) and methyl 4-(2-chloro-3-methyl)pentyloxybenzoate (2). These compounds were synthesized using the procedure described previously [7, 8]. Products were obtained in liquid form, and were purified by chromatography using 2 : 1 *n*-hexane/dichloromethane as eluent. Yields: **1** (98%); **2** (80%).

For **1**, ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.90 (t, J=6.44 Hz, 3H, CH_3), 1.41 (d, J=5.99 Hz, 3H of the methyl branch), 1.40–1.75 (m, 10H, 5 CH_2), 3.90 (s, 3H, CH_3 of the ester group), 4.4 (m, 1H, CH of the chiral chain), 6.80 (d, J=8.76 Hz, 2H, 2 arom. H), 7.90 (d, J=8.61 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 13.8 (CH_3), 19.4 (methyl branch), 22.5, 24.9, 29.6, 31.7, 36.2 (aliph. C), 51.7 (CH_3 of the ester group), 59.6 (CH of the chiral chain), 119.4, 131.5 (arom. C), 122.9, 162.1 (quaternary arom. C), 166.8 (C=O). IR (film, cm^{-1}) 2927 (Csp^3–H), 1724 (C=O), 1602 (C=C).

For **2**, ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.95 (t, J=7.40 Hz, 3H, CH_3), 1.16 (d, J=6.65 Hz, 3H of the methyl branch), 1.30–1.45 (m, 2H, CH_2), 1.80 (m, 1H, *C**H**CH_3), 4.00 (s, 3H, CH_3 of the ester group),

Figure 3. Mesophase textures obtained on cooling: (a) oily-streaks texture (N*) at 166°C for compound **Ie**; (b) oily-streaks texture (N*) at 89°C for compound **III**; (c) mosaic texture (SmX) at 155°C for compound **Ia**; (d) iridescent petal texture (SmC*) at 161°C for compound **Ie**; (e) broken focal-conic texture (SmC*) without electric field for compound **Ie**; (f) broken focal-conic texture (SmC*) with 1 Vpp electric field applied at 155°C for compound **Ie**.



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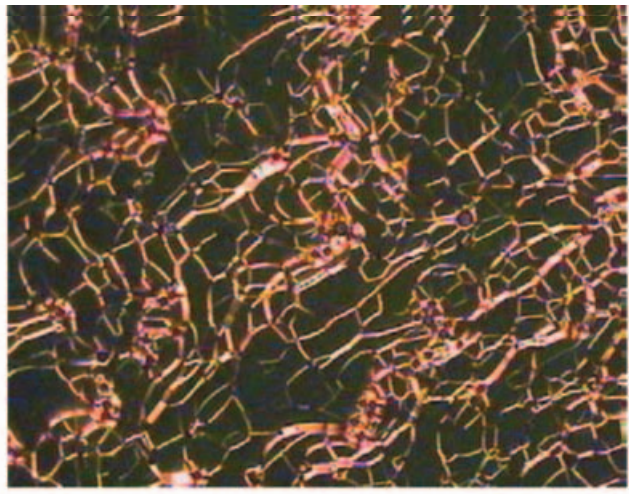

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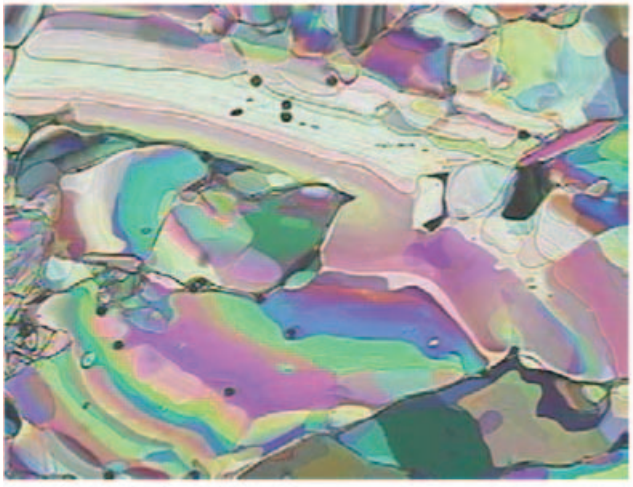

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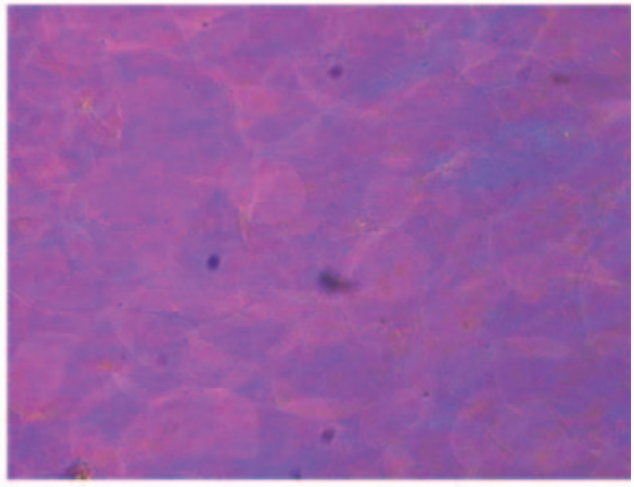

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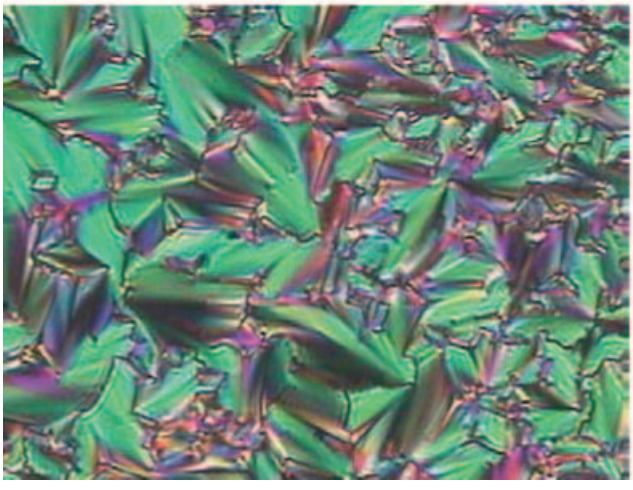

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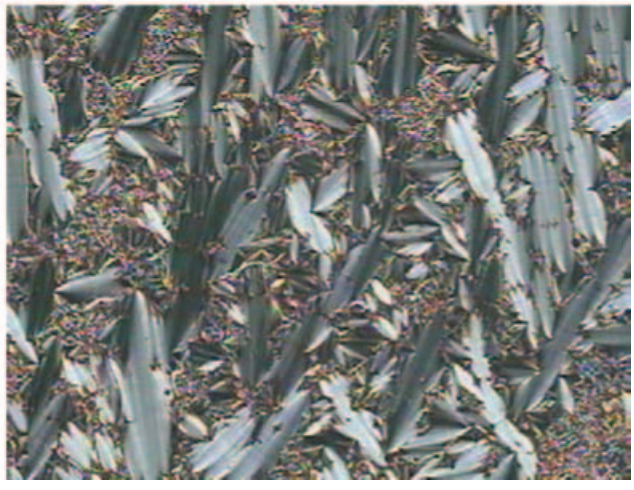

(*f*)

4.45 (m, J=7.03 Hz, 1H, *CHCl), 4.79 (m, 2H, OCH_2), 7.0 (d, J=8.70Hz, 2H, 2 arom. H), 7.90 (d, J=8.62 Hz, 2H, 2 arom. H). ^{13}CNMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 12.1 (CH_3), 16.1 (methyl branch), 23.1 (CH_2), 39.4 (*$\mathbf{C}$HCH_3), 67.9 (OCH_2), 71.7 (*CHCl), 116.1, 136.7 (arom. C), 122.0, 165.1 (quaternary arom. C), 176.8 (C=O). IR (film, cm^{-1}): 2960 (Csp^3–H), 1628 (C=O), 1575 (C=C).

4.2.2. 4-(1-Methyl)heptyloxybenzoic acid chloride (3) and 4-(2-chloro-3-methyl)pentyloxybenzoic acid chloride (4). These compounds were synthesized by saponification of esters **1** and **2**, according to the procedures described in the literature [25, 26], yielding the corresponding chiral benzoic acid, which reacts with thionyl chloride; the resulting chiral benzoic acid chloride (**3** and **4**) were obtained in liquid form, and were used in subsequent reaction without further purification.

The chiral benzoic acids obtained after saponification of the esters **1** and **2** were identified by their characteristic signals in ^{1}H NMR and IR spectra. The signal of the CH_3 of the ester group at 3.9 (ppm)in ester **1** and 4.0 (ppm)in ester **2** disappears in the corresponding chiral benzoic acid and the characteristic signal of the OH, of the carboxylic group, at about 11.0 (ppm)was observed in the spectra. In addition, the IR spectra show a sharp band at 1680 cm^{-1} (C=O) and a very broad and strong band centred at 3000 cm^{-1} (OH).

4.2.3. (1-Methyl)heptyloxybenzene (5) and (2-chloro-3-methyl)pentyloxybenzene (6). These compounds were synthesized using the procedure described previously [7, 8]. Products were obtained in liquid form, and were purified by chromatography using 7 : 3 n-hexane/ethyl acetate as eluent. Yields: **5** (71%); **6** (83%).

For **5**, ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.80 (t, J=6.60 Hz, 3H, CH_3), 1.20 (d, J=6.59 Hz, 3H of the methyl branch), 1.30–1.55 (m, 10H, 5 CH_2), 4.3 (m, 1H, CH of the chiral chain), 6.88 (m, 3H, 3 arom. H), 7.20 (d, J=7.90 Hz, 2H, 2 arom. H).^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 14.1 (CH_3), 19.7 (methyl branch), 22.6, 25.6, 29.3, 31.8, 36.6 (aliph. C), 73.7 (CH of the chiral chain), 115.9, 120.3, 129.4 (arom. C), 129.4 (quaternary arom. C). IR (film, cm^{-1}): 2928 (Csp^3–H), 1594 (C=C), 1239 (C–O).

For **6**, ^{1}HNMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 1.05 (t, J=6.89 Hz, 3H, CH_3), 1.16 (d, J=6.59 Hz, 3H of the methyl branch), 1.35–1.59 (m, 2H, CH_2), 1.30 (m, 1H, *C$\mathbf{H}$$CH_3$), 3.90 (m, 1H, *CHCl), 4.79 (m, 2H, OCH_2), 6.90 (m, 3H, 3 arom. H), 7.20 (d, J=8.88 Hz, 2H, 2 arom. H). ^{13}CNMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 11.2 (CH_3), 15.8 (methyl branch), 25.4 (CH_2), 38.2 (*$\mathbf{C}$HCH_3), 64.8 (OCH_2), 70.6 (*CHCl), 115.2, 120.4, 129.5 (arom. C), 122.0 (quaternary arom. C). IR (film, cm^{-1}): 2930 (Csp^3–H), 1598 (C=C), 1230 (C–O).

4.2.4. Optically active amides Ia–Ie and amide II. Compounds **Ia**–**e** were synthesized by condensation of 5-(4-n-alkoxy)phenyl-2-amino-1,3,4-thiadiazole (n=6–10) with the chiral benzoic acid chloride (**3**) derived from (*R*)-2-octanol and amide **II** was obtained by condensation of 5-(4-n-decyloxy)phenyl-2-amino-1,3,4-thiadiazole with the chiral benzoic acid chloride (**4**) derived from (*S*)-isoleucine, using the procedure described elsewhere [5].

A mixture of 2-amino-thiadiazole derivative (1.96 mmol) and 1.96 mmol of the corresponding chiral benzoic acid chloride (**3** for series **Ia**–**Ie** and **4** for amide **II**) in 20 ml of acetonitrile and 1 ml of triethylamine was heated under reflux for 4 h and then poured into a mixture of water and ice. The products were purified by crystallization on 2-methoxyethanol. The following yields were obtained: **Ia** (70%); **Ib** (71%); **Ic** (71%); **Id** (68%); **Ie** (73%); **II** (70%).

For **Ia** (n=6),^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.90 (t, J=6.62 Hz, 6H, 2 CH_3), 1.20 (d, J=6.75 Hz, 3H of the methyl branch), 1.30–1.62 (m, 18H, 9 CH_2), 4.00 (t, J=6.50 Hz, 2H, OCH_2), 4.50 (m, 1H, C$\underline{\mathrm{H}}$ of the chiral chain), 7.01 (dd, 4H, 4 arom. H), 7.90 (d, J=8.80 Hz, 2H, 2 arom. H), 8.30 (d, J=8.86 Hz, 2H, 2 arom. H), 12.01 (s, 1H, NH).^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 13.9, 14.0 (2 CH_3), 19.6 (methyl branch), 22.5, 25.4, 25.9, 29.2, 31.5, 31.8, 36.3 (aliph. C), 68.2 (OCH_2), 74.1 (CH of the chiral chain), 114.9, 115.0, 128.5, 130.9 (arom. C), 122.9, 123.0, 135.2, 140.8, 161.1, 162.5, (quaternary arom. C), 164.7 (C=O). IR (KBr disk, cm^{-1}): 3141 (N–H), 2925 (Csp^3–H), 1660 (C=O), 1607 (C=C).

For **Ib** (n=7), ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.90 (t, J=6.70 Hz, 6H, 2 CH_3), 1.40 (d, J=6.43 Hz, 3H of the methyl branch), 1.29–1.52 (m, 20H, 10 CH_2), 4.30 (t, J=6.55 Hz, 2H, OCH_2), 4.60 (m, 1H, CH of the chiral chain), 7.00 (dd, 4H, 4 arom. H), 8.00 (d, J=8.45 Hz, 2H, 2 arom. H), 8.28 (d, J=8.32 Hz, 2H, 2 arom. H), 12.10 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 14.1, 14.3 (2 CH_3), 20.1 (methyl branch), 22.8, 25.5, 25.7, 29.0, 30.9, 31.7, 35.9 (aliph. C), 68.4 (OCH_2), 74.5 (CH of the chiral chain), 114.9, 115.4: 128.6, 130.5 (arom. C), 122.8, 125.1, 135.0, 141.1, 161.0, 162.7 (quaternary arom. C), 164.6 (C=O). IR (KBr disk, cm^{-1}): 3142 (N–H), 2926 (Csp^3–H), 1660 (C=O), 1607 (C=C).

For **Ic** (n=8), ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.80 (t, J=6.65 Hz, 6H, 2 CH_3), 1.30 (d, J=6.83 Hz, 3H of the methyl branch), 1.21–1.49 (m, 22H, 11 CH_2), 4.00 (t, J=6.50 Hz, 2H, OCH_2), 4.50 (m,

1H, CH of the chiral chain), 6.90 (dd, 4H, 4 arom. H), 7.90 (d, J=8.62 Hz, 2H, 2 arom. H), 8.30 (d, J=8.77 Hz, 2H, 2 arom. H), 11.90 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 13.9; 14.1 (2 CH_3), 19.6 (methyl branch), 22.5, 25.4, 25.7, 26.0, 29.2, 29.3, 30.9, 31.8, 36.9 (aliph. C), 68.2 (OCH_2), 74.1 (CH of the chiral chain), 114.8, 115.8: 128.3, 130.9 (arom. C), 122.9, 123.0, 135.3, 140.8, 161.0, 162.5 (quaternary arom. C), 164.8 (C=O). IR (KBr disk, cm^{-1}): 3143 (N–H), 2928 (Csp^3–H), 1662 (C=O), 1608 (C=C).

For **Id** (n=9), ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.82 (t, J=6.63 Hz, 6H, 2 CH_3), 1.31 (d, J=6.81 Hz, 3H of the methyl branch), 1.23–1.50 (m, 24H, 12 CH_2), 3.97 (t, J=6.55 Hz, 2H, OCH_2), 4.42 (m, 1H, CH of the chiral chain), 6.88 (dd, 4H, 4 arom. H), 7.80 (d, J=8.79 Hz, 2H, 2 arom. H), 8.20 (d, J=8.83 Hz, 2H, 2 arom. H), 12.50 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 14.0, 14.2 (2 CH_3), 19.7 (methyl branch), 22.6, 25.9, 27.2, 29.3, 29.5, 30.9, 31.7, 36.4 (aliph. C), 68.4 (OCH_2), 74.5 (CH of the chiral chain), 115.0, 115.3, 128.5, 130.8 (arom. C), 122.7, 123.4, 135.5, 141.0, 161.1, 162.6 (quaternary arom. C), 165.0 (C=O). IR (KBr disk, cm^{-1}): 3141 (N–H), 2926 (Csp^3–H), 1659 (C=O), 1609 (C=C).

For **Ie** (n=10), ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.88 (t, J=6.65 Hz, 6H, 2 CH_3), 1.39 (d, J=6.79 Hz, 3H of the methyl branch), 1.28–1.52 (m, 26H, 13 CH_2), 4.01 (t, J=6.50 Hz, 2H, OCH_2), 4.53 (m, 1H, CH of the chiral chain), 6.99 (dd, 4H, 4 arom. H), 7.90 (d, J=8.86 Hz, 2H, 2 arom. H), 8.32 (d, J=8.82 Hz, 2H, 2 arom. H), 12.42 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 13.9, 14.2 (2 CH_3), 19.9 (methyl branch), 22.3, 22.5, 25.3, 26.3, 29.1, 29.5, 30.6, 31.9, 36.4 (aliph. C), 68.9 (OCH_2), 75.6 (CH of the chiral chain), 115.7, 117.6, 127.5, 132.6 (arom. C), 122.1, 123.4, 136.0, 141.2, 161.7, 163.6 (quaternary arom. C), 164.7 (C=O). IR (KBr disk, cm^{-1}): 3139 (N–H), 2924 (Csp^3–H), 1660 (C=O), 1607 (C=C).

For amide **II**, ^{1}HNMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.98 (t, J=6.10 Hz, 6H, 2 CH_3), 1.10 (d, J=6.35 Hz, 3H of the methyl branch), 1.02–1.80 (m, 18H, 9CH_2), 1.90 (m, 1H, *C**H**CH_3), 4.00 (t, J=6.50 Hz, 2H, OCH_2), 4.20 (m, 3H, OCH_2 of the chiral chain and *CHCl), 6.99 (d, J=8.82 Hz, 2H, 2 arom. H), 7.56 (d, J=8.68 Hz, 2H, 2 arom. H), 7.89 (d, J=8.77 Hz, 2H, 2 arom. H), 7.96 (d, J=8.70 Hz, 2H, 2 arom. H), 12.7 (s, 1H, NH). ^{13}CNMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 10.7, 13.1 (2 CH_3), 16.0 (methyl branch), 22.6, 24.6, 25.9, 29.1, 29.2, 29.3, 29.5, 31.8 (aliph. C), 38.7 (*$\mathbf{C}$HCH_3), 66.5 (*CHCl), 67.2, 68.9 (2 OCH_2), 113.9, 115.1, 128.7, 131.3 (arom. C), 123.1, 131.3, 158.0, 159.1, 160.6, 163.2 (quaternary arom. C), 165.0 (C=O). IR (KBr disk, cm^{-1}): 3149 (N–H), 2925 (Csp^3–H), 1663 (C=O), 1617 (C=C).

4.2.5. Optically active azo compounds III and IV. Azo compounds **III** and **IV** were synthesized by condensation of 5-(4-*n*-decyloxy)phenyl-2-amino-1,3,4-thiadiazole with the corresponding chiral alkoxybenzene **5** [derived from (*R*)-2-octanol] and **6** [derived from (S)-isoleucine], respectively, using the procedure described elsewhere [18].

5-(4-*n*-decyloxy)phenyl-2-amino-1,3,4-thiadiazole (1.71 mmol) was dissolved by heating and stirring in 12 ml of 85% phosphoric acid. The solution was cooled in an ice bath, and then concentrated nitric acid (3 ml) and a solution of sodium nitrite (3.48 mmol) in 2 ml of water were added. The mixture was stirred vigorously and maintained below 5°C for 15 min. 1.71 mmol of the corresponding chiral alkoxybenzene (**5** for azo compound **III** and **6** for azo compound **IV**) was then added dropwise with stirring. The orange solid was filtered, washed several times with water. The products were purified by chromatography using 7 : 3 *n*-hexane/ethyl acetate as eluent. Yields: **III** (57%); **IV** (46%).

For **III**, ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.80 (t, J=6.70 Hz, 6H, 2 CH_3), 1.40 (d, J=6.71 Hz, 3H of the methyl branch), 1.50–1.52 (m, 26H, 13 CH_2), 3.90 (t, J=6.60 Hz, 2H, OCH_2), 4.40 (m, 1H, CH of the chiral chain), 6.90 (dd, 4H, 4 arom. H), 7.90 (dd, 4H, 4 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 14.2, 14.9 (2 CH_3), 18.9 (methyl branch), 22.5, 22.6, 25.3, 25.9, 29.1, 29.5, 31.6, 31.9, 36.4 (aliph. C), 68.2 (OCH_2), 74.5 (CH of the chiral chain), 115.0, 115.8, 126.6, 129.6 (arom. C), 116.7, 117.2, 131.9, 134.4, 139.2, 140.1 (quaternary arom. C). IR (KBr disk, cm^{-1}): 2926 (Csp^3–H), 1597 (C=C).

For **IV**, ^{1}HNMR ($CDCl_3$, TMS, 250 MHz): δ (ppm) 0.90 (t, J=6.85 Hz, 6H, 2 CH_3), 1.20 (d, J=6.43 Hz, 3H of the methyl branch), 1.02–1.80 (m, 18H, 9 CH_2), 1.70 (m, 1H, *C**H**CH_3), 3.70 (m, 1H, *CHCl); 4.00 (t, J=6.79 Hz, 4H, 2 OCH_2), 7.00 (dd, 4H, 4 arom. H), 7.99 (dd, 4H, 4 arom. H). ^{13}CNMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) 13.8, 14.0 (2 CH_3), 15.3 (methyl branch), 22.6, 25.8, 29.0, 29.2, 29.4, 29.5, 31.8, 35.4 (aliph. C), 38.7 (*$\mathbf{C}$HCH_3), 66.9, 68.2, (2 OCH_2), 69.5 (*CHCl), 114.5, 115.6, 126.6, 129.6 (arom. C), 122.6, 146.5, 159.4, 162.7, 164.1, 168.3 (quaternary arom. C). IR (KBr disk, cm^{-1}): 2923 (Csp^3–H), 1596 (C=C).

Acknowledgement

This work was supported by FONDECYT (Grant 1030696) and ''Dirección de Investigación, Universidad de Concepción''.

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