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

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Online publication date: 11 November 2010

To cite this Article Garcia, Chantal and Malthête, Jacques(2002) 'Chiralization in mesogenic 1,3-diacylaminobenzenes', Liquid Crystals, 29: 9, 1133 — 1139
To link to this Article: DOI: 10.1080/02678290210160042
URL: http://dx.doi.org/10.1080/02678290210160042

LIQUID CRYSTALS, 2002, VOL. 29, NO. 9, 1133–1139

Chiralization in mesogenic 1,3-diacylaminobenzenes

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(*Received 17 April 2002; accepted 12 June 2002*)

The effect of molecular chirality in thermotropic mesomorphic H-bonded polymeric systems has not really been investigated so far. Therefore, five new chiral mesogenic diamides have been prepared and described. Besides more ordered mesophases, the enantiomers exhibit a chiral nematic polymorphism detected by microcalorimetry and probably corresponding to different modes of chiral coiling to give these singular twisted nematic phases.

1. Introduction

The transfer of molecular chirality to a macroscopic scale in liquid crystals raises fundamental questions and can lead to many applications provided by (i) chiral mesophases such as cholesteric or SmC*, (ii) new mesophases generated by compounds of high enantiomeric purity such as blue phases or TGB phases, or (iii) the polar properties of a SmA phase containing a non-racemic compound or of an untwisted chiral phase [1–3].

Besides chiral rod-like and disc-like liquid crystals derived from natural products such as steroids, sugars or amino acids, most chiral thermotropic mesogens incorporate only one chiral carbon atom in a paraffinic chain, which is commonly obtained from easily available optically pure alcohols. It is worth noting that other chiral centres can be used such as tetrahedral sulphur [4]. Rings with two or more chiral centres can also be introduced into paraffinic chains or within the mesogenic cores (for small cycles such as epoxides, see [5, 6]). Less classical, but no less interesting liquid crystals with axial (allene [7, 8], cyclohexylidene ethanone [9, 10], biphenyl [11], cyclotribenzylidene [12], helicene [13]) or planar [14–16] chirality—which require asymmetric synthesis or chiral separation techniques—have therefore been much less studied. We should add that achiral banana-shaped molecules can also adopt chiral arrangements in lamellar mesophases [17]. On the other hand, the effects of molecular chirality in artificial thermotropic mesomorphic H-bonded polymeric systems have not really been investigated so far†.

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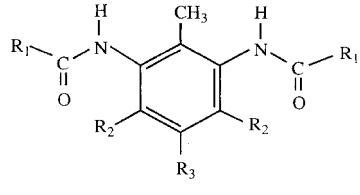
†On the contrary, mesomorphic biological H-bonded polymeric systems can exhibit chiral figures. For example, concentrated solutions of nucleosome core particles exhibit gorgeous chiral discotic columnar nuclei [18].

Depending on the number and relative positions of sites capable of giving rise to hydrogen bonding in a molecule of any shape, mesomorphic polymeric self-assembly can actually be induced. For example, the two polar amide groups of diamide **1** develop intermolecular hydrogen bonds causing the molecules to arrange in infinite, parallel, supramolecular wires which organize themselves in lamello-columnar, columnar or nematic mesophases [19, 20].



1

R_1 = *n*-C_nH_{2n+1}- or 3,5-(*n*-$C_nH_{2n+1}O)_2C_6H_3$-

R_2 = -H or -CH_3

R_3 = -H or *tert*-butyl- or -CO_2Y
(Y = alkyl, alkenyl chains or aromatic groups)

Therefore we have been interested for sometime in effects linked to the introduction of molecular chirality in these H-bonded systems. As a matter of fact, we could expect to observe a macroscopic twist corresponding to a cholesteric phase of a peculiar type. For instance, one among other chiral structures of self-hydrogen-bonded supramolecular wires could look like the structure of a chiral polyacetylene described by Akagi and coworkers [21]. Moreover, in a 2D columnar mesomorphic arrangement, such a chiral system could exhibit asymmetric textures as reported in only two cases: enantiomorphic opposite points and spirals in 2,3,6,7,10,11-hexakis-(3-methylnonanoyloxy) triphenylene enantiomers [22] and a spiral texture in (*S*)-2,3,9,10,16,17,23,24-octakis-(3,7-dimethyloctyloxy) phthalocyanine [23]. Because we

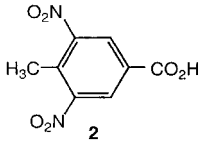
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290210160042

do not know the exact causes of this macroscopic expression of chirality, some further examples in different series of chiral compounds would doubtless contribute to a better understanding of this phenomenon.

2. Results

We report here the synthesis and mesomorphic properties of new chiral diamides **5**, all of which presented mesomorphic properties (see the table). They were prepared by reaction of the diamines **4** with palmitoyl chloride in dry acetone in the presence of Na_2CO_3. Diamines **4** were obtained by reduction of the corresponding dinitro derivatives **3** with H_2 in AcOEt in the presence of Pd/C catalyst. The dinitro esters **3** were prepared by treating the appropriate alcohol, in enantiomerically pure or racemic form, with the acid **2** in CH_2Cl_2 in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and 4-*N*,*N*-dimethylaminopyridine (DMAP). As a first step, we have chosen to graft chains bearing only one chiral centre.

The principle of our study consisted in analysing the changes in the mesomorphic properties according to the length of the grafted chiral alcohol, whose asymmetric carbon position could also vary. The paraffinic chain of the secondary alcohols linked to the asymmetric carbon had two (ester **5a**), three (ester **5b**), four (ester **5c**) or six carbons (**5d**). The chiral carbon can also be in the β-position (**5e**).



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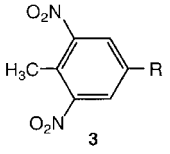

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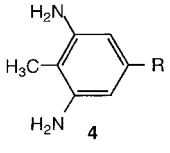

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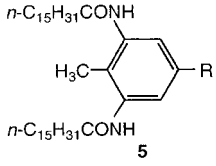
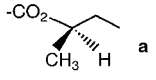
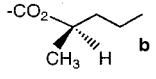


5

R = 

a



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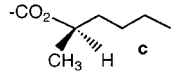

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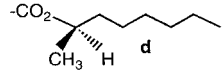

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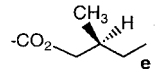


e

Table. Phase transition temperatures (°C) and corresponding enthalpy values (kJ mol^{-1}) in parenthesis for the chiral esters **5**. Abbreviations: Cr = crystalline solid; Col = columnar mesophase; N = nematic phase; N* = chiral nematic phase; M = unidentified mesophase.

(*R*)-(−)-**a**	Cr[a] → N*: 133 (65.5); N* → I: 172 (1.9)
(*R*)-(−)-**b**	Cr → N_1^*: 103 (32.2); N_1^* → N_2^*: 114 (1.6); N_2^* → N_3^*: 130 (1.2); N_3^* → M; 179 (1.8); M → Col[b] 205 (2.6); Col → I: 229 (2.6)
(±)-**b**	Cr → N: 115 (75.0); N → I: 183 (1.6)
(*R*)-(−)-**c**	Cr → N_1^*: 78 (69.6); N_1^* → N_2^*: 126.5 (0.4); N_2^* → I: 173 (1.4)
(±)-**c**	Cr → N: 86–120 (50.9); N → I: 176 (1.8)
(*R*)-(−)-**d**	Cr → Col[b] 88 (66.8); Col → N*: 174 (0.15); N* → I: 186 (2.3)
(±)-**d**	Cr → Col[b] 82 (43.5); Col → N: 126.5 (0.32); N → I: 177 (1.8)
(*S*)-(+)-**e**	Cr^1 → Cr^2: 122 (58.9); Cr^2 → N*: 153 (26.6); N* → I: 157

[a] Metastable ordered mesophases were also present in the whole series, but they are not yet identified.
[b] Columnar mesophase probably of hexagonal symmetry according to its textures observed between crossed polarizers.

An obvious twist appeared in the nematic phase of the shortest ester **5a** in which the helical axis is parallel to the glass plates and the distance between two adjacent stripes is the half pitch (about 3 μm) (figure 1). However, by lengthening the chiral chain, the twist decreased (i.e. the pitch increased) and disappeared for ester **5d**‡. Moreover, esters **5b** and **5c** had three and two chiral nematic phases, respectively. This chiral nematic polymorphism, not clearly observed so far on a thermotropic mesogen, is only detected by microcalorimetry: the N*–N* reversible transitions had enthalpies of about, 1 kJ mol^{-1} and probably corresponded to different packings of helical molecular wires (N*–N* transitions caused no notable texture change between crossed polarizers). Ester **5e**, bearing a chiral carbon in the β-position, showed no characteristic finger prints, as was the case for ester **5d**: only schlieren textures were observed (figure 2). Contrary to the enantiomers, racemic mixtures **5c** and **5d** presented only one nematic phase.

On the other hand, in addition to nematic (esters **5a**–**e**) and low temperture columnar (ester **5d**) mesophases, two further ordered mesophases surprisingly appeared for ester (*R*)-(−)-**5b** above the three chiral nematic states on heating: from 179 to 205°C, a mesophase (M) exhibited a strong homeotropic tendency, while columnar birefringent textures were observable in the highest temperature mesophase (Col).

Unfortunately, as we had previously noticed in the hexagonal columnar mesophases of two compounds quite similar to the diamides **5**—diamides **6** (ester of

‡ The pitch also increased slightly with temperature.

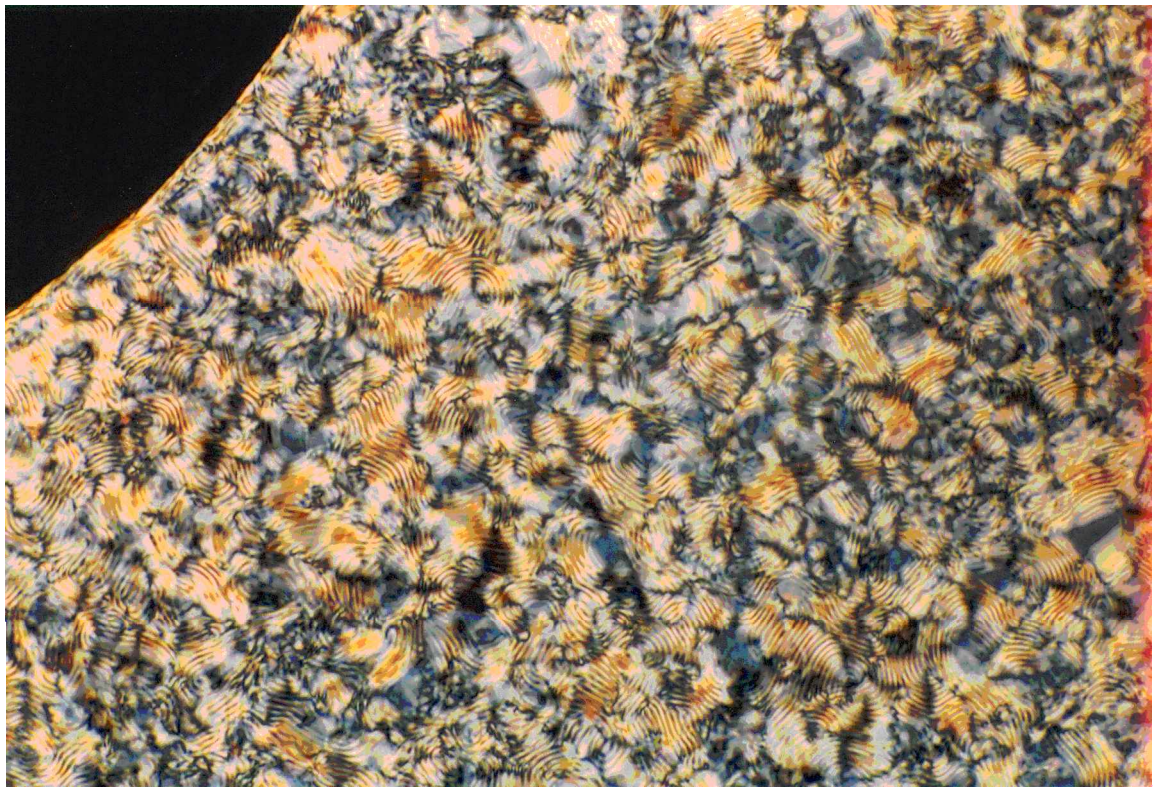


Figure 1. Finger prints in the chiral nematic texture of (*R*)-(−)-**5a** at 147°C between crossed polarizers.

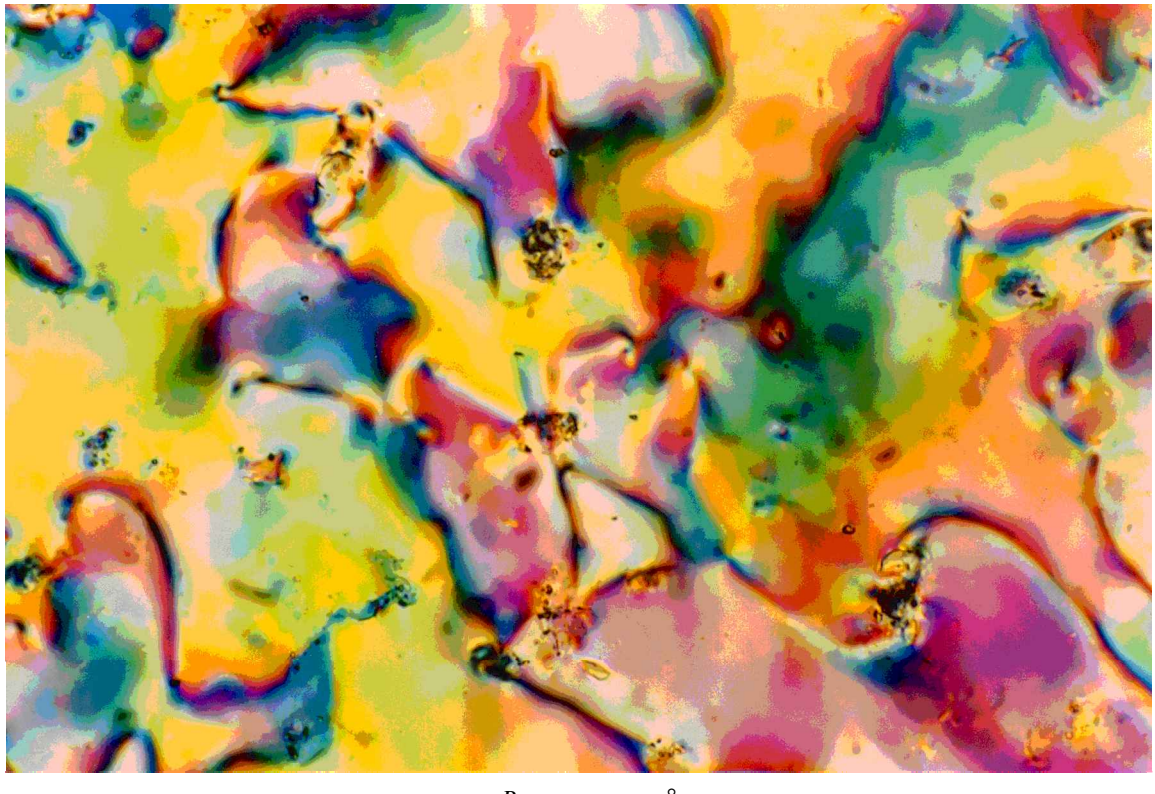
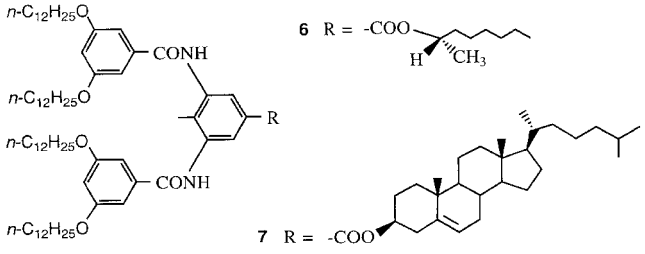


Figure 2. Nematic texture of (*R*)-(−)-**5d** at 181°C between crossed polarizers.

(*R*)-(−)-2-octanol) and **7** (ester of (−)-cholesterol), no chiral textures were observed in the columnar mesophase of **5d**§. X-ray diffraction measurements and optical observations are in progress to determine the different modes of chiral coiling needed to generate these singular twisted nematic phases.



3. Experimental

The products were purified by preparative column chromatography on Merck aluminium oxide 60, 0.063–0.2 mm (70–230 mesh). For TLC Merck aluminium oxide 150 F_{254} neutral (Type T) was used. DSC thermograms were recorded on a Perkin Elmer DSC 7 instrument at a scanning rate of 5°C min^{-1}. ^1H NMR spectra were recorded at 27°C on a AM-Bruker 400 MHz spectrometer using $CDCl_3$ as solvent. Chemical shifts δ are given in ppm relative to the solvent (^1H: $CHCl_3$, 7.24); coupling constants J are given in hertz. Optical rotations were measured using solvent $CHCl_3$ at 27°C on a Perkin Elmer 241 spectropolarimeter and are given in units of 10^{-1} deg cm^2 g^{-1}. Elemental analyses were made at the Service de Microanalyse (ICSN–CNRS). Textures were observed on a Leitz Ortholux polarizing optical microscope carrying a Mettler FP 82 heating stage equipped with a Mettler FP 80 temperature controller.

3.1. *Alkyl 3,5-dinitro-4-methylbenzoates* **3a–e**

3.1.1. *(R)-(−)-2-Butyl 3,5-dinitro-4-methylbenzoate* **3a**

To a stirred mixture of 3,5-dinitro-4-methylbenzoic acid (Aldrich, 5 g, 22 mmol), (*R*)-(−)-2-butanol (Aldrich, 2 ml, 22 mmol), and EDC (Aldrich, 6.7 g, 35.2 mmol) in dry CH_2Cl_2 (35 ml) at r.t. was added DMAP (Aldrich, 1.03 g, 8.4 mmol). After 12 h stirring, water (35 ml) was added to the red limpid solution. The organic layer was washed with water (35 ml), dried over anhydrous $MgSO_4$, filtered, and the solvent removed from the filtrate to give a dark red oily product. This was purified by chromatography on aluminium oxide using CH_2Cl_2 to give 5.5 g (89%) of pure (*R*)-(−)-**3a** (pale yellow solid), m.p. 70°C, $[\alpha]_D$ −33.1 (*c* 0.98). Found: C 50.9, H 4.9, N 9.9; $C_{12}H_{14}N_2O_6$ requires C 51.07, H 5.00, N 9.92%. ^1H NMR: δ 8.56 (s, 2H, ArH), 5.13 (quint., 1H, $J = 6.4$, CH_3–C**H***), 2.61 (s, 3H, $ArCH_3$), 1.76 and 1.69 (2 m, CH*–C**H**$_a$**H**$_b$), 1.35 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 0.95 (t, 3H, $J = 7.5$, CH_3).

§On heating, esters **6** and **7** exhibit the following sequences of phases: (**6**) crystal–51°C → hexagonal columnar mesophase$_1$–149°C → hexagonal columnar mesophase$_2$–164°C → isotropic liquid; (**7**) crystal–166°C → hexagonal columnar mesophase–204°C → isotropic liquid [24].

The following analogues were prepared in a similar manner.

3.1.2. *(R)-(−)-2-Pentyl 3,5-dinitro-4-methylbenzoate* **3b** *and (±)-***3b**

3.1.2.1. *(R)-(−)-***3b**. From (*R*)-(−)-2-pentanol; yield 99%, pale yellow solid, m.p. 25.5°C, $[\alpha]_D$ −35.2 (*c* 2.25). Found: C 52.3, H 5.4, N 9.4; $C_{13}H_{16}N_2O_6$ requires C 52.70, H 5.44, N 9.45%. ^1H NMR: δ 8.55 (s, 2H, ArH), 5.21 (quint., 1H, $J = 6.3$, CH_3–C**H***), 2.61 (s, 3H, $ArCH_3$), 1.71 and 1.61 (2 m, CH*–C**H**$_a$**H**$_b$), 1.35 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 1.43–1.36 (m, 2H, CH_2), 0.93 (t, 3H, $J = 7.4$, CH_3).

3.1.2.2. *(±)-***3b**. From (±)-2-pentanol; yield 90%, pale yellow solid, m.p. 53°C. Found: C 52.7, H 5.5, N 9.6; $C_{13}H_{16}N_2O_6$ requires C 52.70, H 5.44, N 9.45%.

3.1.3. *(R)-(−)-2-Hexyl 3,5-dinitro-4-methylbenzoate* **3c** *and (±)-***3c**

3.1.3.1. *(R)-(−)-***3c**. From (*R*)-(−)-2-hexanol; yield 87%, pale yellow oil, $[\alpha]_D$ −37.5 (*c* 1.53). ^1H NMR: δ 8.55 (s, 2H, ArH), 5.19 (quint., 1H, $J = 6.3$, CH_3–C**H***), 2.61 (s, 3H, $ArCH_3$), 1.73 and 1.63 (2 m, CH*–C**H**$_a$**H**$_b$), 1.35 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 1.33 (m, 4H, CH_2), 0.89 (t, 3H, $J = 7.1$, CH_3).

3.1.3.2. *(±)-***3c**. From (±)-2-hexanol; yield 95%, pale yellow oil.

3.1.4. *(R)-(−)-2-Octyl 3,5-dinitro-4-methylbenzoate* **3d** *and (±)-***3d**

Compound (*R*)-(−)-**3d** and the racemic mixture (±)-**3d** were first prepared using 1,3-dicyclohexylcarbodiimide (DCC). This produces a urea that is difficult to remove after hydrolysis. Therefore, for easy purification EDC was used preferentially, leading to a water-soluble urea.

3.1.4.1. *(R)-(−)-***3d**. To a stirred mixture of 3,5-dinitro-4-methylbenzoic acid (3.4 g, 15 mmol), (*R*)-(−)-2-octanol (Aldrich, 2.4 ml, 15 mmol) and DCC (Aldrich, 5 g, 24 mmol) in dry CH_2Cl_2 (25 ml) at 0°C was added DMAP (0.7 g, 5.7 mmol). After 5 min at 0°C, the heterogeneous mixture was stirred for 3 h at r.t. and then water

(2 ml) was added. The insoluble urea was separated by filtering and washed with CH_2Cl_2. The brown CH_2Cl_2 solution was filtered through a column of aluminium oxide and, after removing the solvent from the filtrate, the remaining oil (5.7 g) was purified by chromatography on aluminium oxide using cyclohexane to give 3 g (60%) of pure (*R*)-(−)-**3d** (pale yellow solid, recrystallized from aq. EtOH), m.p. 41.5°C, $[\alpha]_D$ −37 (*c* 0.99). Found: C 56.8, H 6.6, N 8.1; $C_{16}H_{22}N_2O_6$ requires C 56.80, H 6.55, N 8.28%. ^{1}H NMR: δ 8.55 (s, 2H, ArH), 5.19 (quint., 1H, $J = 6.2$, CH_3–C**H***), 2.61 (s, 3H, $ArCH_3$), 1.74 and 1.63 (2 m, CH*–C**H**$_a$**H**$_b$), 1.35 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 1.36–1.26 (m, 8H, CH_2), 0.86 (t, 3H, $J = 7.0$, CH_3).

3.1.4.2. *(±)-**3d***. From (±)-2-octanol; yield 90%, pale yellow solid, m.p. 19°C. Found: C 56.5, H 6.4, N 8.0; $C_{16}H_{22}N_2O_6$ requires C 56.80, H 6.55, N 8.28%.

3.1.5. *(S)-(+)-1-(2-Methyl)butyl 3,5-dinitro-4-methylbenzoate **3e***

From (*S*)-(+)-1-(2-methyl)butanol; yield 89%, pale yellow solid, m.p. 38.5°C, $[\alpha]_D$ +4.7 (*c* 0.59). Found: C 52.9, H 5.4, N 9.7; $C_{13}H_{16}N_2O_6$ requires C 52.70, H 5.44, N 9.45%. ^{1}H NMR: δ 8.56 (s, 2H, ArH), 4.19 and 4.27 (2 dd, O–C**H**$_c$**H**$_d$–CH*, $J = 10.8$, 6.8, 6.1), 2.62 (s, 3H, $ArCH_3$), 1.87 (m, 1H, CH_3–C**H***), 1.55–1.45 and 1.32–1.22 (2 m, CH*–C**H**$_a$**H**$_b$), 1.0 (t, 3H, $J = 6.7$, C**H**$_3$–CH*), 0.95 (t, 3H, $J = 7.5$, CH_3).

3.2. *Alkyl 3,5-diamino-4-methylbenzoates **4a–e***

3.2.1. *(R)-(−)-2-Butyl 3,5-diamino-4-methylbenzoate **4a***

A solution of the dinitro derivative (*R*)-(−)-**3a** (1.23 g, 4.4 mmol) in AcOEt (50 ml) and 10% Pd/C catalyst (0.4 g) was stirred under H_2 for 4.5 h. The theoretical volume of H_2 (*c*. 500 ml at r.t. and 760 mm Hg) was absorbed in 3 h. The catalyst was filtered off, rinsed with $CHCl_3$ and the solvents were removed from the filtrate to give 0.91 g (95%) of pure diamine (*R*)-(−)-**4a** (colourless oil), $[\alpha]_D$ −26.4 (*c* 0.92). ^{1}H NMR: δ 6.86 (s, 2H, ArH), 5.02 (quint., 1H, $J = 6.3$, CH_3–C**H***), 1.98 (s, 3H, $ArCH_3$), 1.70 and 1.62 (2 m, CH*–C**H**$_a$**H**$_b$), 1.28 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 0.93 (t, 3H, $J = 7.5$, CH_3).

The following analogues were prepared in a similar manner.

3.2.2. *(R)-(−)-2-Pentyl 3,5-diamino-4-methylbenzoate **4b** and (±)-**4b***

3.2.2.1. *(R)-(−)-**4b***. From (*R*)-(−)-**3b**; yield 97%, colourless oil, $[\alpha]_D$ −31.8 (*c* 0.44). ^{1}H NMR: δ 6.85 (s, 2H, ArH), 5.09 (quint., 1H, $J = 6.3$, CH_3–C**H***), 1.98 (s, 3H, $ArCH_3$), 1.65 and 1.53 (2 m, CH*–C**H**$_a$**H**$_b$), 1.28 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), *c*. 1.39 (m, 2H, CH_2), 0.91 (t, 3H, $J = 7.3$, CH_3).

3.2.2.2. *(±)-**4b***. From (±)-**3b**; yield 93%, oil.

3.2.3. *(R)-(−)-2-Hexyl 3,5-diamino-4-methylbenzoate **4c** and (±)-**4c***

3.2.3.1. *(R)-(−)-**4c***. From (*R*)-(−)-**3c**; yield 96%, colourless oil, $[\alpha]_D$ −36.7 (*c* 0.39). ^{1}H NMR: δ 6.85 (s, 2H, ArH), 5.08 (quint., 1H, $J = 7.3$, CH_3–C**H***), 1.98 (s, 3H, $ArCH_3$), 1.67 and 1.60 (2 m, CH*–C**H**$_a$**H**$_b$), 1.28 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), *c*. 1.33 (m, 4H, CH_2), 0.87 (t, 3H, $J = 7.1$, CH_3).

3.2.3.2. *(±)-**4c***. From (±)-**3c**; yield 90%, brown oil.

3.2.4. *(R)-(−)-2-Octyl 3,5-diamino-4-methylbenzoate **4d** and (±)-**4d***

3.2.4.1. *(R)-(−)-**4d***. From (*R*)-(−)-**3d**; yield 98%, beige solid, m.p. 55.5°C, $[\alpha]_D$ −38.7 (*c* 0.58). Found: C 69.1, H 9.4, N 9.9; $C_{16}H_{26}N_2O_2$ requires C 69.03, H 9.41, N 10.06%. ^{1}H NMR: δ 6.86 (s, 2H, ArH), 5.07 (quint., 1H, $J = 6.2$, CH_3–C**H***), 1.99 (s, 3H, $ArCH_3$), 1.55 and 1.65 (2 m, CH*–C**H**$_a$**H**$_b$), 1.28 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 1.37–1.22 (m, 8H, CH_2), 0.85 (t, 3H, $J = 7.1$, CH_3).

3.2.4.2. *(±)-**4d***. From (±)-**3d**; yield 100%, brown solid, m.p. 37°C (broad). Found: C 68.7, H 9.2, N 9.8; $C_{16}H_{26}N_2O_2$ requires C 69.03, H 9.41, N 10.06%.

3.2.5. *(S)-(+)-1-(2-Methyl)butyl 3,5-diamino-4-methylbenzoate **4e***

From (*S*)-(+)-**3e**; yield 91%, beige solid, m.p. 49.5°C, $[\alpha]_D$ +4.0 (*c* 0.57). Found: C 66.3, H 8.5, N 11.7; $C_{13}H_{20}N_2O_2$ requires C 66.07, H 8.53, N 11.85%. ^{1}H NMR: δ 6.86 (s, 2H, ArH), 4.13 and 4.05 (2dd, O–C**H**$_c$**H**$_d$–CH*, $J = 10.8$, 6.6, 6.0), 2.0 (s, 3H, $ArCH_3$), 1.87 (m, 1H, CH_3–C**H***), 1.55–1.45 and 1.30–1.20 (2 m, CH*–C**H**$_a$**H**$_b$), 0.97 (d, 3H, $J = 6.7$, C**H**$_3$–CH*), 0.92 (t, 3H, $J = 7.5$, CH_3).

3.3. *Alkyl 3,5-dipalmitoylamino-4-methylbenzoates **5a–e***

3.3.1. *(R)-(−)-2-Butyl 3,5-dipalmitoylamino-4-methylbenzoate **5a***

A mixture of the diamino derivative (*R*)-(−)-**4a** (0.5 g, 2.26 mmol), Na_2CO_3 (0.62 g, 2.3 equiv.) and palmitoyl chloride (1.43 g, 2.3 equiv.) in dry acetone (60 ml) was heated at reflux with stirring for 5 h. After cooling and adding water (20 ml), the precipitate was separated and crystallized from ethanol to afford 1.03 g (82%) of pure (*R*)-(−)-**5a** (white solid), m.p. 133°C, $[\alpha]_D$ −6.9 (*c* 0.20). Found: C 74.6, H 11.1, N 3.8; $C_{44}H_{78}N_2O_4$. 0.5 H_2O

requires C 74.63, H 11.25, N 3.96%. ^{1}H NMR: δ 7.96 (s, 2H, ArH), 7.07 (broad s, 2H, NH), 5.04 (quint., 1H, $J = 6.4$, CH_3–C**H***), 2.38 (t, 4H, $J = 7.9$, CH_2CO), 2.08 (s, 3H, $ArCH_3$), 1.80–1.70 (m, 4H, C**H**$_2$–CH_2CO), 1.80 and 1.60 (2 m, CH*–C**H**$_a$**H**$_b$), 1.29 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 1.24 (m, 48H, CH_2), 0.93 (t, 3H, $J = 7.5$, CH_3), 0.86 (t, 6H, $J = 6.7$, CH_3).

The following analogues were prepared in a similar manner.

3.3.2. *(R)-(−)-2-Pentyl 3,5-dipalmitoylamino-4-methylbenzoate* ***5b*** *and (±)-****5b***

3.3.2.1. *(R)-(−)-****5b***. From (R)-(−)-**4b**; yield 99%, white solid, m.p. 103°C, $[\alpha]_D$ −10.9 (*c* 0.23). Found: C 73.4, H 11.2, N 3.0; $C_{45}H_{80}N_2O_4$. 1.5 H_2O requires C 73.02, H 11.30, N 3.78%. ^{1}H NMR: δ 7.91 (s, 2H, ArH), 7.15 (broad s, 2H, NH), 5.11 (quint., 1H, $J = 6.3$, CH_3–C**H***), 2.38 (t, 4H, $J = 7.6$, CH_2CO), 2.05 (s, 3H, $ArCH_3$), 1.72 (m, 5H, C**H**$_2$–CH_2CO– + H$_a$), *c*. 1.53 (m, H$_b$), *c*. 1.36 (m, 2H, 1.29, CH_2), 1.29 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 1.40–1.26 (m, 48H, CH_2), 0.91 (t, 3H, $J = 7.3$, CH_3), 0.86 (t, 6H, $J = 7.0$, CH_3).

3.3.2.2. *(±)-****4b***. From (±)-**4b**; yield 86%, white solid, m.p. 115°C. Found: C 75.6, H 11.1, N 4.1; $C_{45}H_{80}N_2O_4$ requires C 75.79, H 11.31, N 3.93%.

3.3.3. *(R)-(−)-2-Hexyl 3,5-dipalmitoylamino-4-methylbenzoate* ***5c*** *and (±)-****5c***

3.3.3.1. *(R)-(−)-****5c***. From (R)-(−)-**4c**; yield 87%, white solid, m.p. 93°C, $[\alpha]_D$ −11.3 (*c* 0.19). Found: C 75.8, H 11.4, N 3.5; $C_{46}H_{82}N_2O_4$ requires C 75.98, H 11.37, N 3.85%. ^{1}H NMR: δ 7.00 (s, 2H, ArH), 7.00 (broad s, 2H, NH), 5.11 (quint., 1H, $J = 6.9$, CH_3–C**H***), 2.38 (t, 4H, $J = 6.2$, CH_2CO), 2.10 (s, 3H, $ArCH_3$), 1.80–1.50 (2 m, 6H, C**H**$_2$–CH_2CO, CH*–C**H**$_a$**H**$_b$), 1.45–1.20 (m, 52H, CH_2), 1.29 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 0.89 (t, 3H, $J = 7.0$, CH_3), 0.86 (t, 6H, $J = 7.0$, CH_3).

3.3.3.2. *(±)-****4c***. From (±)-**4c**; yield 90%, white solid, m.p. 86–120°C. Found: C 76.0, H 11.3, N 4.0; $C_{46}H_{82}N_2O_4$ requires C 75.98, H 11.37, N 3.85%.

3.3.4. *(R)-(−)-2-Octyl 3,5-dipalmitoylamino-4-methylbenzoate* ***5d*** *and (±)-****5d***

3.3.4.1. *(R)-(−)-****5d***. From (R)-(−)-**4d**; yield 74%, white solid, m.p. 88°C, $[\alpha]_D$ −13.4 (*c* 0.16). Found: C 75.2, H 11.4, N 3.6; $C_{48}H_{86}N_2O_4$. 0.5 H_2O requires C 75.44, H 11.47, N 3.67%. ^{1}H NMR: δ 7.90 (s, 2H, ArH), 7.17 (broad s, 2H, NH), 5.10 (quint., 1H, $J = 6.3$, CH_3–C**H***), 2.38 (t, 4H, $J = 7.5$, CH_2CO), 2.04 (s, 3H, $ArCH_3$), 1.72 (m, 4H, C**H**$_2$–CH_2CO), 1.29 (d, 3H, $J = 6.3$, C**H**$_3$–CH*), 1.72 and 1.54 (2 m, CH*–C**H**$_a$**H**$_b$), 1.45–1.24 (m, 56H, CH_2), 0.86 and 0.85 (2t, 9H, $J = 6.8$, CH_3).

3.3.4.2. *(±)-****5d***. From (±)-**4d**; yield 74%, white solid, m.p. 88°C. Found: C 75.5, H 11.5, N 3.5; $C_{48}H_{86}N_2O_4$ requires C 75.44, H 11.47, N 3.67%.

3.3.5. *(S)-(+)-1-(2-Methyl)butyl 3,5-dipalmitoylamino-4-methylbenzoate* ***5e***

From (S)-(+)-**4e**; yield 97%, white solid, m.p. 153°C, $[\alpha]_D$ +28.2 (*c* 0.11). Found: C 75.8, H 11.3, N 3.7; $C_{45}H_{80}N_2O_2$ requires C 75.79, H 11.31, N 3.93%. ^{1}H NMR: δ 7.96 (s, 2H, ArH), 7.11 (broad s, 2H, NH), 4.17 and 4.08 (2dd, O–C**H**$_c$**H**$_d$–CH*, $J = 10.7$, 6.95, 6.0), 2.39 (broad t, 4H, $J = 7.1$, CH_2CO), 2.07 (s, 3H, $ArCH_3$), 1.84 (m, 1H, CH_3–C**H***), 1.73 (m, 4H, C**H**$_2$–CH_2CO), 1.48 and *c*. 1.30 (2 m, CH*–C**H**$_a$**H**$_b$), 1.45–1.18 (m, 48H, CH_2), 0.97 (d, 3H, $J = 6.8$, C**H**$_3$–CH*), 0.92 (t, 3H, $J = 7.5$, CH_3), 0.85 (t, 3H, $J = 7.0$, CH_3).

We are grateful to Dr A.-M. Levelut for helpful discussions.

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