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Heterotrimeric liquid crystalline thiadiazole derivatives

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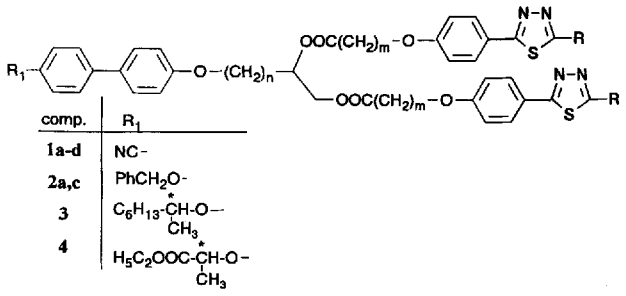
Various trimeric co-oligomers combining 2-phenyl-1,3,4-thiadiazole mesogenic moieties with a biphenyl mesogenic moiety were synthesized and their mesomorphic behaviour investigated by polarizing microscopy, calorimetry and X-ray scattering. Such co-oligomeric structures provide an opportunity to combine different mesogenic units. Thus readily accessible homochiral biphenyl mesogenic units were connected with thiadiazole mesogenic units leading to an oligomeric liquid crystal material with ferroelectric properties.

1. Introduction

The properties of polymeric liquid crystals depend strongly on the degree of polymerization, which often causes unsatisfactory reproducibility. This drawback could probably be circumvented by oligomers with a well-defined molecular structure. The first examples of such compounds were cyclic phosphazenes and the tetrameric liquid crystals based on biphenyl, bicyclohexyl, and phenylcyclohexyl mesogenic groups linked to a pentaerythritol central unit [1]. More recently homo-oligomeric 4-cyanobiphenyl derivatives and Shiffs bases have been described [2,3]. We have reported homotrimeric and homotetrameric oligomers incorporating thiadiazole rigid cores [4], and some of these compounds were found to form a broad smectic C phase.

It should be possible to influence the properties of such materials by combining them with other mesogenic units. Therefore we have synthesized trimeric co-oligomers by linking the 2-phenyl-1,3,4-thiadiazole system to different biphenyl mesogenic units.

At first we were especially interested in the investigation of the influence of the chemical structure of the mesogenic groups on the types of mesophase formed. Therefore cyanobiphenyl derivatives **1a–d**, phenylpyrimidine derivative **2b**, and 4-benzyloxybiphenyl derivatives **2a** and **2c** were synthesized and investigated. However, the major aim of our work was to obtain co-oligomers with a ferroelectric smectic C phase. Therefore the chiral biphenyl derivatives **3** and **4** were synthesized.



comp.	R_1
1a-d	NC–
2a,c	$PhCH_2O$–
3	C_6H_{13}–CH(CH$_3$)–O–
4	H_5C_2OOC–CH(CH$_3$)–O–

2. Synthesis

The co-oligomers **1a–1d** combining 2-phenyl-1,3,4-thiadiazole and 4-cyanobiphenyl units were obtained according to scheme **1** which gives the synthesis of compound **1c** as a representative example. Etherification of 4′-cyano-4-hydroxybiphenyl with 2,2-dimethyl-5-(4-hydroxybutyl)-1,3-dioxolane **6** in the presence of triphenylphosphine and DEAD (diethyl azodicarboxylate) [5] gave the precursor **7** from which 6-(4′-cyanobiphenyl-4-yloxy)-hexan-1,2-diol **8** was obtained by hydrolytic acetal cleavage [6]. The *N,N*-dicyclohexylcarbodiimide mediated esterification of **8** with bromovaleric acid yielded compound **9** which finally was etherified with 4-(5-undecyl-1,3,4-thiadiazol-2-yl)phenol to give **1c**. Compounds **1a**, **1b**, **1d** and the homotrimer **5** (see table 3) were synthesized in an analogous manner.

In order to obtain ferroelectric liquid crystalline materials, we combined two 2-phenyl-1,3,4-thiadiazole mesogenic units with a homochiral biphenyl mesogen (**20**). (The designation of the configuration as (*R*) or (*S*) corresponds only to the homochiral part of the molecule.

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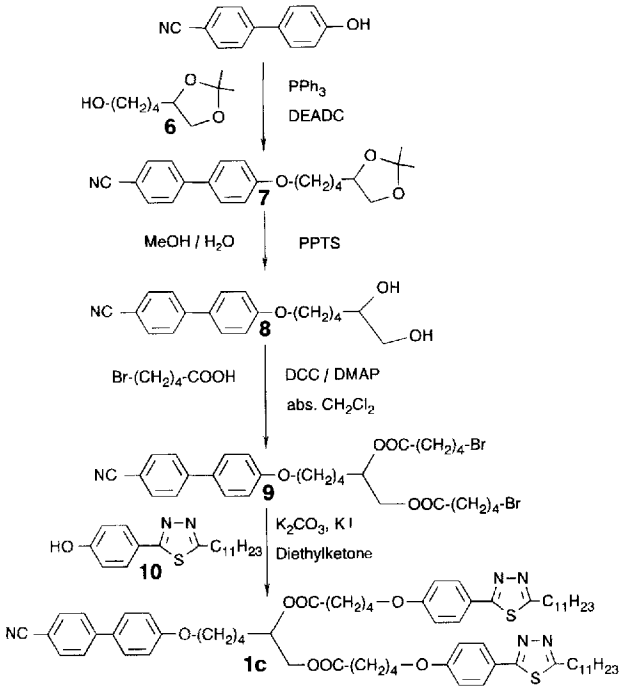
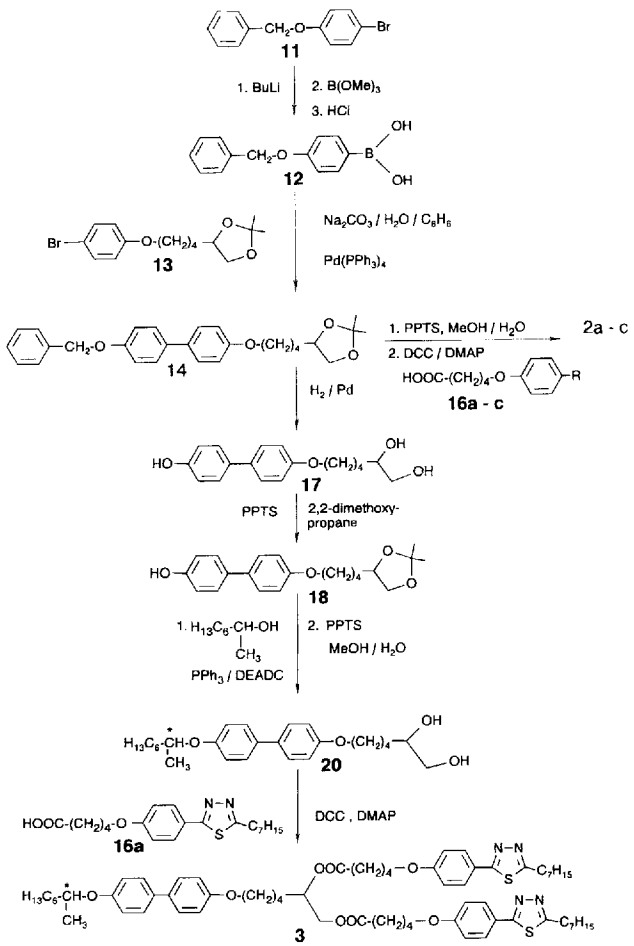


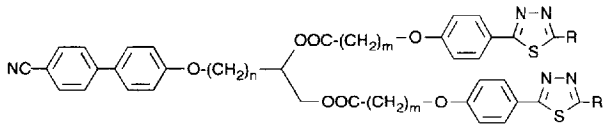
Scheme 1. Synthesis of 1,2,-bis-5-[4-(5-undecyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-6-(4′-cyanobipenyl-4-yloxy)hexane (**1c**).

The 1,2-diol units were racemic in all cases.) The synthesis was designed in such a way that the homochiral compound could be used close towards the end of the reaction cascade (see scheme 2). The Pd-catalysed cross coupling reaction [7, 8] of the 4-benzyloxyphenylboronic acid **12** [9, 10] with the aryl bromide **13** gave the dioxolane derivative **14**, which afterwards was deprotected [6]. The resulting 6-(4′-benzyloxybiphenyl-4-yloxy)hexan-1,2-diol **15** was esterified with various aryloxypentanoic acids **16a–c**, using the carbodiimide method, to yield the co-oligomers **2a–c**. In order to get a precursor for chiral derivatives, **14** was debenzylated. It turned out that the hydrogenolysis gave a mixture of the desired product **18** and, owing to the partial cleavage of the acetonide group, also compound **17**. The diol-group of **17** was reprotected by reacting it with 2,2-dimethoxypropane in the presence of pyridinium tosylate [11, 12]. Mitsunobu etherification [5] of **18** with (*S*)-(+)-octan-2-ol followed by the removal of the acetonide group gave the diol **20** which afterwards was esterified with 5-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoic acid to give the final product **3**. The compounds **4** can be prepared using analogous procedures.



Scheme 2. Synthesis of (*R*)-1,2-bis-{5-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-6-[4′-(oct-2-yloxy)-biphenyl-4-oxy]hexane (**3**).

Table 1. Phase transition temperatures (°C) and enthalpies (ΔH/kJ mol^{-1}) in parentheses of compounds **1a–d** with 2-phenyl-1,3,4-thiadiazole and 4-cyanobiphenyl as mesogenic units.



Compound	*n*	*m*	*R*	C		S_A		I
1a	4	4	C_7H_{15}	•	58 (38·5)	•	122 (19·6)	•
1b	4	10	C_7H_{15}	•	68 (62·0)	•	103 (19·5)	•
1c	4	4	$C_{11}H_{23}$	•	54 (57·3)	•	103 (17·4)	•
1d	6	4	$C_{11}H_{23}$	•	64 (57·2)	•	110 (20·4)	•

3. Discussion of transition temperatures

The liquid crystalline behaviour of the co-oligomers **1a–d** incorporating 2-phenyl-1,3,4-thiadiazole and 4-cyanobiphenyl units is given in table 1. Comparison of the cyanobiphenyl derivatives **1a–d** with the homotrimer **5** [4] (see table 3) shows that the replacement of only one thiadiazole unit by a cyanobiphenyl unit suppresses the smectic C phase and gives rise to the formation of an enantiotropic smectic A phase. Variations of the lengths

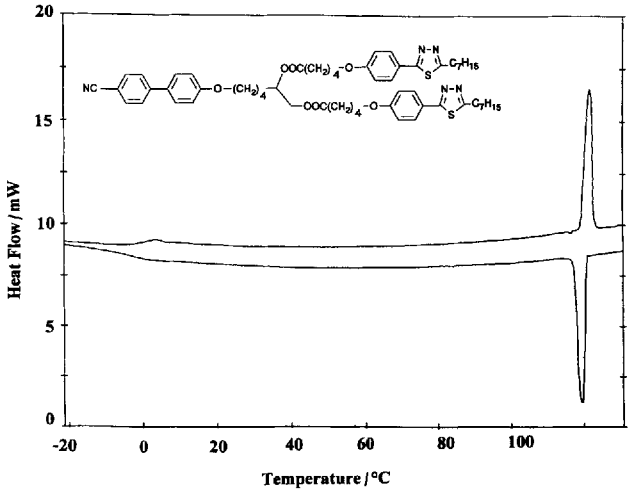


Figure 1. DSC heating and cooling traces (5 K min^{-1}) for compound **1 c**.

of the spacers as well as the side chains have no influence on the phase type. The differences in the melting and clearing temperatures are only small. Supercooling of the mesophases is possible down to 18°C (**1 b**), 32°C (**1 c**) and 36°C (**1 d**). In this temperature range spontaneous crystallization occurs for all the compounds with the exception of **1 a** which only crystallized partly after several months of storage at room temperature. The DSC traces of this compound revealed a glass transition of 5°C (see figure 1). The transition temperatures of the 'mixed' trimers consisting of a 4-benzyloxybiphenyl rigid core and two other heterocyclic mesogenic units are given in table 2. Contrasting compounds **2 a**, **2 b**, and **2 c** shows that the mesomorphic behaviour of these oligomers is strongly influenced by the type of heteroaromatic ring incorporated. It is obvious that replacing the thiadiazole ring of compound **2 a** by a pyrimidine ring (**2 b**) leads to the loss of the smectic C phase, whereas the three-ring thiadiazole derivative **2 c** exhibits an S_C–N polymorphism with high mesophase stability. It is remarkable that the replacement of the bent 2-phenylthiadiazole unit by a linear 2-phenylpyrimidine core gives rise to a decrease in the clearing temperature. If one compares other calamitic liquid crystalline compounds incorporating thiadiazole or pyrimidine units, the reverse order of mesophase stability is usually observed.

The trimers **1 a**, **2 a**, **3**, **4** and **5** which are summarized in table 3 consist of a pair of 4-(5-heptyl-1,3,4-thiadiazole-2-yl)phenoxy mesogenic units linked via flexible spacers to a central unit and a third structurally different calamitic unit. The comparison of these compounds with the homotrimeric compound **5** shows that it is possible to retain the smectic C phase. In the case of the homochiral compound **3**, a bistable switchable ferroelectric smectic C* phase was detected, but the measured value of the spontaneous polarization was very small (0·5 nC cm^{-2} at 72°C). Unfortunately, if the biphenyl core carries a polar substituent such as an (*R*)-1-(ethoxycarbonyl)ethyl group (**4**), the S_C phase is replaced by a S_A phase.

Preliminary X-ray studies of the liquid crystalline phases of **1 c**, **2 a** and **2 b** have been performed using the Guinier method. In all cases, a layer structure without order in the layers has been formed. The classification as S_A or S_C could not be obtained by means of the X-ray studies since oriented samples could not be obtained. This was established by investigations of the textures between crossed polarizers. Comparison between the layer thickness and the molecular length shows that for all the substances investigated so far, the layer periods of the smectic phases (**1 c**: $d = 2{\cdot}58$ nm; **2 a**: $d = 2{\cdot}10$ nm; **2 b**: $d = 2{\cdot}45$ nm) correspond with the averaged values of the lengths of the single calamitic moieties and do not correspond with the total lengths of the molecules in a tuning fork like conformation (**1 c**: $L = 4{\cdot}0$ mm; **2 a**: $L = 4{\cdot}45$ nm; **2 b**: $L = 4{\cdot}6$ nm). Therefore an intercalation of the branched molecules must be assumed.

The molecular model of compound **2 b** in this tuning fork-like conformation is given in figure 2.

4. Experimental

4.1. *General considerations*

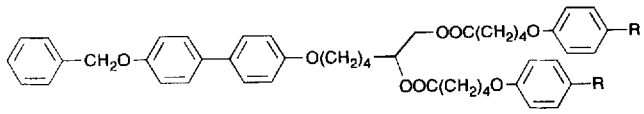
^{1}H NMR spectra were recorded on a Bruker WP-200 or an AC-80 spectrometer with tetramethylsilane as internal standard. IR spectra were recorded by using a Specord 71 IR spectrometer. Transition temperatures were measured using a Mettler FP 82 HT hot stage and control unit, in conjunction with a Nikon Optiphot-2 polarizing microscope, and confirmed using differential scanning calorimetry (Perkin–Elmer DSC-7). Mass spectra were recoreded on an AMD 402 mass spectrometer (70 eV). Thin-layer chromatography was performed on TLC aluminium sheets (silica gel 60 F_{254}) from Merck and visualized by UV-light or by using a spray-solution of 3′,3″-dibromothymolsulphonaphthalene in aqueous KOH and devloping with NH_3. Silica gel 60 (0, 063–0, 200) from Merck was used for column chromatography. Solvents were purified and dried according to standard procedures [14]. The syntheses of compounds **1 c**, **2 b**, and **3** are given as representative examples of the experimental procedures used.

4.2. *Synthesis of 1,2-bis-{5-[4-(5-undecyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy-6-(4′-cyanobiphenyl-4-yloxy)hexane* (**1 c**)

4.2.1. *1,2-bis-(5-Bromopentanoyloxy)-6-(4′-cyanobiphenyl-4-yloxy)hexane* (**9**)

N,N-Dicyclohexylcarbodiimide (0·7 g, 3·45 mmol) was added to a stirred, cooled (0°C) solution of 6-(4′-

Table 2. Phase types, phase transition temperatures (°C) and enthalpies (ΔH/kJ mol^{-1}) in parentheses of compounds **2a–c** with a 4-benzyloxybiphenyl unit.



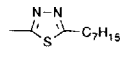
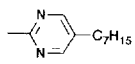
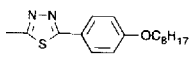
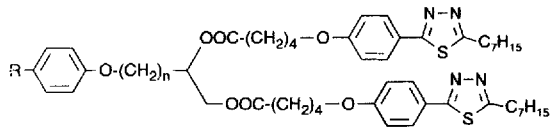
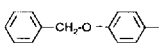
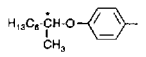
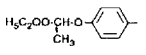
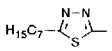
2	*R*	C	S_X	S_C	S_A	N	I
a		• 115 (65·8)	(• 84 (9·3)	• 110) (23·6)	—	—	•
b		• 106 (53·5)	—	—	(• 100) (9·3)	—	•
c		• 149 (59·9)	—	• 197 (9·1)	—	• 206 (4·5)	•

Table 3. Phase types, phase transition temperatures (°C) and enthalpies (ΔH/kJ mol^{-1}) in parentheses of compounds **1a**, **2a**, **3**, **4** and **5** with different mesogenic units.



Compound	*R*	*n*	C	S_X	S_C	S_A	I
1a		4	• 58 (38·5)	—	—	• 122 (19·6)	•
2a		4	• 115 (65·8)	(• 84 (9·3)	• 110) (23·6)	—	•
3		4	• 92 (76·6)	—	(S_C^* 82) (16·7)	—	•
4		1	• 90 (27·3)	—	—	(• 43) (5·2)	•
5		4	• 109 (102·8)	—	(• 92) (22·6)	—	•

cyanobiphenyl-4-yloxy)hexan-1,2-diol **8** [15] (0·46 g, 1·5 mmol), 5-bromovaleric acid (0·57 g, 3·15 mmol) and a catalytic quantity of 4-*N*,*N*-dimethylaminopyridine in 10 ml of dry dichloromethane. The mixture was stirred at room temperature for 24 h. After complete reaction the mixture was filtered, the solvent was removed *in vacuo* and the residue was dissolved in dichloromethane. The organic phase was washed successively with aqueous sodium hydrogen carbonate (3 ×), 10 per cent hydrochloric acid and water. Afterwards, the solution was dried (Na_2SO_4) and the solvent removed *in vacuo*. The product was used as obtained after purification by column chromatography using chloroform/methanol (10:2) as eluent. Yield: 0·45 g (45 per cent).

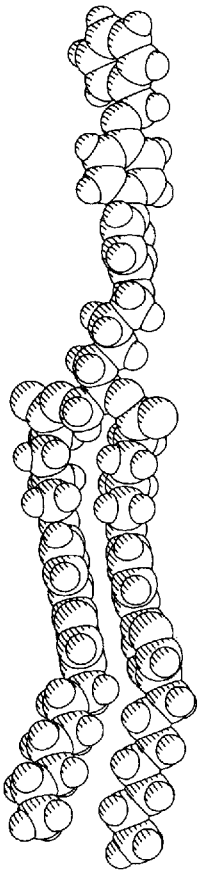


Figure 2. Molecular model of compound **2b** in a tuning fork-like conformation (CERIUS 3·2).

4.2.2. *1,2-bis-{5-[4-(5-Undecyl-1,3,4-thiadiazol-2-yl)-phenoxy]pentanoyloxy}-6-(4'-cyanobiphenyl-4-yloxy)-hexane* (**1c**)

A mixture of compound **9** (0·43 g, 0·68 mmol), 4-(5-undecyl-1,3,4-thiadiazol-2-yl)phenol [13] **10** (0·5 g 1·4 mmol), anhydrous potassium carbonate (1 g, 7 mmol) and potassium iodide (50 mg) in 10 ml of diethyl ketone was stirred and heated at reflux under an argon atmosphere for 30 h. After the reaction was finished, the solvent was removed *in vacuo* and chloroform was added to the residue. The organic phase was filtered and washed with 10 per cent hydrochloric acid, aqueous sodium hydrogen carbonate and water. The solution was dried (Na_2SO_4). before the solvent was removed *in vacuo* to give the crude product which was recrystallized from acetone. Yield: 0·2 g (29 per cent); C 54 S_A 103 I. Elemental analysis (per cent): Found (calculated for $C_{67}H_{89}O_7N_5S_2$): C, 70·27 (70·55); H, 7·88 (7·86); N, 6·17 (6·14); S, 5·69 (5·62), ^{1}H NMR, δ ppm, $CDCl_3$: 0·85 (t, 6 H, $-CH_3$), 1·23–1·60 (m, 36 H, $-CH_2-$), 1·78–1·82 (m, 14 H, $-CH_2-$), 2·38 (t, broad, 4 H, $-OOC-CH_2-$), 3·03 (t, 4 H, thiadiazole–CH_2-), 3·92–4·06 (m, 6 H, $-OCH_2-$), 4·26 (dd, 2 H, $-C\underline{H}_2-$OOC–), 5·08–5·13 (m, 1 H, (–C<u>H</u>–OOC–), 6·90 (d, 4 H, H–ar.), 6·94 (d, 2 H, H–ar.), 7·48 (d, 2 H, H–ar.), 7·59 (d, 2 H, H–ar.), 7·66 (d, 2 H, H–ar.), 7·81 (d, 4 H, H–ar.).

4.3. *Synthesis of (R)-1,2-bis-{5-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-6-[4'-(1-methylheptyloxy)biphenyl-4-yloxy] hexane* (**3**)

4.3.1. *4-Benzyloxyphenylboronic acid* (**12**)

A solution of *n*-butyl lithium (2·5 M solution in hexane, 23·7 ml, 0·06 mol) was added dropwise to a stirred and cooled (− 78°C) solution of 4-bromophenyl benzyl ether **11** (10·6 g, 0·04 mol) [11] in 50 ml of dry THF under dry argon. This mixture was stirred for 2 h at − 78°C. Then a solution of trimethyl borate (13·6 ml), 0·12 mol) in 15 ml of dry THF (cooled to − 30°C) was added at this temperature with stirring. After 1 h at − 78°C, the temperature was allowed to rise to room temperature overnight. The mixture was hydrolyzed with 50 ml of 10 per cent hydrochloric acid at 0°C and was stirred at room temperature for 1 h. The product was extracted into ethyl acetate, and the combined organic extracts were washed with aqueous sodium hydrogen carbonate and water. After the solution had been dried (Na_2SO_4), the solvent was removed *in vacuo* and the residue was treated with boiling methanol. The solution was cooled and the precipitate was filtered with suction. The methanol was removed by evaporation and the monomeric 4-benzyloxyphenylboronic acid was recrystallized from petroleum ether/ethyl acetate (10:1) [7, 8]. Yield: 5·3 g (58 per cent); m.p. 196°C. Elemental analysis (per cent): Found (calculated for $C_{13}H_{13}O_3B$): C, 68·63 (68·46); H, 5·70 (5·74) IR, ν cm^{-1}, (nujol): 3520–3235 (OH). ^{1}H NMR, δ ppm, DMSO: 5·1 (s, 2 H, $-CH_2-O-$), 6·95 (d, 2 H, H–ar.), 7·30–7·45 (m, 5 H, H–ar.), 7·71 (d, 2 H, H–ar.), 7·83 (s, 2 H, –OH). MS *m/z* (rel. intensity, per cent): 228 (M^+) (11), 91 (100), 65 (11).

4.3.2. *2,2-Dimethyl-4-(4'-benzyloxybiphenyl-4-yloxybutyl)-1,3-dioxolane* (**14**)

A solution of compound **12** (4·5 g, 19 mmol) in 40 ml of ethanol was added to a stirred mixture of compound **13** (4·8 g, 14 mmol) and tetrakis(triphenylphosphine)-palladium (0) (0·75 g, 0·65 mmol) [12] in 80 ml of benzene and 80 ml of 2 M aqueous sodium carbonate at room temperature under a dry argon atmosphere. The thoroughly stirred mixture was heated under reflux for 14 h. The product was extracted into dichloromethane and the combined organic extracts were washed with brine and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue was purified by column chromatography using chloroform/methanol (10:0·5) as eluent and finally recrystallized from methanol [7]. Yield: 3 g (50 per cent); m.p. 136°C. Elemental analysis (per cent): Found (calculated for $C_{28}H_{32}O_4$): C, 77·80 (77·74); H, 7·36 (7·45).

^{1}H NMR, δ ppm. $CDCl_3$: 1·34 (s, 3 H, $-CH_3$), 1·39 (s, 3 H, $-CH_3$), 1·54–1·64 (m, 4 H, $-CH_2-$), 1·79–1·85 (m, 2 H, $-CH_2-$), 3·51 (dd, 1 H, $-O-C\underline{H}_2-CH-$, H_{ax}), 3·95–4·10 (m, 4 H, $-OCH_2-$, $-CH-$, $-O-C\underline{H}_2-CH-$, H_{eq}), 5·08 (s, 2 H, $-CH_2-O-$), 6·91 (d, 2 H, H–ar.), 7·0 (d, 2 H, H–ar.), 7·30–7·47 (m, 9 H, H–ar.). MS *m/z* (rel. intensity, per cent): 432 (M^+) (29), 366 (14), 185 (11), 99 (21), 91 (100), 81 (14), 43 (14).

4.3.3. *6-(4′-Hydroxybiphenyl-4-yloxy)hexan-1,2-diol* (**17**)

A mixture of compound **14** (3·95 g, 9 mmol) and palladium on charcoal (0·5 g, 0·45 mmol) in 150 ml of ethyl acetate was shaken for 1 to 2 d in a hydrogen atmosphere. After complete reaction, the mixture was filtered, the methanol was removed by evaporation and the crude product was purified by recrystallization from dichloromethane. Yield: 2 g (73 per cent); C 140 S_C 183 I. ^{1}H NMR, δ ppm, DMSO: 1·08–1·68 (m, 6 H, $-CH_2-$), 3·04–3·32 (m, 3 H, $-C\underline{H}_2-OH$, $-OH$), 3·84 (t, 2 H, $-OCH_2-$), 4·24–4·36 (m, 2 H, $-C\underline{H}-OH$, $-O\underline{H}$), 6·64 (d, 2 H, H–ar.), 6·80 (d, 2 H, H–ar.), 7·24 (d, 2 H, H–ar.), 7·32 (d, 2 H, H–ar.), 9·28 (s, 1 H, –OH). MS *m/z* (rel. intensity, per cent): 302 (M +) (16), 186 (100), 85 (14).

4.3.4. *4-(4′-Hydroxybiphenyl-4-yloxy)butyl-2,2-dimethyl-1,3-dioxolane* (**18**)

The crude product **17** (2 g, 6·6 mmol) and 2,2-dimethoxypropane (8 ml, 66 mmol) in 20 ml of dry acetone was stirred at room temperature for 24 h in the presence of a catalytic quantity of pyridinium tosylate [16, 17]. Afterwards, the solvent and the excess of 2,2-dimethoxypropane were removed *in vacuo*. The precipitate was dissolved in ethyl acetate and the organic phase was washed successively with aqueous sodium hydrogen carbonate and water. After drying the solution (Na_2SO_4), the solvent was removed *in vacuo*. The product was separated by column chromatography (R_f: 0·49) using chloroform/methanol (10:0·5) as eluent. The resulting yellow oil was used as the crude material in the next step. Yield: 1·4 g (63 per cent).

4.3.5. *(R)-4-[4′-(Oct-2-yloxy)biphenyl-4-yloxy]butyl-2,2-dimethyl-1,3-dioxolane* (**19**)

DEADC (1·5 ml, 10 mmol) was added to a stirred solution of **18** (2·3 g, 6·7 mmol), (*S*)-(+)-octan-2-ol (1·5 ml, 10 mmol) and dry triphenylphosphine (2·6 g, 10 mmol) in 15 ml of dry THF at 0°C [5]. Afterwards, the mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the residue was dissolved in cold dry ether. The precipitate was filtered with suction, washed with ether and the solvent evaporated. The crude product was recrystallized from methanol/water (10:1) to yield colourless crystals. Yield: 1·6 g (54 per cent); m.p. 40°C. Elemental analysis (per cent): Found (calculated for $C_{29}H_{42}O_4$): C, 76·37 (76·60); H, 9·26 (9·31). ^{1}H NMR, δ ppm, $CDCl_3$: 0·83 (t, 3 H, $-CH_3$, 1·29 (d, 3 H, $-CH-C\underline{H}_3$), 1·34 (s, 3 H, CH_3), 1·40 (s, 3 H, CH_3), 1·53–1·82 (m, 16 H, $-CH_2-$), 3·51 (dd, 1 H, $-O-C\underline{H}_2-CH-$, $H_{ax.}$), 3·97–4·06 (m, 4 H, $-OCH_2-$, $-O-C\underline{H}-CH_2-$, $-O-C\underline{H}_2-CH-$, $H_{eq.}$), 4·30–4·36 (m, 1 H, $-C\underline{H}-CH_3$), 6·90 (d, 4 H, H–ar.), 7·43 (m, 4 H, H–ar.). MS *m/z* (rel. intensity, per cent): 454 (M^+) (46), 342 (29), 186 (100), 99 (66), 81 (40), 55 (14), 43 (48).

4.3.6. *(R)-6-[4′-(Oct-2-yloxy)biphenyl-4-yloxy]hexan-1,2-diol* (**20**)

Compound **19** (1·4 g, 3 mmol) was heated under reflux in 50 ml of a methanol/water (10:1) mixture in the presence of a catalytic quantity pyridinium tosylate for 3 h [6]. On cooling the solution to room temperature, the product crystallized. The crystals were filtered off, recrystallized once from methanol/water (10:1) and used as such in the next step. Yield: 0·7 g (58 per cent); C 97 S_A 112 I. ^{1}H NMR, δ ppm, DMSO: 0·80 (t, 3 H, $-CH_3$), 1·18–1·80 (m, 19 H, $-CH-C\underline{H}_3$, $-CH_2-$), 3·26 (d, 2 H, $-C\underline{H}_2-OH$), 3·36–3·44 (m, 1 H, $-O-C\underline{H}-CH_2-$), 3·89–4·04 (m, 4 H, $-OCH_2-$, $-OH$), 4·34–4·37 (m, 1 H, $-C\underline{H}-CH_3$), 6·90 (m, 4 H, H–ar.), 7·43 (m, 4 H, H–ar.). MS *m/z* (rel. intensity, per cent): 414 (M^+) (4), 330 (29), 214 (92), 186 (100), 157 (13), 85 (20).

4.3.7. *(R)-1,2-bis-{5-[4-(5-Heptyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-6-[4′-(oct-2-yloxy)biphenyl-4-oxy]hexane* (**3**)

The same experimental procedure as described for the preparation of **9** was used. Quantities: *N,N*-dicyclohexylcarbodiimide (0·23 g, 1·1 mmol), 5-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoic acid (**16 a**) (0·38 g, 1 mmol), compound **20** (0·2 g, 0·48 mmol) and a catalytic quantity of 4-*N,N*-dimethylaminopyridine in 10 ml of dry dichlormethane. The residue was purified by recrystallization from acetone. Yield: 0·35 g (66 per cent); C 93 (S_C^* 79) I. ^{1}H NMR, δ ppm, $CDCl_3$: 0·76 (t, 9 H, $-CH_3$), 1·12–1·40 (m, 29 H, $-CH_2-$, $-CH-C\underline{H}_3$), 1·65–1·75 (m, 18 H, $-CH_2-$), 2·36 (t·broad, 4 H, $-COO-CH_2-$), 3·0 (t, 4 H, thiadiazole–CH_2-), 3·82–4·05 (m, 7 H, $-OCH_2-$, $-C\underline{H}-CH_3$), 4·20 (dd, 2 H, $-CH-C\underline{H}_2-$), 5·04–5·16 (m, 1 H, ($-C\underline{H}-OOC-$), 6·8 (m, 8 H, H–ar.), 7·36 (d, 4 H, H–ar.), 7·72 (d, 4 H, H–ar.). MS *m/z* (rel. intensity, per cent): 1125 (32), 1016 (16), 946 (16), 754 (80), 642 (48), 457 (38), 376 (32), 359 (53), 305 (36), 292 (75), 276 (30), 205 (30), 192, (71), 186 (100), 81 (33), 55 (48).

4.4. *Synthesis of 1,2-bis-{5-[4-(5-heptylpyrimidin-2-yl)-phenoxy]pentanoyloxy}-6-(4'-benzyloxybiphenyl-4-yloxy)hexane* (**2b**)

4.4.1. *6-(4'-Benzyloxybiphenyl-4'-yloxy)hexane-1,2-diol* (**15**)

Compound **14** (1·0 g, 2·3 mmol) was heated under reflux in 50 ml of methanol/water (10:1) after the addition of 10 per cent hydrochloric acid (5 ml). After complete reaction, the solvent was removed *in vacuo* and chloroform was added to the residue. The mixture was heated to reflux temperature and filtered while hot. Upon cooling the chloroform solution, the product crystallized. Yield: 0·75 g (83 per cent), m.p. 193°C. IR $\nu\,cm^{-1}$, (nujol): 3465–3100 (OH). MS *m/z* (rel. intensity, per cent): 392 (M^+) (68), 301 (16), 276 (11), 185 (100), 91 (58).

4.4.2. *1,2-bis-{5-[4-(5-Heptylpyrimidin-2-yl)phenoxy]-pentanoyloxy}-6-(4'-benzyloxybiphenyl-4-yloxy)hexane* (**2b**)

The experimental procedure used was the same as that described for the preparation of **9**. Quantities: compound **15** (70 mg, 0·18 mmol), 5-[4-(5-heptylpyrimidin-2-yl)phenoxy]pentanoic acid **16b** (150 mg, 0·41 mmol), a catalytic amount of DMAP, DCC (90 mg, 0·43 mmol) and dry dichloromethane (10 ml). The crude product was purified by column chromatography (R_f: 0·87) using chloroform/methanol (10:1) as eluent and recrystallized from methanol/chloroform. Yield: 80 mg (42 per cent); C 106 (S_A 100) I. ^{1}H NMR, δ ppm, $CDCl_3$: 0·85 (t, 6H, $-CH_3$), 1·15–1·40 (m, 14H, $-CH_2-$), 1·49–1·71 (m, 10H, $-CH_2-$), 1·71–1·88 (m, 4H, pyrimidine–CH_2-), 3·90–4·01 (m, 6H, $-OCH_2-$), 4·27 (dd, 2H, $-CH-C\underline{H}_2-$), 5·06 (s, 2H, $-CH_2O-$), 5·08–5·19 (m, 1H, $-C\underline{H}-CH_2-$), 6·84–7·15 (m, 8H, H–ar.), 7·29–7·48 (m, 9H, H–ar.), 8·29 (d, 4H, H–ar.), 8·52 (s, 4H, H-pyrimidine). MS *m/z* (rel. intensity, per cent): 1091 (M^+), 551 (18), 368 (41), 313 (37), 236 (28), 185 (18), 135 (23), 123 (33), 109 (53), 95 (88), 83 (100), 57 (95).

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