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Synthesis and liquid crystalline properties of novel laterally connected twins

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Synthesis and liquid crystalline properties of novel laterally connected twins

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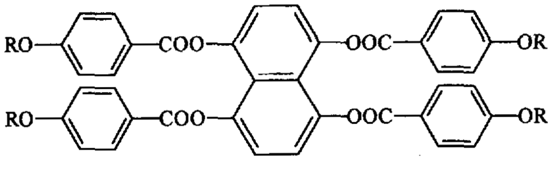
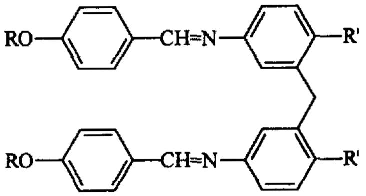
Several laterally connected twin mesogens incorporating rigid *p*-terphenyl units have been synthesized. Their liquid crystalline behaviour was investigated by polarizing microscopy and differential scanning calorimetry. If one compares the twins with their respective halves, the mesophase stabilizing influence of the lateral fixation becomes evident. It obviously pre-organizes the calamitic units and therefore stabilizes smectic phases. The mesophase behaviour of these twins depends strongly on the length and the structure of the spacer. Short as well as highly polar and rigid spacer units give rise to smectic phases with high transition temperatures. By increasing the spacer length the mesophase stability is drastically diminished. Dimesogenic 4,4″-didecyloxyterphenyl derivatives containing spacers consisting of two connecting atoms exhibit smectic C phases exclusively. Elongation of the spacer to three connecting atoms gives an S_A–S_C dimorphism, and in the case of compounds with longer spacers mostly the S_A phase and in one case the nematic phase were found.

1. Introduction

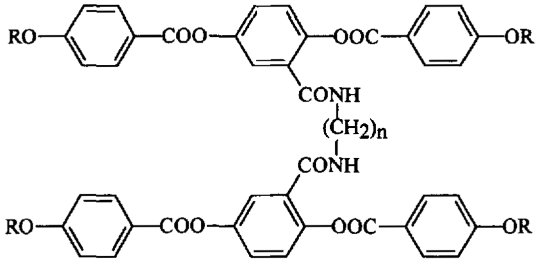
Mesogenic twins, trimesogens, and larger oligomesogens may be considered as prepolymers which are well suited for theoretical modelling. Therefore the investigation of the relationship between the molecular structure and the properties of these compounds is of real interest. In numerous publications, twins with calamitic units connected via their terminal chains have been reported [1–5] because they are interesting as models for main chain and side chain polymers. More recently also, macrocyclic oligomesogens [6] have been described. End-fixed trimesogens and larger defined oligomers have also been reported [7]. Less attention has been drawn to laterally connected mesogens [8–12]. Malthete synthesized tetra-acylated 1,4,5,8-tetrahydroxynaphthalene derivatives, which may be looked



MALTHETE 1975



GRIFFIN 1981



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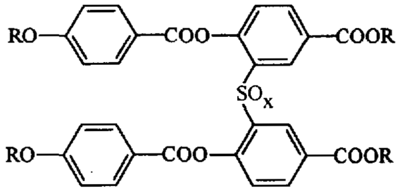

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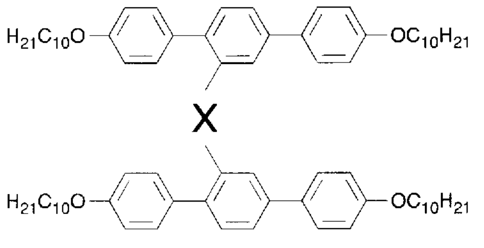
upon as 'fused Siamese twin' [8] mesogens. Later, Griffin prepared methylene bridged 'ligated twins' [9].
Dehne *et al.* [10] described twins which were joined by thio-, sulphinyl- and sulphonyl-bridges. All these twins had only one bridging atom. Weissflog *et al.* [11] reported laterally connected dimesogens with long spacer units, some of them incorporating additional aromatic units. The number of atoms in the spacer units of these compounds amounted to at least seven atoms. However, no laterally connected dimesogens with spacer units incorporating a number of linking atoms in the range two to six have yet been reported.

Herein we describe the synthesis and mesomorphic properties of novel twin mesogens consisting of two *p*-terphenyl mesogens, which are laterally connected by different spacers of medium length.



X = Spacer

2. Synthesis

At first we synthesized the twin **8** according to scheme 1. Here Suzuki cross-coupling reactions [13] of the 4-decyloxyphenyl boronic acid **2** [13(*c*)] with 1,4-dibromo-2-methylbenzene and methyl 2,5-dibromobenzoate (compound **3**) were the key steps in the synthesis of the *p*-terphenyl rigid cores (see table 1). Further functional group transformations yielded the intermediates **5** and **7** which were etherified in the presence of potassium hydride in THF [14] to give the desired dimesogen **8**. (scheme 1)

The benzyl bromide **7** was the key intermediate also in the synthesis of the oligo-oxyethylene bridged twins **10a**, **b**, **c**, the propylene glycol diether **11** and the octan-1,8-diol diether **12** (scheme 2) which were obtained by exhaustive etherification of the appropriate diols with benzyl bromide **7** in the presence of potassium hydride. (scheme 2)

The ethylene bridged dimer **9** was obtained by a cross coupling reaction which was carried out by treatment of the benzyl bromide **7** with one half equivalent of BuLi.

The syntheses of the dimers incorporating carbonyl groups within the spacer units (compounds **18**, **19**, **20** and **21**), as well as the synthesis of the thiadiazole [15] bridged compound **23** are displayed in scheme 3.

The esters **18** and **19** were obtained by the reaction of the benzylalcohol **5** with oxalyl chloride or phosgene in the presence of pyridine.

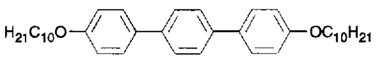
The 4,4″-didecyloxy-2′-nitro-*p*-terphenyl **25** was the key intermediate for the synthesis of the azobenzenene derivative **22** (scheme 4) [16]. It was obtained by Pd^0-catalysed cross coupling of 4-decyloxyphenyl boronic acid **2** with 2,5-dibromonitrobenzene.

In an analogous manner the 2′-amino-4,4″-didecyloxy-*p*-terphenyl **16** and the 4,4″-didecyloxy-*p*-terphenyl **24** were synthesized by cross coupling of boronic acid **2** with 2,5-dibromoaniline or 1,4-dibromobenzene, respectively.

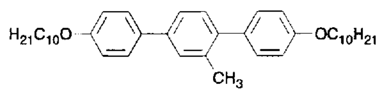
The final products were isolated by column chromatography and further purified by repeated crystallization.

3. Results and discussion

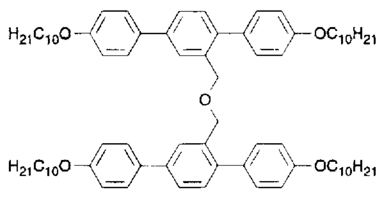
The transition temperatures of the synthesized twins are collected in tabnles 2 and 3. The mesomorphic behaviour of related terphenyl mesogens with different lateral 2′-substituents is given in table 1. From a comparison of the twin **8** with the corresponding 4,4″-didecyloxy-2′-methyl-*p*-terphenyl **6** [17,18], it is obvious that the covalent connection of the two compounds **6** via their methyl groups—mediated by a divalent ether oxygen atom—leads to a considerable increase of the mesophase stability.



24 Cr 129 S_X 172 S_Y 196 S_Z 201 S_C 216 I



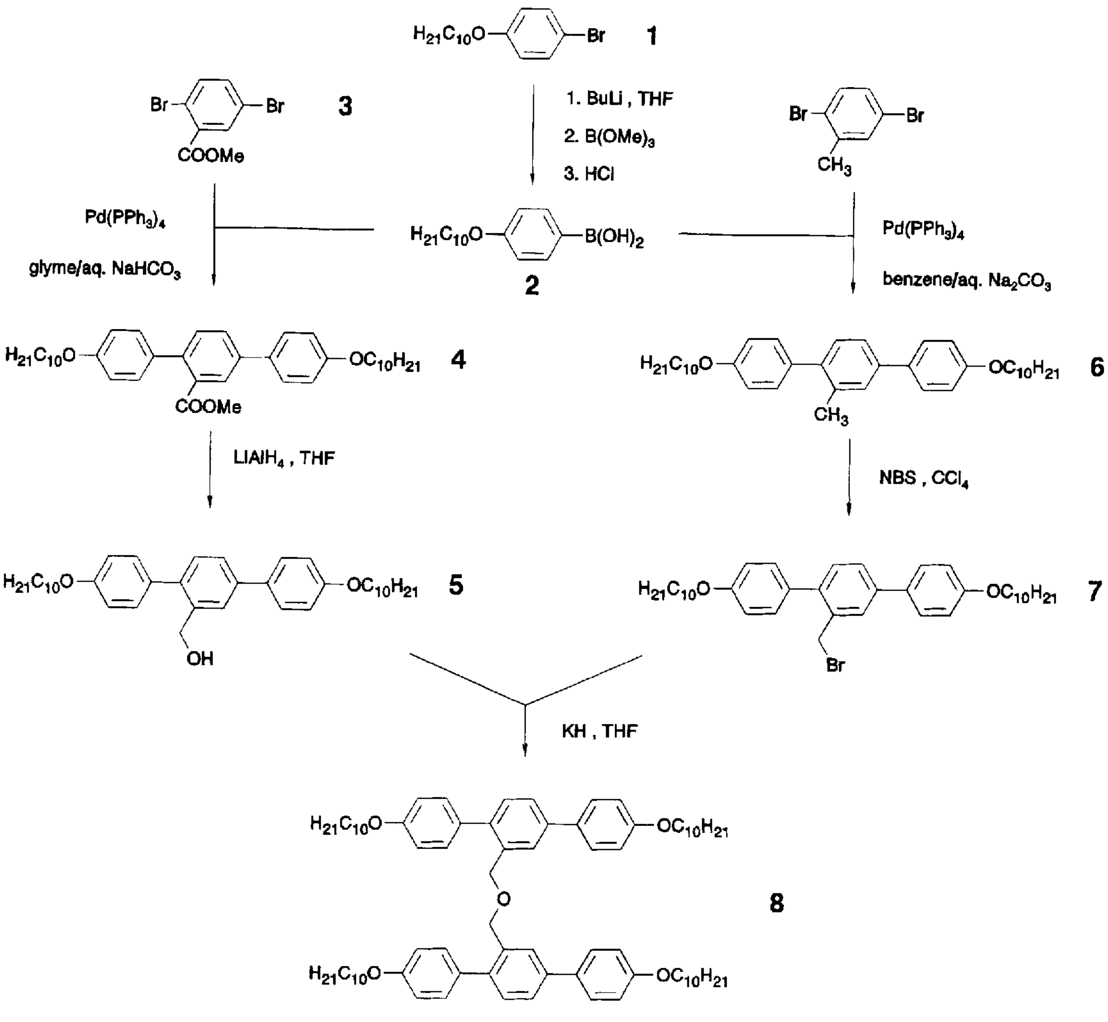
6 Cr 72 (S_C 70) S_A 104 N 109 I



8 Cr 99 S_C 128 S_A 168 I

If, however, one compares the parent terphenyl derivative **24**, without a lateral methyl group, with the dimesogen **8**, a significant mesophase destabilization must be noted. Therefore we have to consider an ambivalent influence of the lateral connecting units. Their steric requirements tend to separate the rigid cores from each other, which gives rise to mesophase destabilization. On the other hand the covalent fixing of the individual molecules stabilizes liquid crystalline phases.

If one compares **6** and **8**, it can also be seen that the lateral connection of the calamitic molecules stabilizes

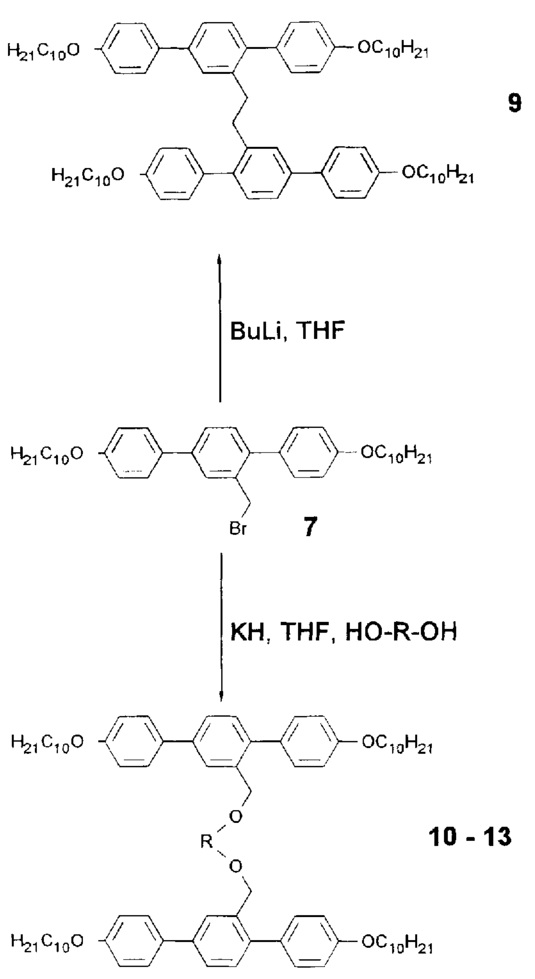


Scheme 1. Synthesis of the twin mesogen **8**.

the layered smectic A phase with respect to the nematic phase of **6**. Furthermore, the tilted smectic C phase is favoured. In order to investigate the influence of the spacer length on the properties of laterally connected dimers, we have synthesized compounds **9**–**12** containing spacer units of different lengths. The transition temperatures of these twins are also shown in table 2.

The dimer **9** with a short $-CH_2-CH_2-$ bridge exhibits a very high melting point. Unfortunately, the melt could be supercooled only for a few degrees. Therefore no statement concerning the monotropic mesophase behaviour of compound **9** can be given. Mesophases can be observed for all the other compounds. Their clearing temperatures decrease with increasing spacer length. The compounds **10a** and **11**, incorporating spacers consisting of six and seven connecting atoms, display only monotropic mesophases and they have a high crystallization tendency. Crystallization sets in at the transition to the smectic A phase. Therefore it is difficult to observe these mesophases. Further elongation of the spacer to nine (compound **10b**), or even twelve connecting atoms (compounds **10c** and **12**) gives compounds with lower melting points and a significantly diminished tendency to crystallization. Some of these compounds display enantiotropic phases and can be supercooled to room temperature without crystallization. The melting process is often accompanied by several solid-state transitions. As an example the first DSC heating and cooling traces of compound **10c** are displayed in the figure.

The compounds **10a**–**c** with oligooxyethylene spacers, and compound **13** incorporating an aromatic unit within the spacer, exhibit exclusively the smectic A phase. This means that the elongation of the spacer unit leads to the loss of the smectic C phase. Only compound **12** incorporating an octamethylene spacer displays a monotropic nematic phase. It seems that smectic phases are



Scheme 2. Syntheses of the twin mesogens **9**–**13** [**10a**: $R = –(CH_2)_2–$; **10b**: $R = –(CH_2)_2–O–(CH_2)_2–$; **10c**: $R = –(CH_2)_2–[O–(CH_2)_2]_2–$; **11**: $R = –(CH_2)_3–$; **12**: $R = –(CH_2)_8–$ and **13**: $R = –CH_2–Ph–CH_2–$].

favoured by more polar spacer units, whereas less polar aliphatic spacers disturb the layer structure and give the nematic phase.

Knowing the mesophase behaviour of dimesogens connected via aliphatic or heteroaliphatic chains, we studied (see table 3) the influence of functional groups like esters (**18** and **19**), amides (**20** and **21**), anhydrides (**17**) and others (azobenzene derivative **22** and thiadiazole **23**). Furthermore these groups allowed us to obtain twins with four (**21**) and five (**18**) connecting atoms.

Compound **17**, in which the two methylene groups within the spacer unit of compound **8** are replaced by carbonyl groups, displays a slightly increased mesophase stability. A larger mesophase stabilization is observed from a comparison of the ethylene glycol ether **10a** and the corresponding oxalate **19**. This is in line with the results obtained for sulphur-ligated twins. Here, increasing the oxidation state of the sulphur atom ($–S– < –SO– < –SO_2–$) gives rise to increased clearing temperatures [10]. It is also remarkable that the anhydride **17**, the amide **20** and the azobenzene derivative **22** display exclusively the smectic C phase. The latter two compounds include rigid spacers consisting of only two atoms, and this obviously leads not only to very high transition temperatures (clearing temperatures and melting points) but also to the exclusive appearance of the smectic C phase. Any further elongation of the spacer drastically decreases the clearing temperature and gives rise to a S_A–S_C dimorphism. The S_A–S_C transition temperature decreases with elongation of the spacer. The influence of an odd–even effect could not be estimated due to the rather different chemical structures of the spacer units.

The very restricted and bent structure of the unusually substituted thiadiazole derivative **23** obviously inhibits mesophase formation.

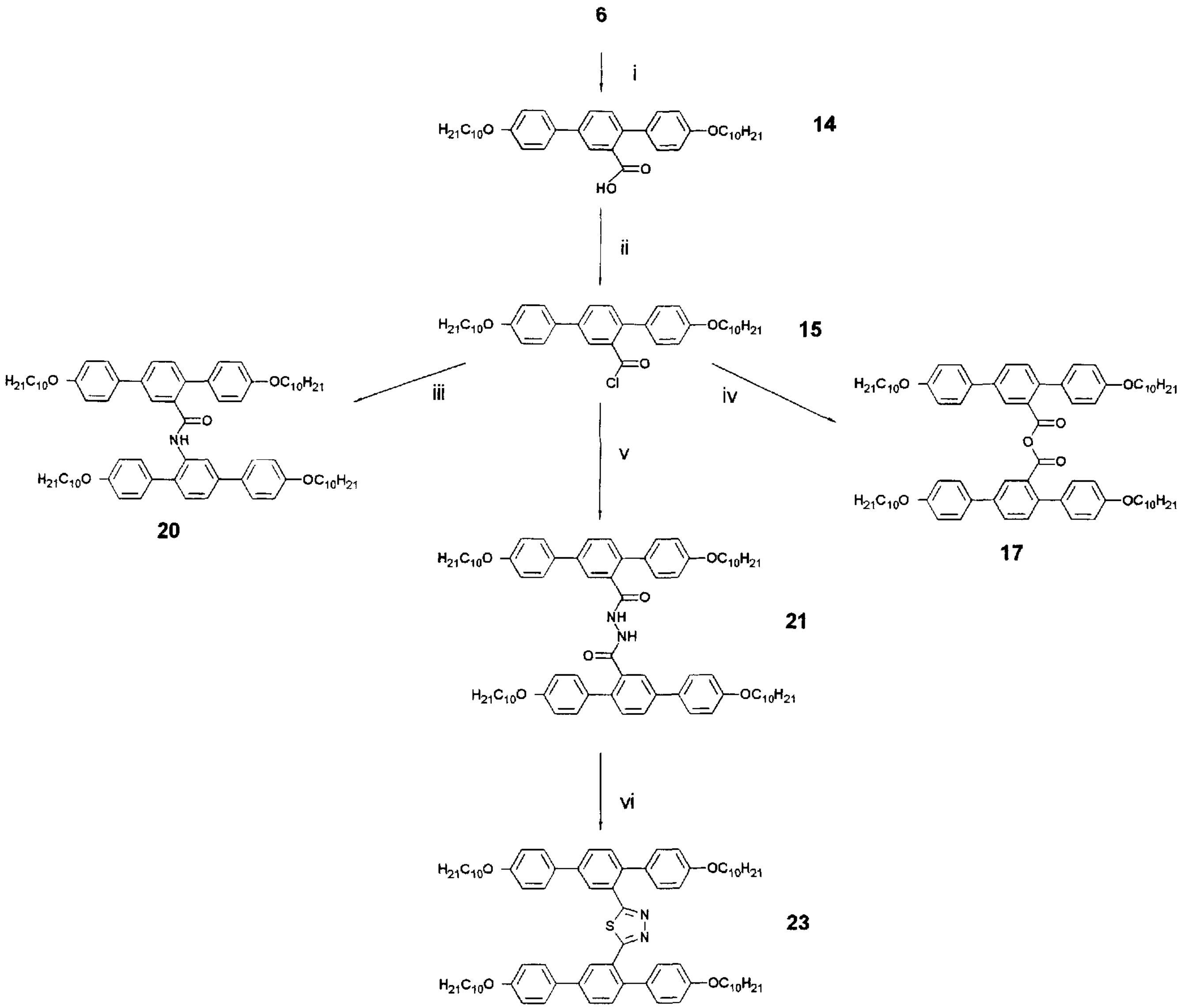
4. Summary

Several laterally connected twin mesogens incorporating rigid *p*-terphenyl units have been synthesized and investigated. Their mesophase behaviour depends strongly on the length and chemical structure of the spacer. Thereby one has to consider an ambivalent influence of the lateral connecting units. Firstly, the steric requirements cause a separation of the rigid cores from each other, giving rise to a mesophase destabilization with respect to the parent compounds without a lateral substituent. Secondly, the covalent connection of the individual molecules stabilizes liquid crystalline phases with respect to the single mesogens with lateral substituents of comparable size.

The most effective mesophase stabilization is observed for twins which are connected by only one atom [9, 10]. These twins often exhibit significantly increased mesophase stabilities even when compared with the parent calamitic single molecule mesogens without a lateral substituent.

By increasing the spacer length, the mesophase stability is drastically diminished. All compounds with spacers consisting of more than two connecting units have clearing temperatures which are below those of the parent calamitic single molecule mesogens without a lateral substituent. The main reason for this must be the increased size of the connecting units. If, however, one compares the twins with their respective halves (e.g. the twin **8** and the laterally methyl substituted compound **6**), the mesophase stabilizing influence of the lateral connection becomes obvious.

It is especially remarkable that this lateral connection pre-organizes the calamitic units and therefore stabilizes the smectic layer structure with respect to that of the nematic mesophase. Furthermore, the 4,4″-didecyloxy-



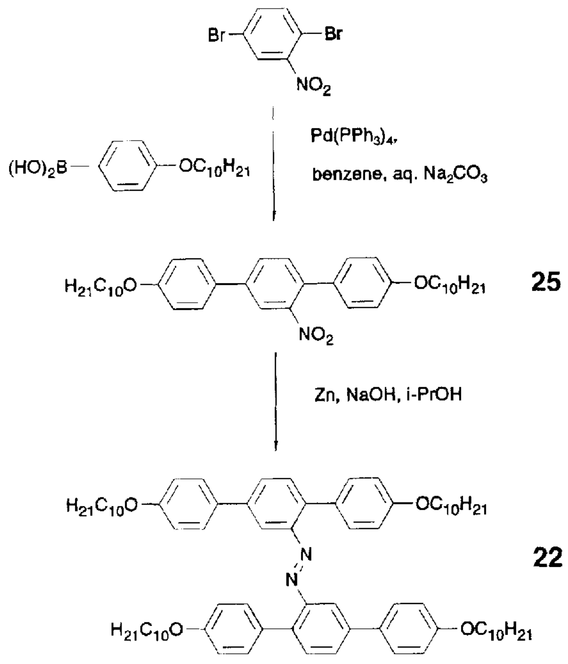
Scheme 3. Syntheses of the twins **17**, **20**, **21** and **23**. Reagents and conditions: (i) EtOH, NaOH, then aq. HCl [18]; (ii) $(COCl)_2$, CH_2Cl_2 [18]; (iii) CH_2Cl_2, 2′-amino-4,4″-didecyloxy-*p*-terphenyl (**16**); (iv) $COCl_2$, NET_3, toluene; (v) CH_2Cl_2, pyridine, $N_2H_4.H_2O$; (vi) Lawesson reagent, pyridine, toluene, then P_4S_{10}.

p-terphenyl derived twins containing short spacer units exhibit the smectic C phase. Elongation of the spacer strongly decreases the stability of the S_C phase. For compounds with long spacers, only the S_A phase and, in one case, the nematic phase were found. Further systematic investigations of mesogenic twins, for example, in relation to the topology of the connecting unit, are in progress.

5. Experimental

5.1. *General considerations*

^1H NMR and ^{13}C NMR spectra were recorded using a Bruker WP 200, a Varian Unity 500 or a Varian Gemini 200 spectrometer with tetramethylsilane as internal standard. 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 were confirmed using differential scanning calorimetry (Perkin Elmer DSC-7). Mass spectra were recorded using an AMD 402 mass spectrometer (70 eV) or an MS Engine 5989 A with Electrospray 59987 A. Thin layer chromatography was performed using coated aluminium plates (silica gel 60 F254) from Merck and visualized by UV light or by spraying with a solution of 3′, 3″-dibromothymolsulphonaphthalene in aqueous KOH and developing with NH_3. Silica gel



Scheme 4. Synthesis of the azobenzene derivative **22**.

60 (0·063–0·200 μm and 0·040–0·063 μm) was used for column chromatography. Solvents were purified and dried according to standard procedures. 1,4-Dibromo-2-methylbenzene (Jannsen), 2,5-dibromobenzoic acid (Lancaster), 2,5-dibromonitrobenzene (Aldrich) and 2,5-dibromoaniline (Aldrich) were used for the various syntheses as received, without further purification.

5.2. *Synthesis of the terphenyl derivatives* **5**, **7**, **16** *and* **25**

5.2.1. *4-Bromodecyloxybenzene* (**1**)

4-Bromophenol (10 g, 58 mmol) was dissolved in 200 ml of DMF. K_2CO_3 (12 g, 87 mmol), 1-bromodecane (19 g, 87 mmol) and Bu_4NI (100 mg) were added and the mixture was heated for 4–8 h at 100°C. The solvent was removed *in vacuo* and the residue was dissolved in ether, and washed with water (100 ml) and then with brine (50 ml). After drying (Na_2SO_4) the solvent was removed *in vacuo*. The product was purified by vacuum distillation. Yield: 16·7 g (92%), colourless oil; b.p. 136–142°C at 0·1 mmHg, (Lit. [19] b.p. 209°C at 20 mmHg). ^1H NMR, δ ppm, $CDCl_3$: 0·89 (t, 3H, $-CH_3$), 1·22–1·44 (m, 14H, $-CH_2-$), 1·74–1·82 (m, 2H, $O{-}CH_2{-}C\underline{H}_2{-}$), 3·89 (t, 2H, $O{-}CH_2{-}$), 6·92 (dd, 2H, H–Ar), 7·38 (dd, 2H, H–Ar).

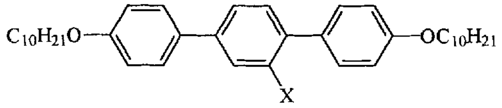
5.2.2. *4-Decyloxyphenylboronic acid* (**2**)

The Grignard reagent was prepared from 4-decyloxybromobenzene **1** (31 g, 0·1 mol) and magnesium (2·9 g, 0·12 mol) in dry THF and the solution was added dropwise to a stirred and cooled (−78°C) solution of trimethyl borate (21 g, 0·2 mol) in THF (150 ml). The temperature was kept below −70°C during the addition. The reaction mixture was stirred overnight and allowed to warm up to room temperature. After addition of 3 M hydrochloric acid (120 ml), the mixture was stirred for 1 h at 20°C. Afterwards it was shaken twice with ether (2 × 100 ml). The combined organic phases were washed with water (100 ml) and dried (Na_2SO_4). After evaporation of the solvent the residue was recrystallized from light petroleum fraction. Yield: 24·6 g (88%); m.p. 86°C, ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, 3H, $-CH_3$), 1·22–1·52 (m, 14H, $-CH_2-$), 1·74–1·82 (m, 2H, $O{-}CH_2{-}C\underline{H}_2{-}$), 4·02 (t, 2H, $O{-}CH_2{-}$), 6·98 (dd, 2H, H–Ar), 8·13 (dd, 2H, H–Ar).

5.2.3. *Methyl 2,5-dibromobenzoate* (**3**)

Concentrated H_2SO_4 (100 ml, 1 mol) was slowly added to a solution of 2,5-dibromobenzoic acid (28 g, 0·1 mol)

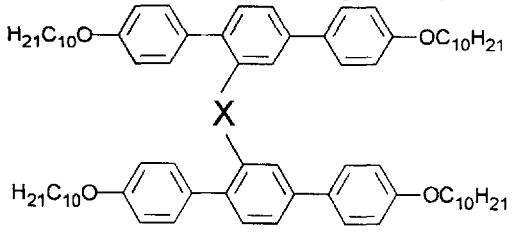
Table 1. Phase transition temperatures[a] (°C) of the laterally substituted *p*-terphenyl derivatives **4–7**, **14–16** and **24–25**.

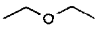
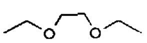
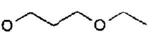
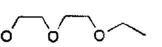
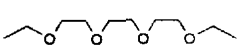
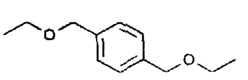


Compound	X	Cr		S_C	S_A	N	I
4	$-COOCH_3$	• 72	–	– –	– –	• 74	•
5	$-CH_2OH$	• 82	–	– –	• 128	– –	•
6 [18]	$-CH_3$	• 72	–	(• 70)	• 104	• 109	•
7	$-CH_2Br$	• 64	–	– –	– –	• 66	•
14 [18]	$-COOH$	• 151	–	– –	(• 125)	– –	•
15 [18]	$-COCl$	• 58	–	– –	–	(• 40)	•
16	$-NH_2$	• 120	–	• 159	• 167	– –	•
24	$-H$	• 129	S_X 172 S_Y 196 S_Z 201	• 216		– –	•
25	$-NO_2$	• 62	–	• 62	• 95	– –	•

[a] Determined by polarizing optical microscopy. S_X, S_Y and S_Z = smectic low temperature mesophases of unknown structure; for an explanation of the other abbreviations see footnote a to Table 2.

Table 2. Phase transition temperatures[a] (°C) and associated enthalpies[b] (ΔH/kJ mol^{-1}, in brackets) of the twins **8–13**.



Compound	X	Cr		S_C		S_A		N		I
9		•	196 (71·6)	–	–	–	–	–	–	•
8		•	99 (31·7)	•	128	•	168 (16·9)	–	–	•
10a		•	108 (71·7)	–	–	(•	97)	–	–	•
11		•	99 (84·7)	–	–	(•	93)	–	–	•
10b		•	74 (72·8)	–	–	•	90 (8·0)	–	–	•
10c		•	70 (73·4)	–	–	•	80 (7·9)	–	–	•
12		•	79 (88·4)	–	–	–	–	(•	65) (4·3)	•
13		•	105 (109·0)	–	–	(•	90) (12·8)			•

[a] Determined by optical microscopy with crossed polarizers: Cr = crystalline, N = nematic phase, S_A = smectic A phase, S_C = smectic C phase, I = isotropic phase. Due to the occurrence of different crystalline modifications, different melting temperatures and solid state transitions were observed depending on the thermal history of the samples. The highest observed melting temperatures are given in the table. The temperatures of the solid state transitions observed during the first heating are given in the experimental section.

[b] Values refer to DSC heating data from the first scan. The melting enthalpies also include the solid state transition enthalpies which were detected down to 20°C.

in methanol (200 ml). The mixture was boiled for 5 h. After cooling to room temperature, the solution was evaporated until crystallization occurred and poured into 500 g of ice. The light yellow precipitate was extracted into ether (3 x 100 ml) and the organic phase dried (Na_2SO_4). The solvent was evaporated and the residue recrystallized from ethanol/ethyl acetate (5:1). Yield: 27·5 g (93%); m.p. 45°C, (Lit. [20] m.p. 42–45°C). ^{1}H NMR, δ ppm, $CDCl_3$: 3·94 (s, 3H, $-CH_3$), 6·86 (d, 1H, H–Ar), 7·51 (dd, 1H, H–Ar), 7·93 (d, 1H, H–Ar).

5.2.4. *Methyl 2,5-bis-(4-decyloxyphenyl)benzoate* (**4**)

In a two necked flask with a reflux condenser and stirrer, $Pd(PPh_3)_4$ (0·5 g, 5 mol %) was added under an argon atmosphere to a mixture consisting of **3** (2·9 g, 10 mmol), **2** (6·7 g, 24 mmol), glyme (50 ml) and 2M aqueous $NaHCO_3$ (50 ml). The mixture was stirred at reflux temperature for 4 h. After cooling, the solvent was evaporated and the residue was treated with diethyl ether (100 ml) and water (100 ml). The organic phase was separated from the aqueous phase which was shaken twice more with diethyl ether (100 ml). The combined organic phases were washed with brine (50 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo* and the crude product obtained was purified by column chromatography (silica gel, chloroform) followed by crystallization from ethanol. Yield: 5·1 g (87%); phase transitions (°C): Cr 72 N 74 I. ^{1}H NMR, δ ppm, $CDCl_3$: 0·87 (t, 6H, $-CH_3$), 1·22–1·54 (m, 28H, $-CH_2-$), 1·75–1·83 (m, 4H, $O-CH_2-C\underline{H}_2-$), 3·67 (s, 3H, $O-CH_3$), 3·98 (t, 2H, $Ph-O-CH_2-$), 3·99 (t, 2H, $Ph-O-CH_2-$), 6·91 (dt, 2H, H(3″,5″)–Ar), 6·96 (dt, 2H, H(3,5)–Ar), 7·24 (dt, 2H,

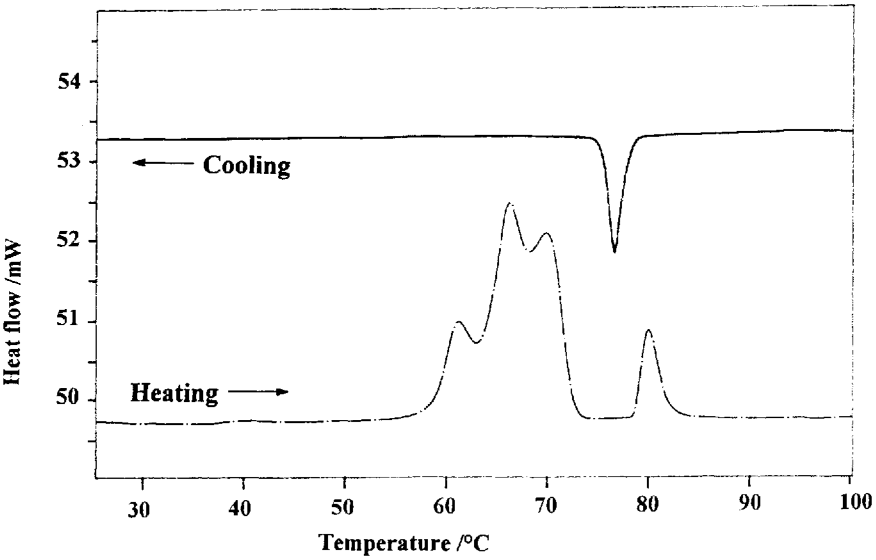


Figure 1. The first DSC heating and cooling scans for compound **10c** (10 K min^{-1}).

H(2″,6″)-Ar), 7·39 (d, 1H, H(6′)-Ar), 7·55 (dt, 2H, H(2,6)-Ar), 7·67 (dd, 1H, H(5′)-Ar), 7·94 (d, 1H, H(3′)-Ar).

5.2.5. *4,4″-Didecyloxy-2′-hydroxymethyl-*p*-terphenyl (*5*)*

In a three necked 1000 ml round bottomed flask, equipped with stirrer, reflux condenser and dropping funnel, $LiAlH_4$ (0·57 g, 15 mmol) was suspended under an argon atmosphere in dry ether (300 ml). While stirring, a suspension of **4** (15 g, 25 mmol) in dry ether (150 ml) was carefully added without external cooling. The reaction mixture was heated under reflux for an additional 10 h. After cooling to room temperature, water (100 ml) was carefully added dropwise with stirring. The organic phase was separated, dried (Na_2SO_4) and the solvent evaporated. The crude product was crystallized from petroleum fraction (b.p. 60–80°C). Yield: 12·9 g (90%); phase transitions (°C): Cr 82 S_A 128 I. ^{1}H NMR, δ ppm, $CDCl_3$: 0·88 (t, 6H, $-CH_3$), 1·24–1·41 (m, 24H, $-CH_2-$), 1·45–1·51 (m, 4H, $O-CH_2-CH_2-\underline{CH_2}-$), 1·77–1·83 (m, 4H, $O-CH_2-\underline{CH_2}-$), 4·00 (t, 4H, $Ph-O-CH_2-$), 4·67 (d, 2H, $-\underline{CH_2}-OH$), 6·95 (dt, 2H, H(3″,5″)-Ar), 6·97 (dt, 2H, H(3,5)-Ar), 7·30 (dt, 2H, H(2″,6″)-Ar), 7·31 (d, 1H, H(6′)-Ar), 7·50 (dd, 1H, H(5′)-Ar), 7·55 (dt, 2H, H(2,6)-Ar), 7·71 (d, 1H, H(3′)-Ar).

5.2.6. *4,4″-Didecyloxy-2′-methyl-*p*-terphenyl* (**6**)

This was prepared as described for **4** from dibromotoluene (2·5 g, 10 mmol) and **2** (6·7 g, 24 mmol), using benzene (50 ml) as solvent and 2M aqueous Na_2CO_3 (50 ml) as base. After chromatographic separation the product was crystallized from petroleum fraction (b.p. 60–80°C). Yield: 5·4 g (98%); phase transitions (°C): Cr 72 (S_C 70) S_A 104 N 109 I. ^{1}H NMR, δ ppm, $CDCl_3$: 0·87 (t, 6H, $-CH_3$), 1·28–1·48 (m, 28H, $-CH_2-$), 1·71–1·80 (m, 4H, $O-CH_2-\underline{CH_2}-$), 2·26 (s, 3H, $-CH_3$), 4·04 (t, 4H, $Ph-O-CH_2-$), 6·92 (dt, 2H, H(3″,5″)-Ar), 6·97 (dt, 2H, H(3,5)-Ar), 7·04 (dt, 2H, H(2″,6″)-Ar), 7·17 (d, 1H, H(6′)-Ar), 7·27 (d, 1H, H(3′)-Ar), 7·41 (dd, 1H, H(5′)-Ar), 7·53 (dt, 2H, H(2,6)-Ar).

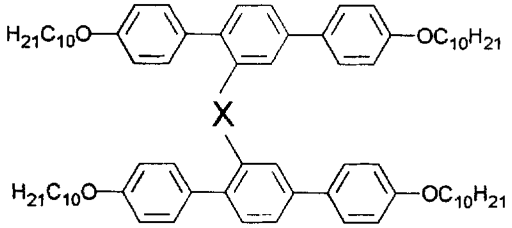
5.2.7. *2′-Bromomethyl-4,4″-didecyloxy-*p*-terphenyl (*7*)*

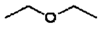
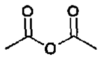
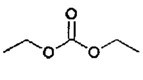
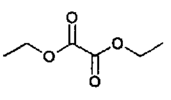
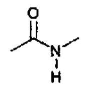
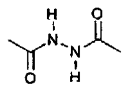
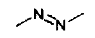
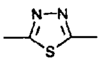
A solution of **6** (8·3 g, 15 mmol) and *N*-bromosuccinimide (3·2 g, 18 mmol) in dry tetrachloromethane (125 ml) was placed in a quartz flask and heated to boiling. A catalytic amount of dibenzoylperoxide (50 mg) was added and the boiling mixture irradiated with UV light (366 nm). After 2 h, the mixture was cooled to room temperature and the succinimide formed was filtered off. The solvent was removed *in vacuo* and the residue purified by column chromatography (silica gel, chloroform/methanol 10:0·5) followed by crystallization from light petroleum fraction. Yield: 8·1 g (85%); phase transitions (°C): Cr 58 N 65 I. ^{1}H NMR, δ ppm, $CDCl_3$: 0·88 (t, 6H, $-CH_3$), 1·28–1·56 (m, 28H, $-CH_2-$), 1·77–1·83 (m, 4H, $O-CH_2-\underline{CH_2}-$), 3·99 (t, 2H, $Ph-O-CH_2-$), 4·00 (t, 2H, $Ph-O-CH_2-$), 4·51 (s, 2H, $-CH_2-Br$), 6·97 (d, 4H, H(3,3″)-Ar, H(5,5″)-Ar), 7·27 (d, 1H, H(6′)-Ar), 7·38 (d, 2H, H(2″,6″)-Ar), 7·49 (dd, 1H, H(5′)-Ar), 7·54 (d, 2H, H(2,6)-Ar), 7·68 (d, 1H, H(3′)-Ar).

5.2.8. *4,4″-Didecyloxy-2′-nitro-*p*-terphenyl* (**25**)

This was prepared as described for **4** from 2,5-dibromonitrobenzene (2·8 g, 10 mmol) and **2** (6·9 g, 25 mmol) using benzene (50 ml) as solvent and 2M

Table 3. Phase transition temperatures[a] (°C) and associated enthalpies[b] (ΔH/kJ mol^{-1}, in brackets) of the twins **8** and **17–23**.



Compound	X	Cr	S_C	S_A	I
8		● 99 (31·7)	● 128	● 168 (16·9)	●
17		● 144 (39·5)	● 172 (26·3)	– –	●
18		● 105 (84·2)	– –	● 116 (15·9)	●
19		● 133 (121·4)	– –	(● 119)	●
20		● 196 (112·2)	(● 193)	– –	●
21		● 141 (22·5)	– –	● 159 (12·0)	●
22		● 178 (73·3)	● 237 (18·1)	– –	●
23		● 110 (53·0)	– –	– –	●

[a] Determined by optical microscopy with crossed polarizers; for an explanation of the abbreviations see footnote a to table 1.
[b] See footnote b to table 1.

aqueous Na_2CO_3 (50 ml) as base. After chromatographic separation ($CHCl_3$) the product was crystallized from acetone/methanol (1 : 1). Yield: 3·5 g (60%); yellow needles; phase transitions (°C): Cr_1 54 Cr_2 59 Cr_3 62 S_C 62 S_A 95 I. ^1H NMR, δ ppm, $CDCl_3$: 0·88 (t, 6H, $-CH_2$), 1·22–1·38 (m, 24H, $-CH_2-$), 1·43–1·50 (m, 4H, $O{-}CH_2{-}CH_2{-}C\underline{H}_2{-}$), 1·76–1·83 (m, 4H, $O{-}CH_2{-}C\underline{H}_2{-}$), 3·97 (t, 4H, Ph–O–$CH_2$–), 4·00 (t, 4H, Ph–O–$CH_2$–), 6·93 (dt, 2H, H(3,5)–Ar), 6·99 (dt, 2H, H(3″,5″)–Ar), 7·25 (dt, 2H, H(2,6)–Ar), 7·43 (d, 1H, H(6′)–Ar), 7·54 (dt, 2H, H(2″,6″)–Ar), 7·73 (dd, 1H, H(5′)–Ar), 7·94 (d, 1H, H(3′)–Ar).

5.2.9. *2′-Amino-4,4″-didecyloxy-*p*-terphenyl* (**16**)

This was prepared as described for **4** from 2,5-dibromoaniline (2·5 g, 10 mmol) and **2** (6·9 g, 25 mmol), using benzene (50 ml) as solvent and 2M aqueous Na_2CO_3 (50 ml) as base. After chromatographic separation ($CHCl_3$) the product was crystallized from hexane/ethyl acetate (10 : 1). Yield: 4·3 g (77%); phase transitions (°C): Cr 120 S_C 159 S_A 167 I. ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, 6H, $-CH_3$), 1·26–1·48 (m, 28H, $-CH_2-$), 1·72–1·82 (m, 4H, $O{-}CH_2{-}C\underline{H}_2{-}$), 3·80 (s.broad, 2H, $-NH_2$), 3·98 (t, 4H, Ph–O–CH_2–), 6·92 (dt, 2H, H(2″,6″)–Ar), 6·93 (d, 1H, H(3′)–Ar), 6·96 (dt, 2H, H(2,6)–Ar), 6·99 (dd, 1H, H(5′)–Ar), 7·14 (d, 1H, H(6′)–Ar), 7·38 (dt, 2H, H(3″,5″)–Ar), 7·50 (dt, 2H, H(3,5)–Ar).

5.2.10. *4·4″-Didecyloxy-*p*-terphenyl* (**24**)

This was prepared as described for **4** from 2,5-dibromobenzene (2·4 g, 10 mmol) and **2** (6·9 g, 25 mmol), using benzene (50 ml) as solvent and 2M aqueous Na_2CO_3 (50 ml) as base. The product was crystallized from chloroform. Yield: 4·6 g (85%); transitions (°C): C 129 S_X 172 S_Y 196 S_Z 201 S_C 216 I. ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, 6H, $-CH_2$), 1·26–1·49 (m, 28H, $-CH_2-$), 1·72–1·82 (m, 4H, $O-CH_2-C\underline{H}_2-$), 3·97 (t, 4H, $Ph-O-CH_2-$), 6·96 (dt, 4H, H(3,3″)–Ar, H(5,5″)–Ar), 7·53 (dt, 4H, H(2,2″)–Ar, H(6,6″)–Ar), 7·58 (s, 4H, H′–Ar).

5.3. *1,2-bis-(4,4″-Didecyloxy-*p*-terphenyl-2′-yl)ethane* (**9**)

Compound **7** (0·64 g, 1 mmol) was dissolved in dry THF (20 ml). At −78°C, BuLi (0·34 ml, 1·6 M in THF, 0·55 mmol) was added under an argon atmosphere over a period of 30 min. The solution was kept at −78°C for 3 h and was allowed to warm up to room temperature overnight. Diethyl ether (20 ml) and water (20 ml) were added, and the organic phase was separated. The light yellow precipitate in the organic phase was filtered off and crystallized from hexane. Yield: 50 mg (6%); m.p. 196°C. Elemental analysis (%): found (calculated for $C_{78}H_{110}O_4$): C, 84·10 (84·27); H, 9·83 (9·97). ^1H NMR, δ ppm, $CDCl_3$: 0·89 (t, 12H, $-CH_3$), 1·24–1·40 (m, 48H, $-CH_2$), 1·45–1·53 (m, 8H, $Ph-O-CH_2-CH_2-C\underline{H}_2-$), 1·78–1·84 (m, 8H, $Ph-O-CH_2-C\underline{H}_2-$), 2·85 (s, 4H, $Ph-CH_2-CH_2-Ph-$), 3·95 (t, 4H, $Ph-O-CH_2-$), 4·01 (t, 4H, $Ph-O-CH_2-$), 6·86 (dt, 4H, H–Ar), 6·96 (dt, 4H, H–Ar), 7·04 (dt, 4H, H–Ar), 7·16 (d, 2H, H(6′)–Ar), 7·19 (d, 2H, H(3′)–Ar), 7·37 (dd, 2H, H(5′)–Ar), 7·44 (dt, 4H, H–Ar). MS *m/z* (relative intensity, %): 1111 (100), 970 (5), 570 (8), 556 (17), 275 (30).

5.4. *General procedure for synthesis of the ethers* **8** *and* **10–13**

In a two-necked flask with inert gas inlet, septum and magnetic stirring bar, potassium hydride (100 mg, 2·5 mmol, washed with dry hexane prior to use) was suspended in dry THF (5 ml). The resulting suspension was cooled to 0°C and the corresponding alcohol (1 mmol), dissolved in dry THF (10 ml) was slowly added using a syringe. The mixture was stirred at room temperature for 4 h. A solution of the appropriate bromide (2·4 mmol) in dry THF (10 ml) and dry NBu_4I (40 mg, 0·1 mmol) were added. The reaction mixture was stirred for 10–60 h at 20–40°C. Diethyl ether (20 ml) and water (20 ml) were then carefully added, the organic phase was separated and the aqueous phase was shaken twice with ether (50 ml). The combined organic phases were dried with Na_2SO_4, the solvent was removed *in vacuo* and the residue was purified by column chromatography followed by crystallization.

5.4.1. *1,3-bis-(4,4″-Didecyloxy-*p*-terphenyl-2′-yl)-2-oxapropane* (**8**)

This was synthesized from **5** and **7**. Eluent: chloroform/methanol (10:0·5). Crystallized from light petroleum fraction. Yield: 56%; phase transitions (°C): Cr 99 S_C 128 S_A 168 I. Elemental analysis (%): found (calculated for $C_{78}H_{110}O_5$): C, 82·88 (83·07); H, 9·66 (9·83). ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, 12H, CH_3), 1·27–1·48 (m, 56H, $-CH_2-$), 1·69–1·79 (m, 8H, $Ph-O-CH_2-C\underline{H}_2-$), 3·88 (t, 4H, $Ph-O-CH_2-$), 3·91 (t, 4H, $Ph-O-CH_2-$), 4·47 (s, 4H, $Ph-CH_2-O$), 6·86–7·44 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1124 (20), 570 (29), 556 (100), 276 (38).

5.4.2. *1,6-bis-(4,4″-Didecyloxy-*p*-terphenyl-2′-yl)-* 2,5-dioxahexane (**10a**)

This was synthesized from dry ethylene glycol and **7**. Eluent: chloroform. Crystallized from light petroleum fraction. Yield: 68%; phase transitions (°C): Cr_1 80 Cr_2 108 (S_A 97) I. Elemental analysis (%): found (calculated for $C_{80}H_{114}O_6$): C, 82·05 (82·00); H, 9·81 (9·81). ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, 12H, $-CH_3$), 1·27–1·42 (m, 56H, $-CH_2-$), 1·72–1·82 (m, 8H, $O-CH_2-C\underline{H}_2-$), 3·62 (s, 4H, $-O-CH_2-CH_2-O-$), 3·90 (t, 4H, $Ph-O-CH_2-$), 3·95 (t, 4H, $Ph-O-CH_2-$), 4·48 (s, 4H, $Ph-CH_2-O-$), 6·84–7·73 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1171 (24), 630 (4), 614 (16), 600 (48), 570 (100), 553 (44).

5.4.3. *1,7,bis-(4,4″-Didecyloxy-*p*-terphenyl-2′-yl)-* 2,6-dioxaheptane (**11**)

This was synthesized from dry propan-1,3-diol and **7**. Eluent: chloroform/methanol (10:2). Crystallized from hexane. Yield: 22%; phase transitions (°C): Cr_1 85 Cr_2 99 (S_A 93) I. Elemental analysis (%): found (calculated for $C_{81}H_{116}O_6$): C, 81·97 (82·04); H, 9·67 (9·86). ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, 12H, $-CH_3$), 1·26–1·49 (m, 56H, $-CH_2-$), 1·72–1·82 (m, 8H, $Ph-O-CH_2-C\underline{H}_2-$), 1·86–1·92 (m, 2, $-O-CH_2-C\underline{H}_2-CH_2-O-$), 3·54 (t, 4H, $-O-C\underline{H}_2-CH_2-CH_2-O-$), 3·92 (t, 4H, $Ph-O-CH_2-$), 3·96 (t, 4H, $Ph-O-CH_2-$), 4·40 (s, 4H, $Ph-CH_2-O-$), 6·86–7·67 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1185 (7), 630 (8), 614 (11), 570 (100), 553 (84).

5.4.4. *1,9-bis-(4,4″-Didecyloxy-*p*-terphenyl-2′-yl)-* 2,5,8-trioxanonane (**10b**)

This was synthesized from dry diethylene glycol and **7**. Eluent: chloroform/methanol (10:0·5). Crystallized from hexane. Yield: 22%; phase transitions (°C): Cr_1 60 Cr_2 67 Cr_3 74 S_A 90 I. Elemental analysis (%): found (calculated for $C_{82}H_{118}O_7$): C, 80·77 (81·01); H, 9·61 (9·78). ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, 12H, –CH_3), 1·22–1·38 (m, 48H, –CH_2–), 1·40–1·48 (m, 8H, O–CH_2–CH_2–$C\underline{H}_2$–), 1·73–1·80 (m, 8H, Ph–O–CH_2–$C\underline{H}_2$–), 3·58 (t, 4H, Ph–CH_2–O–CH_2–$C\underline{H}_2$–O–), 3·64 (t, 4H, Ph–CH_2–O–$C\underline{H}_2$–CH_2–O–), 3·94 (t, 4H, Ph–O–CH_2–), 3·96 (t, 4H, Ph–O–CH_2–), 4·47 (s, 4H, Ph–CH_2–O–), 6·89–7·70 (m, 22H, H–Ar). MZ *m/z* (relative intensity, %): 1215 (18), 660 (30), 644 (29), 616 (38), 570 (100), 556 (78).

5.4.5. *1,12-bis-(4,4″-Didecyloxy*-p-*terphenyl-2′-yl)*-2,5,8,11-tetroxadodecane (**10c**)

This was synthesized from dry triethylene glycol and **7**. Eluent: chloroform and chloroform/methanol (10:2). Crystallized from light petroleum fraction. Yield: 66%; phase transitions (°C): Cr_1 61 Cr_2 66 Cr_3 70 S_A 80 I. Elemental analysis (%): found (calculated for $C_{84}H_{122}O_8$): C, 79·77 (80·08); H, 9·52 (9·76). ^1H NMR, δ ppm, $CDCl_3$: 0·88 (t, 12H, –CH_3), 1·28–1·57 (m, 56H, –CH_2–), 1·73–1·86 (m, 8H, Ph–O–CH_2–$C\underline{H}_2$–), 3·56–3·65 (m, 12H, –O–CH_2–CH_2–O–), 3·98 (t, 8H, Ph–O–CH_2–), 4·47 (s, 4H, Ph–CH_2–O–), 6·90–7·71 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1259 (22), 704 (10), 688 (26), 570 (52), 553 (100).

5.4.6. *1,12-bis-(4,4″-Didecyloxy*-p-*terphenyl-2′-yl)*-2,11-dioxadodecane (**12**)

This was synthesized from 1,8-dihydroxyoctane and **7**. Eluent: chloroform. Crystallized from light petroleum fraction. Yield: 22%; phase transitions (°C): Cr_1 68 Cr_2 79 (N 65) I. Elemental analysis (%): found (calculated for $C_{86}H_{126}O_6$): C, 81·71 (82·24); H, 10·01 (10·11). ^1H NMR, δ ppm, $CDCl_3$: 0·88 (t, 12H, –CH_3), 1·24–1·40 (m, 56H, –CH_2–), 1·43–1·49 (m, 8H, Ph–O–CH_2–CH_2–$C\underline{H}_2$–), 1·53–1·59 (m, 4H, –CH_2–O–CH_2–$C\underline{H}_2$–), 1·75–1·82 (m, 8H, –O–CH_2–$C\underline{H}_2$–), 3·41 (t, 4H, Ph–CH_2–O–$C\underline{H}_2$–), 3·97 (t, 4H, Ph–O–CH_2–), 3·98 (t, 4H, Ph–O–CH_2–), 4·40 (s, 4H, Ph–CH_2–O–), 6·91–7·69 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1255 (48), 698 (20), 570 (100), 556 (63).

5.4.7. *1,4-bis-[3-(4,4″-Didecyloxy*-p-*terphenyl-2′-yl)-2-oxaprop-1-yl]benzene* (**13**)

This was synthesized from **5** and α,α'-dibromo-*p*-xylene. Eluent: chloroform. Crystallized from light petroleum fraction. Yield: 55%; phase transitions (°C): Cr_1 90 Cr_2 105 (S_A 90) I. Elemental analysis (%): found (calculated for $C_{86}H_{118}O_6$): C, 82·62 (82·78); H, 9·46 (9·53). ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, 12H, –CH_3), 1·27–1·49 (m, 56H, –CH_2–), 1·72–1·82 (m, 8H, Ph–O–CH_2–$C\underline{H}_2$–), 3·97 (t, 4H, Ph–O–CH_2–), 3·98 (t, 4H, Ph–O–CH_2–), 4·49 (s, 4H, Ph–CH_2–O–), 4·51 (s, 4H, Ph–CH_2–O–), 6·89–7·72 (m, 26H, H–Ar). MS *m/z* (relative intensity, %): 1247 (38), 690 (29), 570 (36), 556 (100), 276 (35).

5.5. *2,5-bis-(4-Decyloxyphenyl)benzoic acid anhydride* (**17**)

2,5-bis-(4-Decyloxyphenyl)benzoic acid [18] (0·18 g, 0·3 mmol) was dissolved in dry toluene (20 ml). Triethylamine (0·33 g, 0·33 mmol) was added at 0°C. After stirring for 10 min, phosgene (0·1 ml of a 1·93M solution in toluene, 0·18 mmol) was added by syringe. Stirring was continued for 30 min at 0°C and for one additional hour at 20°C. The solvent was removed *in vacuo* and the residue was immediately purified by column chromatography with chloroform. Yield: 90 mg (52%); phase transitions (°C): Cr_1 113 Cr_2 142 Cr_3 144 S_C 172 I. Elemental analysis (%): found (calculated for $C_{78}H_{106}O_7$): C, 80·92 (81·06); H, 9·36 (9·24). ^1H NMR, δ ppm, $CDCl_3$: 0·88 (t, 12H, –CH_3), 1·22–1·34 (m, 48H, –CH_2–), 1·32–1·40 (m, 4H, O–CH_2–CH_2–$C\underline{H}_2$–), 1·43–1·50 (m, 4H, O–CH_2–CH_2–$C\underline{H}_2$–), 1·66–1·72 (m, 4H, O–CH_2–$C\underline{H}_2$–), 1·77–1·83 (m, 4H, O–CH_2–$C\underline{H}_2$–), 3·81 (t, 4H, Ph–O–CH_2–), 4·00 (t, 4H, Ph–O–CH_2–), 6·81–7·75 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1155 (63), 586 (100), 568 (60).

5.6. *bis-[(4,4″-Didecyloxy*-p-*terphenyl-2′-yl)methyl] carbonate* (**18**)

4,4″-Didecyloxy-2′-hydroxymethyl-*p*-terphenyl **5** (1·9 g, 3·3 mmol) was dissolved in a mixture of dry toluene (20 ml) and dry pyridine (0·3 ml). The mixture was cooled to −10°C and phosgene (0·77 ml of a 1·93M solution in toluene, 1·5 mmol) was slowly added by syringe. Stirring was continued at 0°C for 2 h. The reaction mixture was allowed to warm up to room temperature and was stirred for an additional 24 h. The solution was washed twice with 10 ml of aqueous HCl (10%) and the solvent was removed *in vacuo*. The solid residue was crystallized from dichloromethane/methanol (1:1). Yield: 0·9 g (52%); phase transitions (°C): Cr_1 94 Cr_2 105 S_A 116 I. Elemental analysis (%): found (calculated for $C_{79}H_{110}O_7$): C, 80·99 (80·98); H, 9·45 (9·46). ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, 12H, –CH_3), 1·22–1·38 (m, 48H, –CH_2–), 1·40–1·48 (m, 8H, Ph–O–CH_2–CH_2–$C\underline{H}_2$–), 1·74–1·81 (m, 8H, Ph–O–CH_2–$C\underline{H}_2$–), 3·93 (t, 4H, Ph–O–CH_2–), 3·97 (t, 4H, Ph–O–CH_2–), 5·12 (s, 4H, Ph–CH_2–O–), 6·89–7·69 (m, 22H, H–Ar). Electrospray-MS: 1233·3 $(M+K)^+$, 1210·4 $(M+Na)^+$, 1193·9 $(M+H)^+$.

5.7. *bis-[(4,4″-Didecyloxy*-p-*terphenyl-2′-yl)methyl] oxalate* (**19**)

4,4″-Didecyloxy-2′-hydroxymethyl-*p*-terphenyl **5** (1·2 g, 2 mmol) was dissolved in a mixture of dry toluene

(20 ml) and dry pyridine (0·3 ml). The mixture was cooled to 0°C and oxalyl chloride (0·16 g, 0·9 mmol) was slowly added by syringe. Afterwards the reaction mixture was stirred for 3 h at 20°C. The solution was washed twice with 10 ml of aqueous HCl (10%) and the solvent was removed *in vacuo*. The white residue was crystallized from chloroform/methanol (2:1). Yield: 0·49 g (45%); phase transitions (°C): Cr_1 65 Cr_2 133 (S_A 119) I. Elemental analysis (%): found (calculated for $C_{80}H_{110}O_8$): C, 79·87 (80·09); H, 9·16 (9·24). ^{1}H NMR, δ ppm, $CDCl_3$: 0·87 (t, 12H, $-CH_3$), 1·23–1·38 (m, 48H, $-CH_2-$), 1·40–1·48 (m, 8H, $Ph-O-CH_2-CH_2-C\underline{H}_2-$), 1·72–1·81 (m, 8H, $Ph-O-CH_2-C\underline{H}_2-$), 3·90 (t, 4H, $Ph-O-CH_2-$), 3·97 (t, 4H, $Ph-O-CH_2-$), 5·25 (s, 4H, $Ph-CH_2-O-$), 6·84–7·68 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1199 (2), 600 (25), 572 (32), 554 (100).

5.8. *2′-(4,4″-Didecyloxy-*p*-terphenyl-2′-carbonylamino)-4,4″-didecyloxy-*p*-terphenyl* (**20**)

2,5-bis-(4-Decyloxyphenyl)benzoyl chloride **15** [19] (0·1 g, 0·16 mmol) was dissolved in dry dichloromethane (10 ml). 2′-Amino-4,4″-didecyloxy-*p*-terphenyl **16** (0·14 g, 0·26 mmol) dissolved in dichloromethane (10 ml) was added by syringe at 20°C. The reaction mixture was heated to 30°C and stirred until no amine could be detected by thin layer chromatography (20 h). The precipitate formed was filtered off and purified by column chromatography with dichloromethane followed by crystallization from ethyl acetate/light petroleum fraction. Yield: 0·11 g (60%); transitions (°C): Cr_1 128 Cr_2 186 Cr_3 191 Cr_4 196 (S_C 193) I. Elemental analysis (%): found (calculated for $C_{77}H_{107}NO_5$): C, 81·90 (82·08); H, 9·38 (9·57); N, 1·23 (1·24). ^{1}H NMR, δ ppm, $CDCl_3$: 0·85–0·88 (m, 12H, $-CH_3$), 1·24–1·38 (m, 48H, $-CH_2-$), 1·41–1·50 (m, 8H, $O-CH_2-CH_2-C\underline{H}_2-$), 1·73–1·82 (m, 8H, $O-CH_2-C\underline{H}_2-$), 3·92–3·96 (m, 4H, $Ph-O-CH_2-$), 3·97–4·01 (m, 4H, $Ph-O-CH_2-$), 6·81–7·82 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1126 (84), 586 (100), 569 (24), 557 (10), 429 (60).

5.9. *N,N′-bis-(4,4″-Didecyloxy-*p*-terphenyl-2′-carbonyl)hydrazine* (**21**)

2,5-bis-(4-Decyloxyphenyl)benzoyl chloride **15** [19] (0·3 g, 0·5 mmol) was dissolved in dry dichloromethane (10 ml) and added at 0°C via a syringe to a solution of hydrazine hydrate (13 mg, 0·25 mmol) in a mixture consisting of dry dichloromethane (10 ml) and dry pyridine (10 ml). The reaction mixture was stirred at 20°C for 5 h. Afterwards the solvent was evaporated and the residue was purified by column chromatography using chloroform/methanol (10:0·5), followed by crystallization from light petroleum fraction. Yield: 0·14 g (47%); phase transitions (°C): C 141 S_A 159 I. Elemental analysis (%): found (calculated for $C_{78}H_{108}N_2O_6$): C, 79·65 (80·09); H, 9·58 (9·31); N, 2·07 (2·39). ^{1}H NMR, δ ppm, $CDCl_3$: 0·84–0·90 (m, 12H, $-CH_3$), 1·22–1·38 (m, 48H, $-CH_2-$), 1·41–1·49 (m, 8H, $O-CH_2-CH_2-C\underline{H}_2-$), 1·76–1·82 (m, 8H, $O-CH_2-C\underline{H}_2-$), 3·97 (t, 4H, $Ph-O-CH_2-$), 3·99 (t, 4H, $Ph-O-CH_2-$), 6·92–7·85 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1150 (16), 583 (100), 569 (44), 554 (42).

5.10 *2,5,2′,5′-tetrakis-(4-Decyloxyphenyl)azobenzene* (**22**)

4,4″-Didecyloxy-2′-nitro-*p*-terphenyl **25** (1·5 g, 2·6 mmol) and zinc powder (0·33 g, 5·2 mmol) were suspended in isopropanol (10 ml). A solution of NaOH (0·4 g, 10·4 mmol) in water (2 ml) was added and the resulting mixture was heated at reflux for 8 h. After evaporation of the solvent, a light yellow residue was obtained, which was treated with 5M aqueous hydrochloric acid (10 ml) and boiled for 4 h. After cooling, the mixture was poured onto 50 g of crushed ice. The precipitate produced was filtered off and crystallized from chloroform. Yield: 0·48 g (34%); phase transitions (°C): Cr_1 113 Cr_2 178 S_C 237 I. Elemental analysis (%): found (calculated for $C_{76}H_{106}N_2O_4$): C, 81·88 (82·11); H, 9·38 (9·61); N, 2·31 (2·52). ^{1}H NMR, δ ppm, $CDCl_3$: 0·88 (t, 12H, $-CH_3$), 1·24–1·35 (m, 48H, $-CH_2-$), 1·41–1·50 (m, 8H, $O-CH_2-CH_2-C\underline{H}_2-$), 1·72–1·83 (m, 8H, $O-CH_2-C\underline{H}_2-$), 3·91–3·95 (m, 4H, $Ph-O-CH_2-$), 3·98–4·01 (m, 4H, $Ph-O-CH_2-$), 6·89–7·63 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1111 (18), 557 (100), 542 (33).

5.11. *2,5-bis-(4,4″-Didecyloxy-*p*-terphenyl-2′-yl)-*1,3,4-thiadiazole (**23**)

Under an argon atmosphere *N,N′*-bis-(4,4″-didecyloxy-*p*-terphenyl-2′-carbonyl)hydrazine **21** (0·47 g, 0·4 mmol) was added to a solution of Lawesson reagent (0·21 g, 0·52 mmol) in dry toluene (5 ml) and dry pyridine (0·1 ml). The reaction mixture was heated at reflux for 5 h. After evaporation of the solvent *in vacuo* pyridine (10 ml) and P_4S_{10} (0·05 g, 0·13 mmol) were added. After stirring at 90°C for 5 h, ethanol (1 ml) was added and the yellow solution was poured onto 50 g of ice. A light yellow precipitate was obtained, which was filtered off and purified by column chromatography with light petroleum fraction/ethyl acetate (10:1), followed by crystallization from ethyl acetate/ethanol (1:1). Yield: 0·35 g (78%); phase transitions (°C): Cr_1 99 Cr_2 110 I. Elemental analysis (%): found (calculated for $C_{78}H_{106}N_2SO_4$): C, 79·88 (80·23); H, 9·09 (9·15); N, 2·30 (2·40); S, 2·97 (2·75). ^{1}H NMR, δ ppm, $CDCl_3$: 0·87 (t, 12H, $-CH_3$), 1·22–1·52 (m, 56H, $-CH_2-$), 1·72–1·86 (m, 8H, $O-CH_2-C\underline{H}_2-$), 3·97 (t, 4H, $Ph-O-CH_2-$), 4·00 (t, 4H, $Ph-O-CH_2-$), 6·74–8·29 (m, 22H, H–Ar). MS *m/z* (relative intensity, %): 1166 (100), 567 (3).

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