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Synthesis and liquid crystalline properties of novel laterally connected trimesogens and tetramesogens

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Three types of laterally connected triplet mesogens and one quadruplet mesogen incorporating rigid *p*-terphenyl units have been synthesized. Their liquid crystalline behaviour was investigated by polarizing microscopy, differential scanning calorimetry and X-ray scattering. The lateral fixation of three rod-like 4,4″-didecyloxy-*p*-terphenyl units mostly gives liquid crystalline materials with considerably increased mesophase stabilities with respect to the parent 4,4″-didecyloxy-2′-methyl-*p*-terphenyl. The mesophase stability strongly depends on the type of connection. The highest clearing temperatures were observed for triplets which are connected in line with each other (type **I**) and triplets which are laterally connected in a peripheral manner. Only the oligomesogens of type **III** are not liquid crystalline. All compounds incorporating exclusively decyloxy chains exhibit smectic phases (S_A and S_C). For the ethoxy derivatives the nematic phase was found.

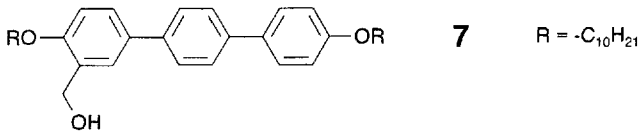
1. Introduction

Mesogenic twins, trimesogens, tetramesogens and larger oligomesogens have attracted some interest during the last decade. This has been promoted both by their ability to act as model compounds for liquid crystalline polymers and by their quite different properties in comparison to conventional low molecular weight mesogens.

In most cases these oligomesogens consist of calamic units which are connected via their terminal chains [1]. Only a few laterally connected mesogenic twins [2–6] have been described. Herein we report on new oligomesogens in which three or four calamitic terphenyl rigid cores are laterally attached to each other by means of different topologies [7]. Three different connecting topologies were realized (figure 1). Type **I** represents trimesogens in which the calamitic units are connected in line with each other. In type **II** the rigid cores are connected *via* an aromatic central unit. The terphenyl units of the oligomesogens of type **III** are connected *via* a branched hetero-aliphatic chain.

2. Synthesis

The monomeric *p*-terphenyl derivatives **1–7** were synthesized according to schemes 1 and 2 using Pd°-catalysed cross coupling reactions as the key steps [8]. Some of these syntheses have been described in previous papers [7, 9, 10].



7 R = -$C_{10}H_{21}$

Scheme 3 displays the synthesis of selected oligomesogens. The ethers **11–13**, **15**, **17**, **20** and **21** (see also the table and figure 2) were obtained by etherification reactions in the presence of potassium hydride. The esters **14**, **16** and **18** (see also figure 2) were synthesized by the reaction of the benzyl alcohols **6b** [7] or **7** [10] (see formula above) with trimesoyl trichloride or terephthaloyl dichloride in the presence of pyridine.

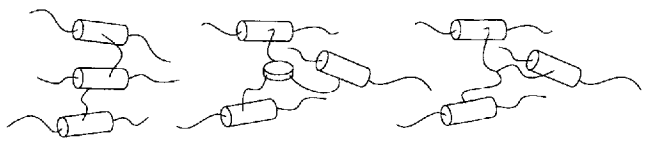


Figure 1. The different types of laterally attached oligomesogens.

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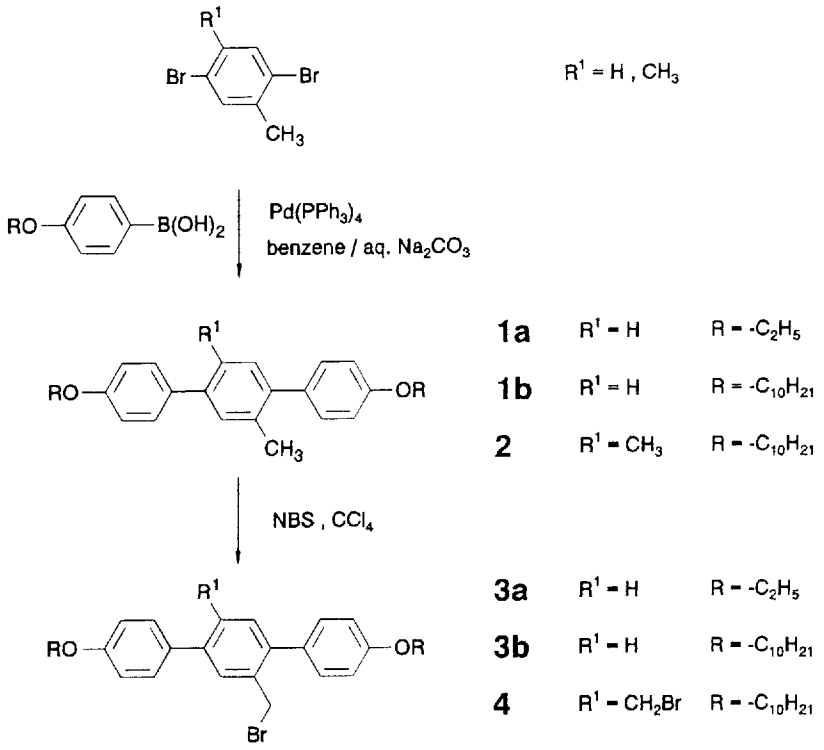
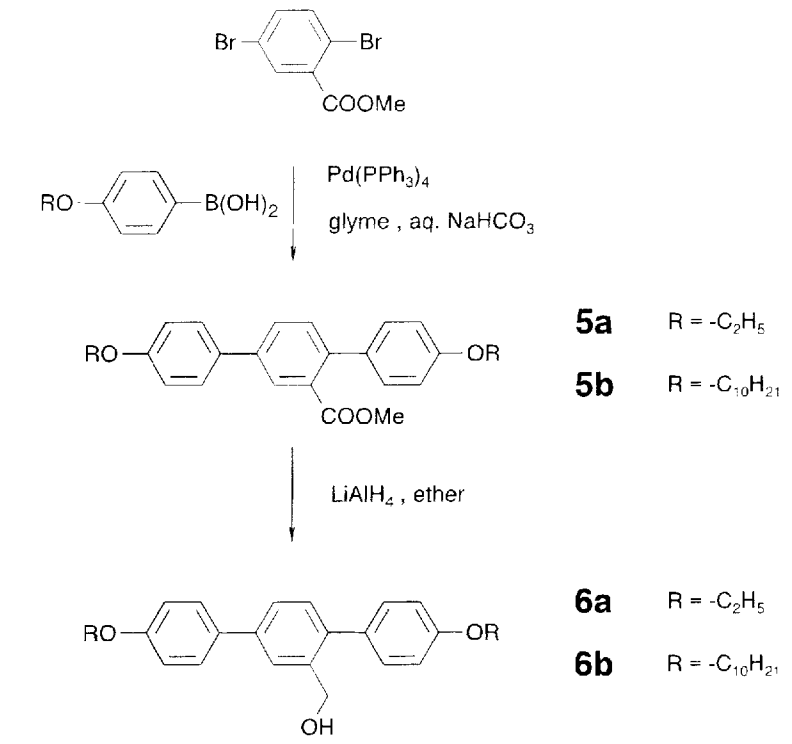


Scheme 1. Synthesis of the *p*-terphenyl derivatives **3** and **4**.

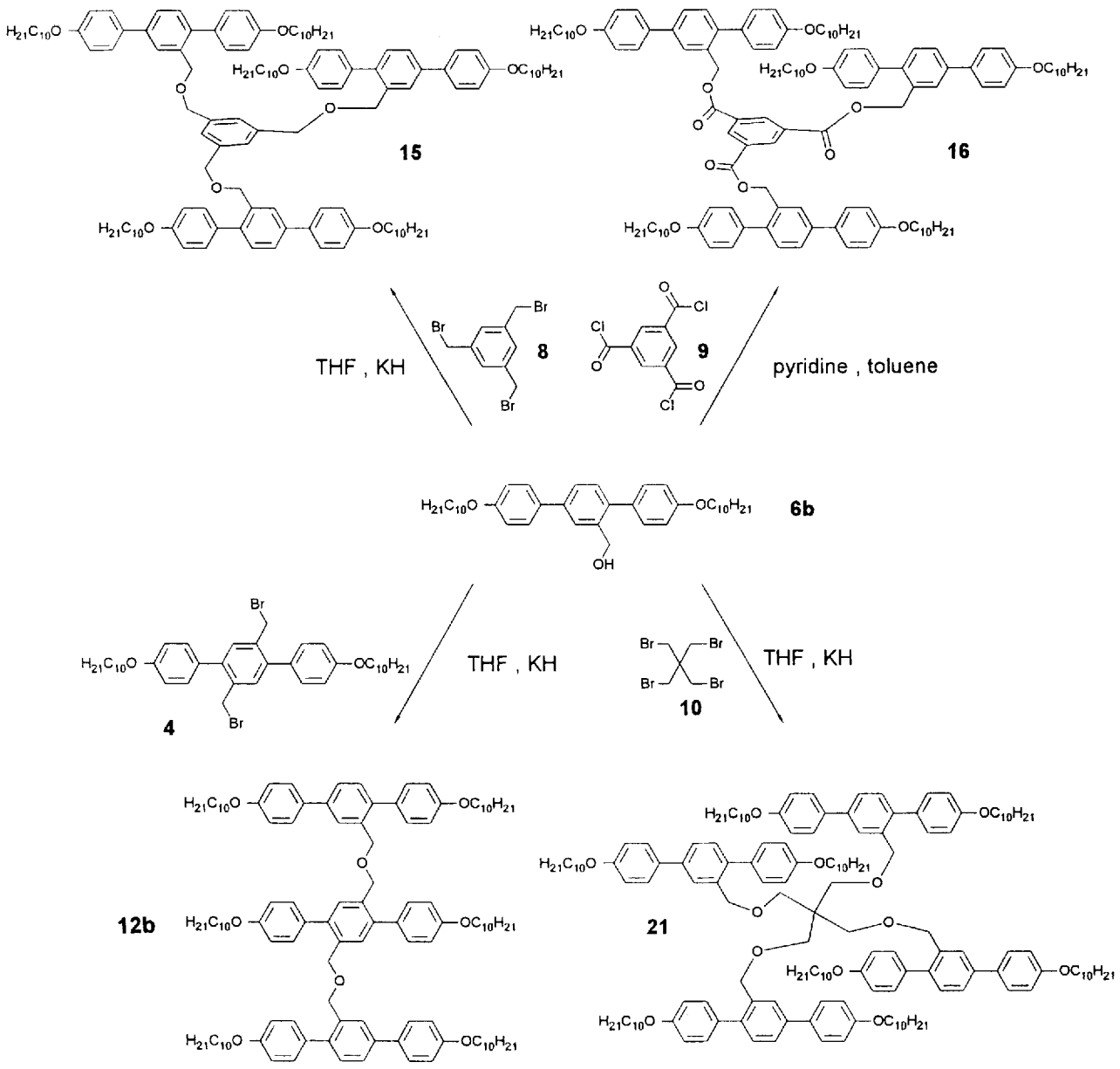


Scheme 2. Synthesis of the *p*-terphenyl derivatives **6**.

3. Experimental

3.1. *General considerations*

^{1}H NMR spectra were recorded on a VARIAN Gemini 200 or a VARIAN Unity 500 spectrometer with tetramethylsilane as internal standard. Mass spectra were recorded on an AMD 402 mass spectrometer (70 eV). Microanalyses were performed using a LECO CHNS-932 elemental analyser. Transition temperatures



Scheme 3. Synthesis of oligomesogens **12b**, **15**, **16** and **21**.

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). X-Ray studies were performed by means of a Guinier goniometer. Thin layer chromatography was performed using TLC aluminium sheets (silica gel 60 F254) from Merck and visualized by UV light. Silica gel 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.

The compounds **1b**, **3b**, **5b**, **6b** and **7** (see schemes 1 and 2 and formula) were synthesized according to recently reported procedures [7, 9, 10]. Mesitylene tribromide **8** [11], trimesoyl trichloride **9** [12] and tetrakis-bromomethylmethane **10** [13] were synthesized according to literature procedures. Terephthaloyl dichloride (Acros) and 1,1,1-trishydroxymethylpropane (Merck) were used as obtained.

3.2. *Synthesis of the terphenyl derivatives* **1a**, **2** *and* **5a** *(see schemes 1 and 2)*

In a two-necked flask equipped with a reflux condenser and a magnetic stirring bar, $Pd(PPh_3)_4$ (0·5 g,

0·5 mmol, 5 mol %) was added under an argon atmosphere to a mixture consisting of the appropriate bromobenzene derivative (10 mmol), the boronic acid (24 mmol), benzene (50 ml) and 2M Na_2CO_3 solution (50 ml). The mixture was stirred at reflux temperature for 4 h. After cooling, the solvent was evaporated and the residue dissolved in diethyl ether (100 ml) and water (100 ml). The organic phase was separated and the aqueous phase shaken twice with diethyl ether (100 ml). The combined organic phases were washed with brine (50 ml) and dried with Na_2SO_4. The solvent was removed *in vacuo* and the crude product obtained was purified by column chromatography (silica gel, chloroform).

3.2.1. *4,4″-Diethoxy-2′-methyl-p-terphenyl (* **1a** *)*

This was prepared from 2,5-dibromotoluene (2·5 g, 10 mmol) and 4-ethoxyphenyl boronic acid (3·7 g, 24 mmol). After chromatographic separation the product was crystallized from petroleum fraction (b.p. 60–80°C). Yield: 3·2 g (98 per cent); transitions (°C): Cr 142 N 179 I. ^{1}H NMR, δ ppm, $CDCl_3$: 1·43 (t, 3H, O–CH_2–CH_3), 1·44 (t, 3H, O–CH_2–CH_3), 2·32 (s, 3H, Ph–CH_3), 4·05, (t, 2H, Ph–O–CH_2–), 4·09 (t, 2H, Ph–O–CH_2–), 6·92 (m, 2H, H(3″,5″)ar), 6·96 (m, 2H, H(3,5)ar), 7·04 (m, 2H, H(2″,6″)ar), 7·14 (d, 1H, H(6′)ar), 7·22 (d, 1H, H(3′)ar), 7·40 (dd, 1H, H(5′)ar), 7·55 (m, 2H, H(2,6)ar).

3.2.2. *4,4″-Didecyloxy-2′,5′-dimethyl-p-terphenyl (* **2** *)*

This was prepared from 2,5-dibromo-*p*-xylene (2·6 g, 10 mmol) and 4-decyloxyphenyl boronic acid (6·7 g, 24 mmol). After chromatographic separation the product was crystallized from petroleum fraction (b.p. 60–80°C). Yield: 5·1 g (90 per cent); m.p. 76°C. ^{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–CH_2–), 2·26 (s, 6H, –CH_3), 3·95 (t, 4H, Ph–O–CH_2–), 6·92 (m, 2H, H(3″,5″)ar), 6·97 (m, 2H, H(3,5)ar), 7·04 (m, 2H, H(2″,6″)ar), 7·17 (d, 1H, H(6′)ar), 7·27 (d, 1H, H(3′)ar), 7·41 (dd, 1H, H(6′)ar), 7·53 (m, 2H, H(2,6)ar).

3.2.3. *Methyl 2,5-bis-(4-ethoxyphenyl)benzoate (* **5a** *)*

This was synthesized from methyl 2,5-dibromobenzoate (2·9 g, 10 mmol) and 4-ethoxyphenyl boronic acid (3·7 g, 24 mmol) using glyme (50 ml) as solvent and $NaHCO_3$ solution (50 ml, 2M) as base; the product was crystallized from ethanol. Yield: 3·1 g (83 per cent); transitions (°C): Cr 137 (N 93) I. ^{1}H NMR, δ ppm, $CDCl_3$: 1·45 (t, 6H, –CH_3), 3·69 (s, 3H, O–CH_3), 4·07 (t, 2H, Ph–O–CH_2–), 4·11 (t, 2H, Ph–O–CH_2–), 6·94 (m, 2H, H(3″,5″)ar), 6·99 (m, 2H, H(3,5)ar), 7·27 (m, 2H, H(2″,6″)ar), 7·41 (d, 1H, H(6′)ar), 7·46 (m, 2H, H(2,6)ar), 7·61 (dd, 1H, H(5′)ar), 7·97 (d, 1H, H(3′)ar).

3.3. *Syntheses of the benzyl bromides* **3a** *and* **4** *(see scheme 1)*

A solution of the appropriate 2,5-disubstituted toluene (15 mmol) and *N*-bromosuccinimide (3·2 g, 18 mmol for each methyl group) in dry tetrachloromethane (125 ml) was placed in a quartz flask and heated to boiling. Dibenzoyl peroxide (50 mg) was added and the refluxing 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 residues were purified by column chromatography (silica gel, chloroform/methanol 10:0·5) followed by crystallization from petroleum fraction.

3.3.1. *2′-Bromomethyl-4,4″-diethoxyterphenyl (* **3a** *)*

Yield: 5·2 g (85 per cent); m.p. 128°C. ^{1}H NMR, δ ppm, $CDCl_3$: 1·43 (t, 3H, O–CH_2–CH_3), 1·44 (t, 3H, O–CH_2–CH_3), 4·00 (t, 2H, Ph–O–CH_2–), 4·12 (t, 2H, Ph–O–CH_2–), 4·58 (s, 2H, –CH_2–Br), 6·96 (m, 2H, H(3″,5″)ar), 6·96 (m, 2H, H(3,5)ar), 7·04 (m, 2H, H(2″,6″)ar), 7·14 (d, 1H, H(6′)ar), 7·24 (d, 1H, H(3′)ar), 7·46 (dd, 1H, H(5′)ar), 7·63 (m, 2H, H(2,6)ar).

3.3.2. *2′,5′-Dibromomethyl-4,4″-didecyloxyterphenyl (* **4** *)*

Yield: 8·2 g (75 per cent); m.p. 91°C. ^{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–CH_2–), 3·98 (t, 4H, Ph–O–CH_2–), 4·51 (s, 4H, –CH_2–Br), 7·05 (d, 4H, H(3,3″)ar, H(5,5″)ar), 7·38 (s, 2H, H(2′,6′)ar), 7·42 (d, 4H, H(2,2″)ar, H(6,6″)ar).

3.4. *4,4″-Dietoxy-2′-hydroxymethylterphenyl (* **6a** *) (see scheme 2)*

In a three-necked 1 litre round bottomed flask equipped with mechanical stirrer, reflux condenser and dropping funnel, $LiAlH_4$ (0·57 g, 15 mmol) was suspended under an argon atmosphere in dry diethyl ether (300 ml). A suspension of methyl 2,5-bis-(4-ethoxyphenyl)benzoate (9·4 g, 25 mmol) in dry diethyl ether (150 ml) was carefully added dropwise with stirring without external cooling. The reaction mixture was heated under reflux for an additional 10 hours. 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 purified by column chromatography (silica gel, chloroform) and crystallized from petroleum fraction/ethyl acetate (1:3). Yield: 7·7 g (88 per cent); transitions (°C): Cr 159 (N 156) I. ^{1}H NMR, δ ppm, $CDCl_3$: 1·43 (t, 6H, O–CH_2–CH_3), 4·05 (t, 2H, Ph–O–CH_2–), 4·09 (t, 2H, Ph–O–CH_2–), 4·67 (d, 2H, –CH_2–OH), 6·94 (m, 2H, H(3″,5″)ar), 6·96 (m, 2H, H(3,5)ar), 7·31 (m, 2H, H(2″,6″)ar), 7·32 (d, 1H, H(6′)ar),

7·51 (dd, 1H, H(5′)ar), 7·56 (m, 2H, H(2,6)ar), 7·71 (d, 1H, H(3′)ar).

3.5. *General procedure for the synthesis of the ethers* **11a**, **12a**, **12b**, **15**, **17**, **20** *and* **21** *(see also the table, scheme 3, figures 3 and 4)*

In a two-necked flask fitted with an 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 (1·1 mmol for each OH-group of the alcohol) in dry THF (10 ml) and dry NBu_4I (40 mg, 0·1 mmol) were added. The reaction mixture was stirred for an additional 24 h at room temperature. Afterwards diethyl ether (20 ml) and water (20 ml) were carefully added, the organic phase was separated and the aqueous phase was shaken twice with diethyl ether (50 ml). The combined organic phases were dried with Na_2SO_4, the solvent was removed *in vacuo* and the residue purified by column chromatography, followed by crystallization.

3.5.1. *1-(4,4″-Didecyloxy-p-terphenyl-2′-yl)-3-(4,4″-diethoxy-p-terphenyl-2′-yl)-2-oxapropane (***11a***)*

This was synthesized from **3a** and **6b**. Eluent: chloroform/methanol (10:0·5). Crystallized from petroleum fraction. Yield: 78 per cent; transitions (°C): Cr 112 (S_C 75) S_A 165 N 172 I. Elemental analysis (per cent): found (calculated for $C_{62}H_{78}O_5$): C, 82·07 (82·44); H, 8·83 (8·70). ^{1}H NMR, δ ppm, $CDCl_3$: 0·87 (t, 6H, $-CH_3$), 1·28–1·55 (m, 28H, $-CH_2-$), 1·44 (t, 6H, $-CH_3$), 1·77–1·89 (m, 4H, $O-CH_2-CH_2-$), 3·92–4·12 (m, 8H, $Ph-O-CH_2-$), 4·49 (s, 4H, $Ph-CH_2-O-$), 6·89–7·75 (m, 22H, Har). MS *m/z* (relative intensity, per cent): 902 (90), 570 (28), 556 (100), 332 (94), 276 (30).

3.5.2. *2′,5′-Bis[3-(4,4″-diethoxy-p-terphenyl-2′-yl)-2-oxaprop-1-yl]-4,4″-didecyloxy-p-terphenyl (***12a***)*

This was synthesized from **4** and **6a**. Eluent: chloroform/methanol (10:0·5). Crystallized from petroleum fraction/ethyl acetate (5:1). Yield: 74 per cent; transitions (°C): Cr 162 (N 155) I. Elemental analysis (per cent): found (calculated for $C_{86}H_{102}O_8$): C, 81·50 (81·74); H, 8·11 (8·14). ^{1}H NMR, δ ppm, $CDCl_3$: 0·89 (t, 6H, $-CH_3$), 1·28–1·54 (m, 28H, $-CH_2-$), 1·42 (t, 6H, $-CH_3$), 1·44 (t, 6H, $-CH_3$), 1·74–1·84 (m, 4H, $O-CH_2-CH_2-$), 3·92–4·13 (m, 12H, $Ph-O-CH_2-$), 4·46 (s, 8H, $Ph-CH_2-O-$), 6·85–7·71 (m, 32H, Har).

3.5.3. *2′,5′-Bis[3-(4,4″-didecyloxy-p-terphenyl-2′-yl)-2-oxaprop-1-yl]-4,4″-didecyloxy-p-terphenyl (***12b***)*

This was synthesized from **4** and **6b**. Eluent: chloroform. Crystallized from petroleum fraction. Yield: 56 per cent; transitions (°C): Cr 117 S_A 162 I. Elemental analysis (per cent): found (calculated for $C_{118}H_{166}O_8$): C, 82·99 (82·75); H, 9·63 (9·78). ^{1}H NMR, δ ppm, $CDCl_3$: 0·88 (t, 18H, $-CH_3$), 1·22–1·38 (m, 72H, $-CH_2-$), 1·42–1·50 (m, 12H, $O-CH_2-CH_2-CH_2-$), 1·74–1·82 (m, 12H, $O-CH_2-CH_2-$), 3·92–4·00 (m, 12H, $Ph-O-CH_2-$), 4·44 (s, 4H, $Ph-CH_2-O-$), 4·46 (s, 4H, $Ph-CH_2-O-$), 6·85–7·68 (m, 32H, Har).

3.5.4. *1,3,5-Tris[3-(4,4″-didecyloxy-p-terphenyl-2′-yl)-2-oxaprop-1-yl]benzene (***15***)*

This was synthesized from α,α′,α″-trisbromomesitylene (**8**) and **6b**. Eluent: chloroform/methanol (10:0·5). Crystallized from petroleum fraction. Yield: 60 per cent; transitions (°C): Cr 73 (g 8) S_A 124 I. Elemental analysis (per cent): found (calculated for $C_{126}H_{174}O_9$): C, 82·24 (82·57); H, 9·21 (9·57). ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, 18H, $-CH_3$), 1·18–1·53 (m, 84H, $-CH_2-$), 1·68–1·79 (m, 12H, $O-CH_2-CH_2-$), 3·88 (t, 6H, $Ph-O-CH_2-$), 3·91 (t, 6H, $Ph-O-CH_2-$), 4·46 (s, 12H, $Ph-CH_2-O-$), 6·82–7·68 (m, 36H, Har).

3.5.5. *1,3,5-Tris[3-(4,4″-didecyloxy-p-terphenyl-3-yl)-2-oxaprop-1-yl]benzene (***17***)*

This was synthesized from α,α′,α″-trisbromomesitylene (**8**) and **7**. Eluent: chloroform. Crystallized from petroleum fraction. Yield: 85 per cent; transitions (°C): Cr 80 (S_C 67) S_A 156 I. Elemental analysis (per cent): found (calculated for $C_{126}H_{174}O_9$): C, 82·30 (82·57); H, 9·48 (9·57). ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, 9H, $-CH_3$), 0·89 (t, 9H, $-CH_3$), 1·25–1·53 (m, 84H, $-CH_2-$), 1·68–1·82 (m, 12H, $O-CH_2-CH_2-$), 3·96 (t, 6H, $Ph-O-CH_2-$), 3·97 (t, 6H, $Ph-O-CH_2-$), 4·66 (s, 6H, $Ph-CH_2-O-$), 4·68 (s, 6H, $Ph-CH_2-O-$), 6·91–7·60 (m, 36H, Har).

3.5.6. *1,1,1-Tris[3-(4,4″-didecyloxy-p-terphenyl-2′-yl)-2-oxaprop-1-yl]propane (***20***)*

This was synthesized from 1,1,1-trishydroxymethylpropane and **3b**. Eluent: chloroform/methanol (10:0·5). Crystallized from petroleum fraction. Yield: 77 per cent; m.p. 156°C. Elemental analysis (per cent): found (calculated for $C_{123}H_{176}O_9$): C, 81·82 (82·12); H, 9·58 (9·87). ^{1}H NMR, δ ppm, $CDCl_3$: 0·87 (t, 21H, $-CH_3$), 1·27–1·54 (m, 86H, $-CH_2-$), 1·74–1·84 (m, 12H, $O-CH_2-CH_2-$), 3·41 (s, 6H, $Ph-CH_2-O-CH_2-$), 3·80–4·00 (m, 12H, $Ph-O-CH_2-$), 4·37 (s, 6H, $Ph-CH_2-O-$), 6·79–7·66 (m, 33H, Har).

3.5.7. *Tetrakis[3-(4,4″-didecyloxy-p-terphenyl-2′-yl)-2-oxaprop-1-yl]methane (**21**)*

This was synthesized from terakisbromomethylmethane (**10**) and **6b**. Eluent: chloroform. Crystallized from hexane. Yield: 6 per cent; m.p. 80°C. Elemental analysis (per cent): found (calculated for $C_{161}H_{228}O_{12}$): C, 82·11 (82·09); H, 9·87 (9·76). ^{1}H NMR, δ ppm, $CDCl_3$: 0·87 (t, 24H, $-CH_3$), 1·24–1·40 (m, 96H, $-CH_2-$), 1·42–1·50 (m, 16H, O–CH_2–CH_2–CH_2–), 1·76–1·83 (m, 16H, O–CH_2–CH_2–), 3·21 (s, 8H, Ph–CH_2–O–CH_2–), 3·99 (t, 16H, Ph–O–CH_2–), 4·42 (s, 8H, Ph–CH_2–O–), 6·92–7·71 (m, 44H, Har).

3.6. *Synthesis of the esters* **14**, **16** *and* **18** *(see also figure 2)*

The carboxylic acid chloride (1 mmol) was dissolved in dry toluene (10 ml). The appropriate hydroxymethyl-*p*-terphenyl derivative **6b** or **7** (1·1 equivalent per carboxylic acid chloride group) was dissolved in a mixture of dry toluene (20 ml) and dry pyridine (0·3 ml). The mixture was slowly added *via* a syringe. Afterwards the reaction mixture was stirred for 4 h at reflux temperature. After cooling to room temperature the solution was washed twice with HCl (10 ml, 10 per cent) and the solvent was removed from the organic phase *in vacuo*. The white residue was crystallized from hexane/ethyl acetate (5:1).

3.6.1. *1,4-Bis[3-(4,4″-didecyloxyterphenyl-2′-yl)-1-oxy-2-oxaprop-1-yl]benzene (**14**)*

This was synthesized from terephthaloyl dichloride and **6b**. Yield: 94 per cent; transitions (°C): Cr 132 (S_A 94) I. Elemental analysis (per cent): found (calculated for $C_{86}H_{114}O_8$): C, 80·63 (80·96); H, 9·06 (9·01). ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, 12H, $-CH_3$), 1·25–1·54 (m, 56H, $-CH_2-$), 1·73–1·80 (m, 8H, O–CH_2–CH_2–), 3·95 (t, 4H, Ph–O–CH_2–), 3·97 (t, 4H, Ph–O–CH_2–), 5·34 (s, 4H, Ph–CH_2–O–), 6·89–7·73 (m, 22H, Har), 8·05 (s, 4H, Har). MS *m/z* (relative intensity, per cent): 1275 (18), 720 (60), 676 (48), 570 (43), 556 (100), 276 (25).

3.6.2. *1,3,5-Tris[3-(4,4″-didecyloxy-p-terphenyl-2′-yl)-1-oxy-2-oxaprop-1-yl]benzene (**16**)*

This was synthesized from trimesoyl trichloride (**9**) and **6b**. Yield: 75 per cent; m.p. 121°C. Elemental analysis (per cent): found (calculated for $C_{126}H_{168}O_{12}$): C, 80·72 (80·73); H, 9·17 (9·03). ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, 18H, $-CH_3$), 1·26–1·53 (m, 84H, $-CH_2-$), 1·68–1·81 (m, 12H, O–CH_2–CH_2–), 3·86 (t, 6H, Ph–O–CH_2–), 3·94 (t, 6H, Ph–O–CH_2–), 5·36 (s, 6H, Ph–CH_2–O–), 6·81–7·70 (m, 33H, Har), 8·76 (s, 3H, Har).

3.6.3. *1,3,5-Tris[3-(4,4″-didecyloxy-p-terphenyl-3-yl)-1-oxy-2-oxaprop-1-yl]benzene (**18**)*

This was synthesized from trimesoyl trichloride (**9**) and **7**. Yield: 38 per cent; transitions (°C): Cr 135 S_A 161 I. Elemental analysis (per cent): found (calculated for $C_{126}H_{168}O_{12}$): C, 80·40 (80·73); H, 9·06 (9·03). ^{1}H NMR, δ ppm, $CDCl_3$: 0·82 (t, 9H, $-CH_3$), 0·86 (t, 9H, $-CH_3$), 1·17–1·53 (m, 84H, $-CH_2-$), 1·66–1·82 (m, 12H, O–CH_2–CH_2–), 3·93 (t, 6H, Ph–O–CH_2–), 3·96 (t, 6H, Ph–O–CH_2–), 5·48 (s, 6H, Ph–CH_2–O–), 6·87–7·62 (m, 33H, Har), 8·91 (s, 3H, Har).

4. Results and discussion

The transition temperatures of the synthesized compounds are collected in the table and in figures 2 and 4. For comparison the corresponding 4,4″-dialkoxy-2′-methyl-*p*-terphenyls **1a** and **1b** [7, 14] and some twins (compounds **11a**, **11b** [9], **13** [9], **14** and **19** [9]) are also included.

4.1. *Type **I** triplets*

From a comparison of the triplets **12a** and **12b** with the corresponding methyl substituted *p*-terphenyls **1a** and **1b**, it is obvious that the lateral covalent connection of three *p*-terphenyl units in line with each other (type **I**) leads to a considerable increase of the mesophase stability. However, if one compares **12a** and **12b** with the related twins **11**, a certain mesophase destabilization is observed.

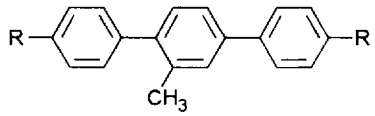
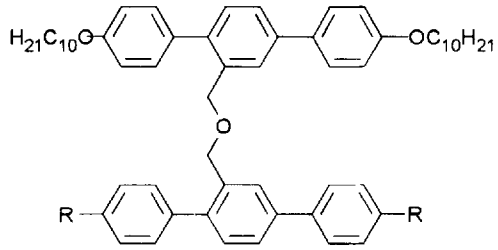
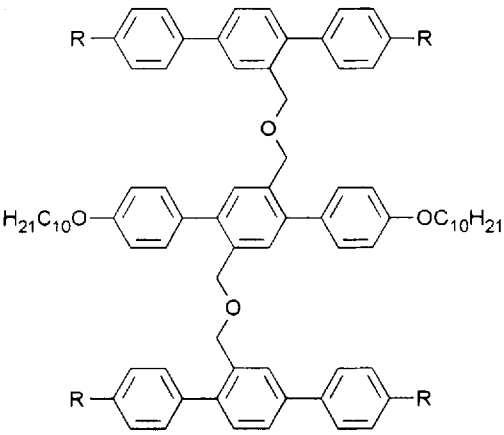
As found during the investigation of mesogenic twins [9, 10] an ambivalent influence of the lateral connecting unit has to be considered. On the one hand, the steric requirements tend to separate the rigid cores from each other, which gives rise to mesophase destabilization. On the other hand, the covalent fixing of the individual molecules stabilizes smectic liquid crystalline phases. Obviously the lateral connection of only two terphenyl units allows a better molecular packing than the in-line connection of three of them.

If one compares the mesomorphic properties of the twins **11a** and **11b** with those of 4,4″-didecyloxy-2′-methyl-*p*-terphenyl **1b**, a certain stabilization of the layered smectic A phase with respect to the nematic phase is found. Only, the trimesogen **12a** with a central 4,4″-didecyloxy-*p*-terphenyl unit and two peripherally attached 4,4″-diethoxy-*p*-terphenyl units exhibits exclusively the nematic mesophase. It seems that the oligomesogens behave like mixtures of individual mesogens. Increasing the ratio of short chain derivatives to long chain derivatives increases the tendency to form the nematic phase.

4.2. *Type **II** triplets*

Another type of triplet mesogen is represented by compounds **15** and **16** (figure 2). Here the calamitic units

Phase transition temperatures (°C) of the 2′-methyl substituted 4,4″-dialkoxy-*p*-terphenyl derivatives **1a** and **1b** [7,14], the twins **11a** and **11b** [9] and the triplets **12a** and **12b** [7]. Determined by microscopy using crossed polarizers. Cr = crystalline, S_C = smectic C phase, S_A = smectic A phase, N = nematic phase, I = isotropic phase.

	Compound	Cr	S_C	S_A	N	I
	**1a** R = $-OC_2H_5$	• 142	— —	— —	• 179	•
	1b R = $-OC_{10}H_{21}$	• 72	(• 70)	• 104	• 109	•
	**11a** R = $-OC_2H_5$	• 112	(• 75)	• 165	• 172	•
	11b R = $-OC_{10}H_{21}$	• 99	• 128	• 168	— —	•
	**12a** R = $-OC_2H_5$	• 162	— —	— —	(• 155)	•
	12b R = $-OC_{10}H_{21}$	• 117	— —	• 162	— —	•

are connected via an aromatic linking unit. Their mesophase stability is considerably lower than that of the type **I** triplets.

Nevertheless, one of them (compound **15**) forms a mesophase with a clearing temperature significantly above that of 4,4″-didecyloxy-2′-methyl-*p*-terphenyl **1b**. The S_A phase of this compound can be supercooled to room temperature without crystallization.

The triplet **15** has a higher clearing temperature than the respective twin **13**, which is in contrast to the behaviour of the triplets of type **I**. Due to poor supercooling of **16** (down to 107°C), no mesophase could be observed for this compound incorporating ester groups instead of ether linkages.

In a previous paper [10] we have shown, that the connecting position at the rigid *p*-terphenyl core has a great influence on the mesomorphic behaviour. Shifting the lateral linking unit from the central to a more peripheral position increases the mesophase stability and can give rise to the formation of smectic C phases. The same is true for the trimesogens. The peripherally connected triplets **17** and **18** exhibit enantiotropic mesophases with clearing temperatures approximately 40 K above that of the S_A phase of the centrally connected triplet **15**. Furthermore, a smectic C phase was found below the S_A-phase of compound **17**.

4.3. *Oligomesogens of type III*

In order to obtain quadruplet mesogens we synthesized the pentaerythritol derivative **21** (figure 4). Unfortunately this compound and also the triplet **20** are only crystalline solids. No monotropic mesophases could

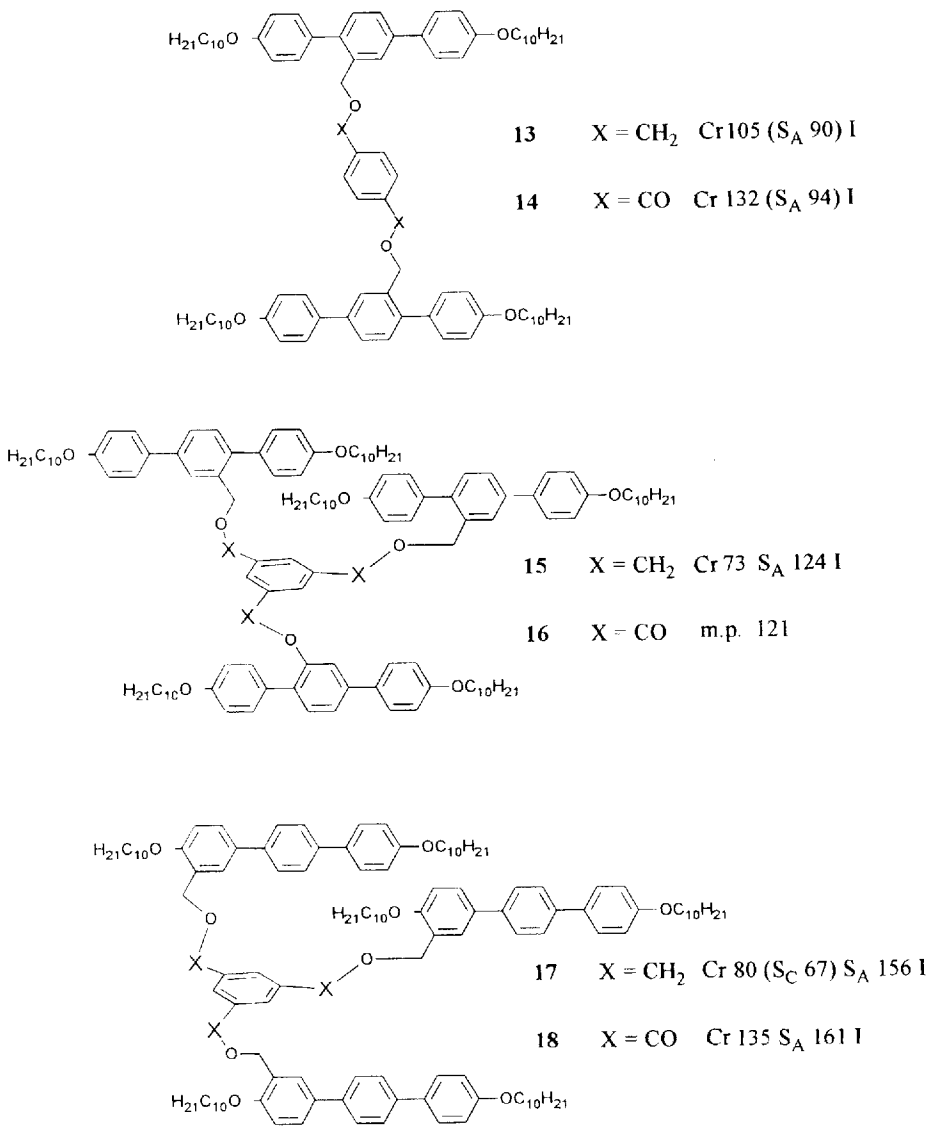


Figure 2. Phase transition temperatures (°C) of the twins **13** [9] and **14** and the triplets **15** [7], **16**, **17** and **18** incorporating aromatic central units. Determined by microscopy using crossed polarizers. Cr = crystalline, S_A = smectic A phase, S_C = smectic C phase, I = isotropic phase.

be detected by supercooling the quadruplet **21** to 35°C. The triplet **20** can be supercooled down to 140°C. Unlike these two compounds, the twin **19** [13] gives a monotropic liquid crystal phase. It seems that connecting the individual mesogenic units via aliphatic groups is less effective than their connection *via* the more polar aromatic units. The reason for the absence of liquid crystalline phases in these compounds is not yet clear.

4.4. *X-ray studies*

The mesomorphic properties of these new compounds were investigated by polarizing microscopy and calorimetry. The compounds **12b**, **15** and **17** were additionally investigated by X-ray diffraction. Their layer thicknesses (compound **12b**: $d = 3{\cdot}60$ nm at 60°C; compound **15**: $d = 3{\cdot}44$ nm at 60°C; compound **17**: $d = 3{\cdot}54$ nm at 107°C) are of the same order of magnitude as that of 4,4″-didecyloxy-2′-methyl-*p*-terphenyl **1b** ($d = 3{\cdot}63$ nm at 89°C) which may be considered as a single calamitic unit of the trimesogens **12b**, **15** and **17**.

Using CPK models and assuming an all *trans*-conformation of the alkyl chains, the molecular length of compound **1b** was found to be 4·1 nm.

The thickness of the smectic layers of compounds **12b**, **15** and **17** is therefore smaller than the length of their single calamitic units. This is in agreement with our

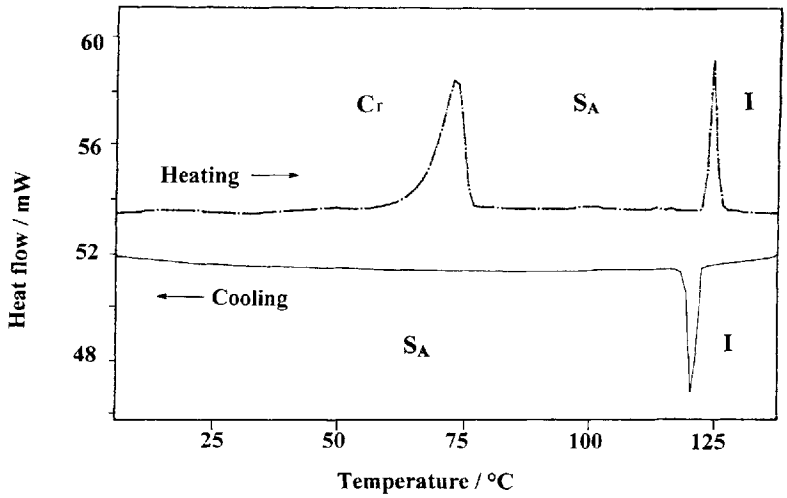


Figure 3. DSC heating (first heating) and cooling (first cooling) traces of compound **15** (10 K min^{-1}).

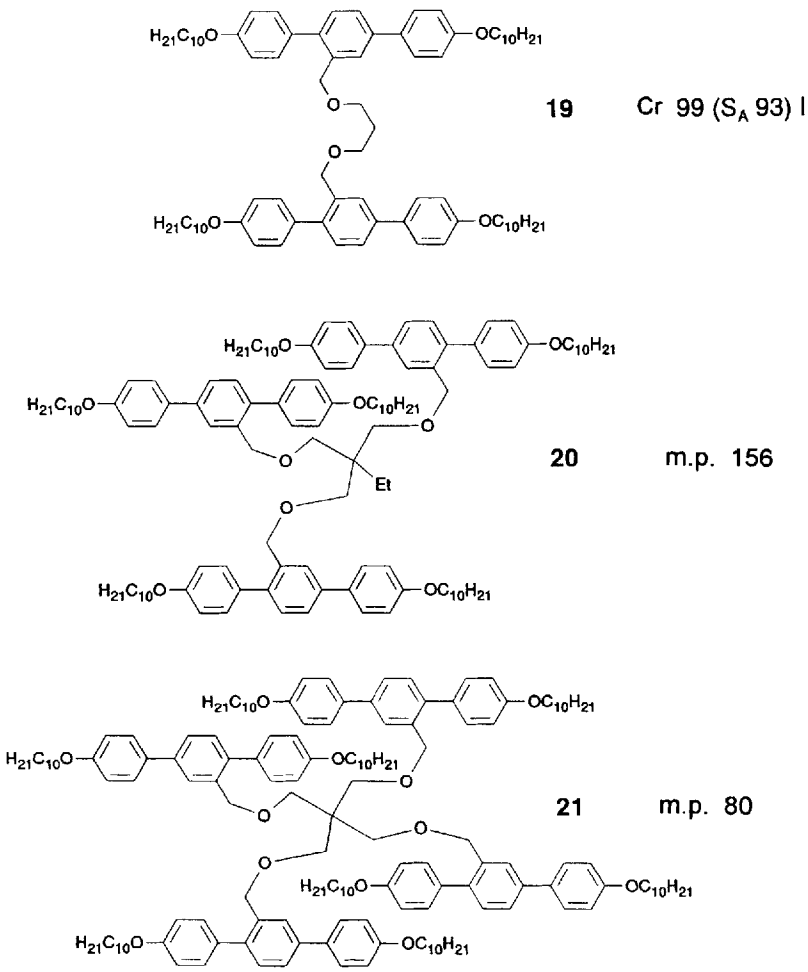


Figure 4. Phase transition temperatures of the oligomesogens **19** [9], **20** and **21** incorporating hetero-aliphatic connecting units.

model in which the single calamitic units of the trimesogens are arranged parallel to the layer normal in the S_A phase. The difference between the layer thickness and the estimated molecular length can be explained by a high number of *gauche*-linkages in the chains. The bulky central part of the trimers leads to a free volume in the chain region, which is compensated by the fluidity of the chains. Increasing the bulkiness of the central parts (compare **12b** and **15**) gives rise to a larger free volume and consequently to a decreased layer thickness. Furthermore, it seems that shifting the connecting unit from the central to a more peripheral position (compare for example compounds **15** and **17**) not only increases the mesophase stability, but also increases the layer thickness, which means that the mesophase disturbing influence is less pronounced for the peripherally connected triplets. Thus the mesophase disturbing influence of lateral substituents depends on their position on the rigid core; those in peripheral positions have the more pronounced stabilizing influence. The reason may be that the spacer units in a central position are forced to be located between the rigid terphenyl cores, whereas those in a peripheral position can be more easily expelled into the region of the flexible terminal chains.

5. Summary

Three types of laterally connected triplet mesogens incorporating rigid *p*-terphenyl units have been synthesized and investigated. The highest clearing temperatures were observed for the triplets of type **I** and the peripherally connected type **II** triplets **17** and **18**. Only the oligomesogens of type **III** are not liquid crystalline. All the compounds with decyloxy chains exhibit exclusively smectic phases. For the ethoxy derivatives the nematic phase was found.

The oligomesogens of types **II** and **III** may be considered as model compounds for mesogenic polymers with rigid cores laterally attached to a polymeric backbone (type **A**) [15, 16]. The triplets **12** (type **I**) can be looked upon as low molecular weight analogues of main chain polymers with perpendicularly connected rigid cores (type **B**) [17].

Though these oligomers differ from existing polymers in the type of mesogenic units and in the structures of the linking units, they have some structural features resembling those of the polymers of types **A** and **B**, respectively.

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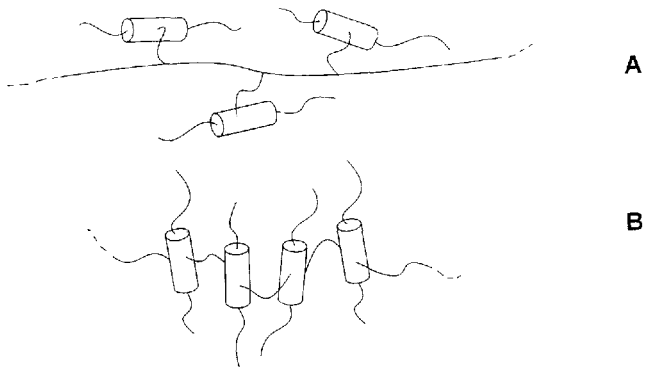

Figure 5. Structural types of laterally connected liquid crystalline polymers.

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