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Trimeric and tetrameric liquid crystalline thiadiazole derivatives

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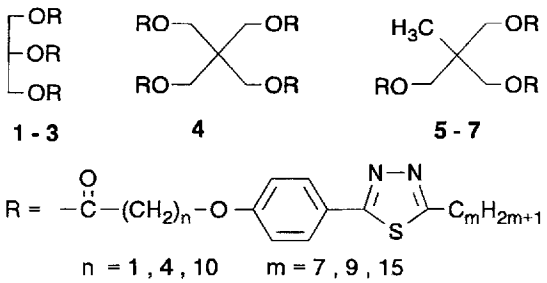
Novel liquid crystalline 2-phenyl-1,3,4-thiadiazole based oligomers with three and four rigid aromatic units linked by a flexible central unit have been investigated by polarizing microscopy. The synthesis of these compounds and the influence of structural variations on the mesomorphic properties are described. The combination of suitable mesogenic moieties with appropriate central units leads to oligomers which exhibit S_C phases.

1. Introduction

Surprisingly, oligomeric liquid crystals which could possibly bridge the gap between low molecular weight and polymeric liquid crystals have attracted only scant attention until recently. One of the interesting properties of many polymers is their ability to form stable glassy states, making them promising materials for reversible data storage. However, the properties of polymers depend strongly on the degree of polymerization, which often causes unsatisfactory reproducibility. This drawback could be circumvented by oligomers with a well-defined molecular structure. The first examples of such compounds were the cyclic phosphatenes, and the tetrameric liquid crystals based on biphenyl, bicyclohexyl, and phenylcyclohexyl mesogenic groups linked to a pentaerythrityl central unit [1]. More recently oligomeric 4-cyanobiphenyl derivatives have been reported to exhibit a nematic phase with a glass transition [2].

We have synthesized various oligomeric compounds by combining the 2-phenyl-1,3,4-thiadiazole system as the rigid core with central linking units such as glycerol, pentaerythritol and 1,1,1-tris-(hydroxymethyl)ethane—see the structures below. We chose the thiadiazole unit because it is one of the most powerful molecular tools for the induction of the S_C phase.



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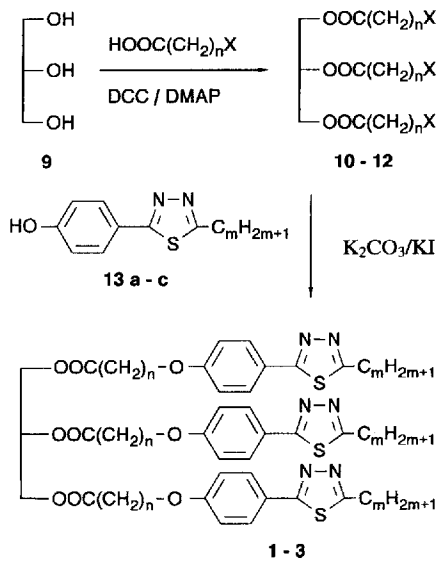
2. Synthesis

We started our investigations with the synthesis of various oligomeric liquid crystals, using glycerol as starting material according to scheme 1. Esterification of glycerol with 5-bromopentanoic acid, 11-bromo-undecanoic acid and chloracetic acid, respectively, in the presence of DCC and catalytic amounts of DMAP [3] gave the tris-(ω-bromoalkanoyl)glycerides **10–12**. The synthesis of the oligomers **1–3** was achieved by etherification of **10–12** with the respective 4-(5-alkyl-1,3,4-thiadiazol-2-yl)phenols **13a–13c** [4] in acetone or diethyl ketone with anhydrous potassium carbonate as base [5].

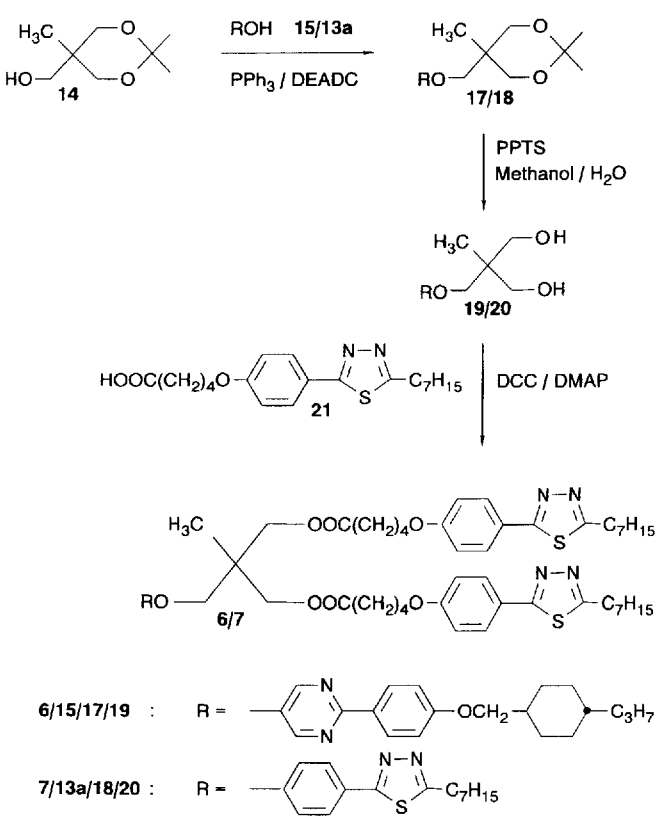
In the next stage of our investigations we were interested in oligomers containing four identical thiadiazole units. Therefore, the tetrameric compound **4** was



Compound	n	x
10	10	Br
11	4	Br
12	1	Cl

Compound	n	m
1a	4	7
1b	4	9
1c	4	15
2	1	9
3	10	9

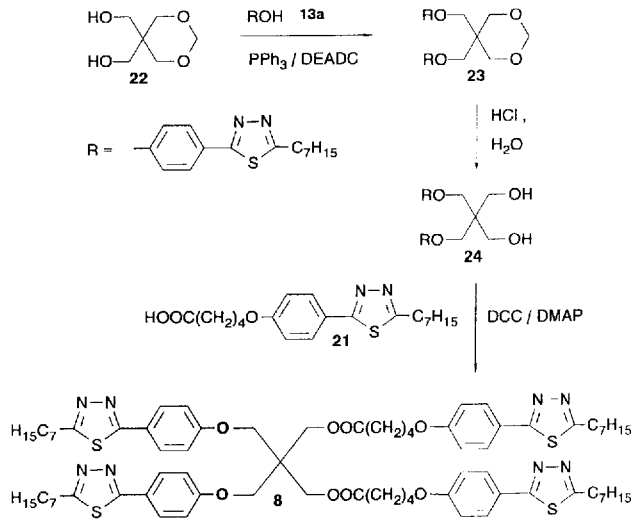
Scheme 1. Synthesis of the triglycerides **1–3**.



Scheme 2. Synthesis of the 1,1,1-tris-(hydroxymethyl)ethane triesters **6** and **7**.

synthesized using a reaction sequence similar to that in scheme 1, but using pentaerythritol as starting material. Furthermore we wanted to learn how the replacement of one thiadiazole unit by a methyl substituent at the central unit affected the liquid crystalline properties. The trimeric compound **5** was obtained by esterification of 1,1,1-tris-(hydroxymethyl)ethane with 4-[4-(heptyl-1,3,4-thiadiazol-2-yl)phenoxy]butanoic acid **21**. The synthesis of the trimeric compounds **6** and **7** is given in scheme 2. A Mitsunobu etherification [6] of 5-hydroxymethyl-5-methyl-1,3-dioxan **14** [7, 8] with an appropriate phenol (**15** or **13a**), subsequent deprotection with aqueous acid and esterification of the resulting alcohol (**19** or **20**) with 4-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenyloxy]-butanoic acid **21**, applying the DCC/DMAP method, constitute the key steps of this reaction pathway.

As an example of a tetrameric compound with four mesogenic groups linked by two sets of differently lengthed spacers to the central unit, we have synthesized compound **8**. The synthesis (scheme 3) was achieved starting from 5,5-bis-(hydroxymethyl)-1,3-dioxan **22**, which was etherified with two equivalents of 4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenol **13a** according to the Mitsunobu procedure [6], followed by aqueous acidic



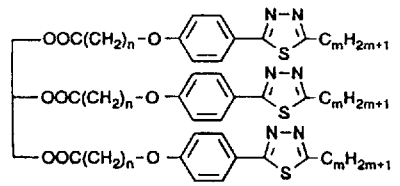
Scheme 3. Synthesis of the neopentane derivative **8**.

cleavage of the dioxan ring [9]. In the final step the 1,3-diol **24** was esterified with the carboxylic acid **21**, applying the same procedure as that described for **6** and **7**.

3. Discussion of transition temperatures

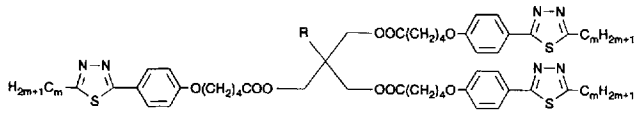
The transition temperatures of the compounds synthesized are given in tables 1–3. The phase transitions were determined by polarizing microscopy, in combination with DSC measurements. According to textural investigations, in most cases smectic C phases are formed on cooling the isotropic liquids. The glycerol derivatives **1–3**, differing in various structural features, are listed in table 1. The trimers **1b**, **2** and **3** differ only in the lengths of their spacers. The number of methylene groups in these spacers has a strong influence on the liquid crystalline behaviour. Formation of a smectic C phase was found in the case of the thiadiazole derivative **1b** possessing alkylene spacers of medium length. Preliminary X-ray

Table 1. Transition temperatures for the triglycerides **1–3**.



Compound	*n*	*m*	C	S_X	S_Y	S_C	I
1a	4	7	• 83	—	—	• 98	•
1b	4	9	• 88	—	—	• 113	•
1c	4	15	• 95	—	—	• 130	•
2	1	9	• 260	• 270	• —	300	•
3	10	9	• 103	—	—	—	•

Table 2. Transition temperatures (°C) of tetramer **4** and trimer **5**.



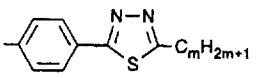
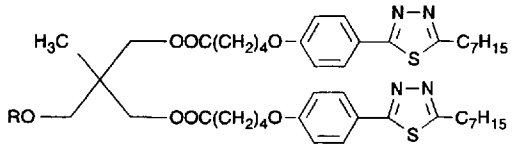
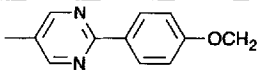
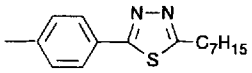
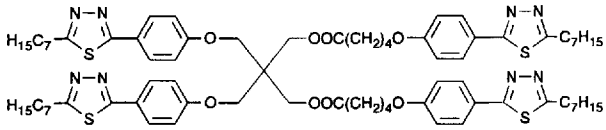
Compound	m	*R*	Transition temperatures
4	9	$-CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-O-$ 	C 122 (S_C 118) I
5	7	$-CH_3$	M.p. 87

Table 3. Transition temperatures (°C) of **6**, **7** and **8**.



Compound	*R*	Transition temperatures
6		C 130 (S_C 111) I
7		M.p. 137



8

M.p. 158°C

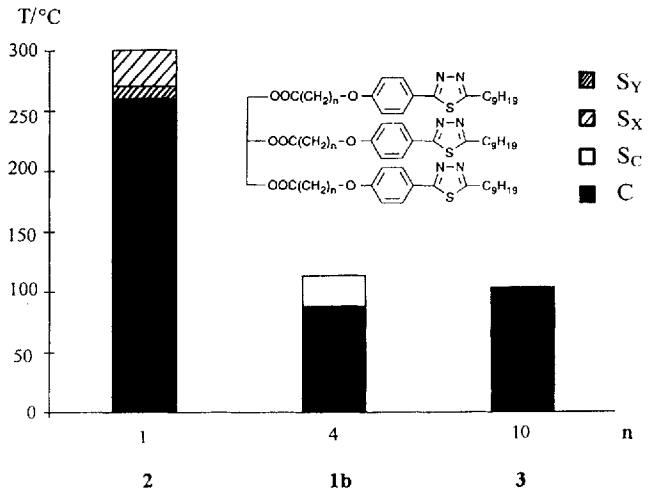
studies suggest that increasing the spacer length (compound **3**) leads to the formation of a highly ordered, probably crystalline phase. Compound **2** with only an acetoxy group between the central unit and the rigid core exhibits two liquid crystalline phases (S_x and S_y) with very high transition temperatures. Because of the commencement of decomposition, the determination of the phase types was impossible.

From this it may be concluded that alkylene spacers of medium length ($n = 4$) are most suitable for the formation of a smectic C phase in such materials.

Comparison of the thiadiazole derivatives **1a**, **1b** and **1c** reveals the influence of the lengths of the alkyl side chains on the thermal stability of their smectic C phases. The melting and clearing temperatures and the mesomorphic ranges increase with increasing length of the side chain.

The results from the investigation of the homotrimeric glycerol derivatives **1–3** show that variation of the number of methylene groups has a much stronger impact on the liquid crystalline behaviour when this occurs in the spacer region, rather than in the side chains, presumably because the number of methylene groups in the spacer strongly influences the molecular flexibility of these trimeric compounds.

Simultaneously with our studies of homosubstituted glycerol derivatives, we have investigated the influence of the structure of the linking unit on the mesomorphic properties. Our special interest was focused on the structure/property relationships of derivatives of pentaerythritol (compound **4**) and 1,1,1-tris-(hydroxymethyl)-ethane (compound **5**). First the glycerol derivative **1b** will be compared with the tetramer **4** and the trimer **5**. The compounds consist of identical rigid cores but have different central units. Only compound **1b** containing three phenylthiadiazole units, combined via a glycerol derived central unit, exhibits an enantiotropic smectic C phase. The introduction of a fourth phenylthiadiazole unit (compound **4**) causes a significant increase of the melting temperature, leading to a monotropic smectic C phase.



Comparison of the phase transition temperatures (°C) of the glycerol derivatives **1 b**, **2** and **3**, which differ only in the lengths of the spacer units (S_X and S_Y are unidentified liquid crystalline phases).

Finally, the introduction of a non-mesogenic substituent, for example, a methyl group, into the central unit (compound **5**) disturbs the molecular packing so strongly that mesomorphic properties are lost.

Compound **7** in which only one of the thiadiazole units is directly linked to the central unit shows no mesomorphic properties, not even upon supercooling of the isotropic liquid, which is possible down to 95°C. However, if one of the mesogenic units of **7** is replaced by a larger rigid core the liquid crystalline behaviour can be restored (compound **6**). Linking two of four identical calamatic thiadiazole mesogenic groups directly to a pentaerythritol derived central unit (scheme 3) leads to compound **8**, which is structurally related to the tetrasubstituted neopentane derivative **4**. Compound **8** has a melting point of 158°C and the isotropic liquid may be supercooled down to 100°C. Liquid crystalline phases could not however be detected in this temperature range. Obviously, this structural variation does not provide access to low melting materials. However, our investigations have shown that the mesomorphic behaviour of such oligomers is affected by the kind of central unit, the lengths of the side chains and mainly by the lengths of the spacers between the central unit and the rigid cores. We have demonstrated, that it is possible to make defined oligomers which exhibit smectic C phases (compounds **1 a–1 c**, **4** and **6**). Unfortunately, supercooling of these materials did not lead to glassy smectic phases.

4. Experimental

4.1. *General considerations*

The proton NMR spectra were obtained on a Bruker WP-200 or an AC-80 spectrometer with tetramethylsilane as internal standard and deuteriochloroform as solvent. Infrared spectra were recorded using a Specord 71 IR spectrometer. Mass spectra were recorded on an AMD 402 Intectra (70 eV) mass spectrometer. Transition temperatures were measured using a Mettler FP 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).

Thin-layer chromatography was performed on aluminium TLC plates (silica gel 60 F_{254}) from Merck and the spots were visualized with UV light or by spraying with a solution of bromothymol blue and developing the plates in an NH_3 atmosphere. Silicagel 60 (0·063–0·200) from Merck was used for column chromatography. Solvents were purified and dried according to standard procedures [10]. In the following account, for each synthetic route, one representative example is given.

4.2. *Synthesis of 1,2,3-tris-{11-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]undecanoyloxy}propane* (**3**)

4.2.1. *1,2,3-Tris-(11-bromo-undecanoyloxy)propane* (**10**)

A solution of *N,N'*-dicyclohexylcarbodiimide (3·39 g, 16·5 mmol) in anhydrous chloroform (25 ml) was added dropwise to a stirred, cooled (5°C) solution of glycerol (0·46 g, 5 mmol), 11-bromo-undecanoic acid (4·37 g, 16·5 mmol) and 4-*N,N*-dimethylaminopyridine (0·2 g, 1·65 mmol) in chloroform (25 ml). The mixture was stirred at room temperature for 72 h. The precipitate was filtered with suction (through a 2–3 cm thick layer of silica gel) and washed with chloroform. The solutions were combined and the solvent was removed *in vacuo* to give the crude product which was purified by column chromatography using petroleum ether/ethyl acetate (10:4) as eluent. Yield: 3·0 g (74 per cent). Elemental analysis. Found (calculated for $C_{36}H_{65}O_6Br_3$): C 52·07 (51·87), H 7·79 (7·86), Br 28·58 (28·76) per cent. IR, ν cm^{-1}, $CHCl_3$: 2920, 1740 (C=O), 1460, 1350. ^{1}H NMR, δ ppm, $CDCl_3$: 1·26–1·43 (m, 36 H, $-CH_2-$), 1·55–1·62 (m, 6 H, $-CH_2-$), 1·75–1·89 (m, 6 H, $-CH_2-$), 2·29 (t, 6 H, OOC–CH_2-), 3·38 (t, 6 H, $-CH_2$–Br), 4·11 (dd, 2 H, –CH–C<u>H</u>$_2-$), 4·27 (dd, 2 H, –CH–C<u>H</u>$_2-$), 5·21–5·26 (m, 1 H, –CH–).

4.2.2. *1,2,3-Tris-{11-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)-phenoxy]undecanoyloxy}propane* (**3**)

A mixture of compound **10** (0·63 g, 0·76 mmol), 4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenol **13 b** (0·82 g, 2·7 mmol), anhydrous potassium carbonate (3·72 g, 27 mmol) and potassium iodide (0·13 g, 0·06 mmol) in diethyl ketone (20 ml) was stirred and heated at reflux under an argon atmosphere for 48 h. The solvent was removed *in vacuo* and chloroform was added to the residue. After acidifying with 2 M hydrochloric acid, the

organic phase was washed with aqueous sodium hydrogen carbonate (3 ×) and brine. The solution was dried (Na_2SO_4) before the solvent was removed *in vacuo* to give the crude product which was recrystallized from dry ethanol. Yield 0·66 g (58 per cent); m.p. 103°C. Elemental analysis. Found (calculated for $C_{87}H_{134}N_6O_9S_3$): C 69·18 (69·47), H 8·80 (8·98), N 5·42 (5·59), S 6·10 (6·39) per cent. ^{1}H NMR, δ ppm, $CDCl_3$: 0·85 (t, 9H, CH_3), 1·13–1·50 (m, 74H, $-CH_2-$), 1·51–1·67 (m, 6H, $-CH_2-$), 2·29 (t, 6H, OOC–CH_2-), 3·08 (t, 6H, thiadiazole–CH_2-), 3·97 (t, 6H, $-OCH_2-$), 4·12 (dd, 2H, –CH–C$\underline{H}_2-$), 4·27 (dd, 2H, –CH–C$\underline{H}_2$), 5·18–5·30 (m, 1H, –CH–), 6·92 (d, 6H, aromatic H), 7·83 (d, 6H, aromatic H).

4.3. *Synthesis of 1,2,3,4-tetrakis-{5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}neopentane* (**4**)

4.3.1. *1,2,3,4-Tetrakis-(5-bromopentanoyloxy)neopentane* (**16**)

The experimental procedure described for the preparation of compound **10** was used. Quantities: pentaerythritol (0·81 g, 6·0 mmol), bromovaleric acid (4·77 g, 26·4 mmol), DMAP (0·32 g, 2·6 mmol), dry chloroform (20 ml) and DCC (5·44 g, 2·64 mmol). Reaction time: 69 h. The crude product was purified by column chromatography using a chloroform/methanol (10:1) mixture as eluent. Yield: 2·41 g, (51 per cent). Elemental analysis: Found (calculated for $C_{25}H_{40}Br_4O_8$): C 37·94 (38·10), H 5·09 (5·12), Br 40·25 (40·55) per cent. IR, ν cm^{-1}, $CHCl_3$: 2960, 1740 (C=O), 1460, 1350. ^{1}H NMR, δ ppm, $CDCl_3$: 1·67–1·93 (m, 16H, $-CH_2-$), 2·34 (t, 8H, OOC–CH_2-), 3·38 (t, 8H, $-CH_2$–Br), 4·04 (s, 8H, $-OCH_2-$).

4.3.2. *1,2,3,4-Tetrakis-{5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}neopentane* (**4**)

This compound was synthesized from **16** and **13 b** using the same procedure as for **3**. Yield: 0·47 g (37 per cent); transitions (°C): C 122 (S_C 118) I. Elemental analysis. Found (calculated for $C_{93}H_{132}N_8O_{12}S_4$): C 66·25 (66·40), H 7·79 (7·91), N 6·50 (6·66), S 7·59 (7·62) per cent. ^{1}H NMR, δ ppm, $CDCl_3$: 0·85 (t, 12H, CH_3), 1·2–1·49 (m, 48H, $-CH_2-$), 1·7–1·9 (m, 24H, $-CH_2-$), 2·45 (br t, 8H, OOC–CH_2-), 3·12 (t, 8H, thiadiazole–CH_2-), 3·97 (br t, 8H, $-OCH_2-$), 4·15 (s, 8H, $-OCH_2-$), 6·91 (d, 8H, aromatic H), 7·83 (d, 8H, aromatic H).

4.4. *Synthesis of 1,3-bis-{5-[4-(heptyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-2-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxymethyl]-2-methylpropane* (**7**)

4.4.1. *5-[4-(5-Heptyl-1,3,4-thiadiazol-2-yl)phenoxymethyl]-2,2,5-trimethyl-1,3-dioxan* (**18**)

A solution of 5-hydroxymethyl-2,2-dimethyl-1,3-dioxan **14** (1·2 g, 7·5 mmol), 4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenol **13 a** (1·4 g, 5 mmol) and dry triphenylphosphine (1·96 g, 7·5 mmol) in dry THF (20 ml) was stirred at 0°C and DEADC (1·3 g, 7·5 mmol) was added [6]. This mixture was stirred at room temperature overnight. Then the solvent was removed *in vacuo*, the residue was dissolved in a mixture of methanol/water (10:1) and the product was extracted into hexane. The combined organic extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo*. The crude product was recrystallized from a methanol/water (3:1) mixture. Yield: 0·95 g (48 per cent); m.p. 70°C; ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, 3H, CH_2–C$\underline{H}_3$); 0·94 (s, 3H, C$\underline{H}_3$), 1·25–1·36 (m, 8H, $-CH_2-$), 1·39 (s, 3H, CH_3), 1·45 (s, 3H, CH_3), 1·73–1·87 (m, 2H, $-CH_2-$), 3·08 (t, 2H, thiadiazole–CH_2-), 3·72 (dd, 4H, $-OCH_2-$, 4·05 (s, 2H, $-OCH_2-$), 7·12 (d, 2H, aromatic H), 7·84 (d, 2H, aromatic H). MS *m/z* 418 (M^+), 334, 192, 85.

4.4.2. *1,3-Bis-(hydroxymethyl)-2-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxymethyl]-2-methylpropane* (**20**)

Compound **18** was heated under reflux in the presence of a catalytic amount of pyridinium tosylate in a mixture of methanol/water (10:1) for 3·5 h. The solvent was removed *in vacuo*; the residue was dissolved in ethyl acetate, washed with water (3 ×) and the organic phase dried (Na_2SO_4). The solvent was removed *in vacuo* and the crude product was recrystallized from a methanol/water (10:1) mixture. Yield: 0·55 g (69 per cent); m.p. 103°C. Elemental analysis. Found (calculated for $C_{20}H_{30}O_3N_2S$): C 63·72 (63·46), H 8·15 (7·99), N 7·12 (7·41), S 8·45 (8·45) per cent. IR, ν cm^{-1}, (nujol): 3120–3515 (OH), 1605 (C=N), 1520 (C=C). ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, 3H, $-CH_2-C\underline{H}_3$), 0·95 (s, 3H, CH_3), 1·27–1·36 (m, 8H, $-CH_2-$), 1·72–1·86 (m, 2H, $-CH_2-$), 2·73 (br t, 2H, –OH), 3·11 (t, 2H, thiadiazole–CH_2-), 3·70–3·82 (m, 4H, $-OCH_2-$, 4·03 (s, 2H, $-OCH_2-$), 6·96 (d, 2H, aromatic H), 7·80 (d, 2H, aromatic H).

4.4.3. *1,3-Bis-{5-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)-phenoxy]pentanoyloxy}-2-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxymethyl]-2-methylpropane* (**7**)

The experimental procedure used was that described for the preparation of compound **10**. Quantities: compound **20** (0·5 g, 1·3 mmol), 5-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoic acid **21** (1·2 g, 3·25 mmol), a catalytic quantity of DMAP, DCC (0·67 g, 3·25 mmol) and dry dichloromethane (20 ml). The crude product was purified by column chromatography using a chloroform/methanol (10:1) mixture and recrystallized from petroleum ether/ethyl acetate (1:2). Yield: 0·35 g (25 per cent); m.p. 137°C. ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, 9H, $-CH_2-C\underline{H}_3$), 1·13 (s, 3H, CH_3, 1·26–1·54 (m, 24H, $-CH_2-$), 1·70 (m, 14H, $-CH_2-$), 2·40 (br t, 4H, OOC–CH_2-), 3·04 (2t, 6H, thiadiazole-CH_2-), 3·89–3·94 (m, 6H, $-CH_2O-$, $-OCH_2-$,

4·14 (s, 2 H, $-OCH_2-$), 6·90 (d, 6 H, aromatic H), 7·64 (d, 6 H, aromatic H). MS *m/z* 1091 (M^+), 1022, 938, 866, 781, 665, 547, 359, 289, 277, 205, 192, 55, 41.

4.5. *Synthesis of 1,3-bis-{5-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-2,2-bis-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxymethyl]propane* (**8**)

4.5.1. *5,5-Bis-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)-phenoxymethyl]-1,3-dioxan* (**23**)

The experimental procedure described for the preparation of compound **18** was used. Quantities: 5,5-bis-(hydroxymethyl)-1,3-dioxan **22** (1 g, 6·7 mmol), compound **13a** (3·7 g, 13·4 mmol), triphenylphosphine (5·24 g, 20 mmol), DEADC (3·48 g, 20 mmol) and dry THF (25 ml). The crude product was purified by recrystallization from methanol/water (10:1). Yield: 1·4 g (31 per cent); m.p. 119°C. Elemental analysis. Found (calculated for $C_{36}H_{48}O_4N_4S_2$): C 65·00 (65·03), H 7·41 (7·28), N 8·25 (8·43), S 9·49 (9·64) per cent. ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, 6 H, CH_3), 1·27–1·37 (m, 16 H, $-CH_2-$), 1·73–1·80 (m, 4 H, $-CH_2-$), 3·07 (t, 4 H, thiadiazole–CH_2-), 4·02 (s, 4 H, $-OCH_2-$), 4·17 (s, 4 H, $-OCH_2-$), 4·88 (s, 2 H, O–CH_2–O), 6·97 (d, 4 H, aromatic H), 7·83 (d, 4 H, aromatic H).

4.5.2. *2,2-Bis-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)-phenoxymethyl]-1,3-dihydroxypropane* (**24**)

Compound **23** (1·3 g, 1·9 mmol) was heated under reflex in methanol (15 ml) in the presence of concentrated hydrochloric acid (5 ml) for 2 h [9]. The methanol was removed by evaporation, followed by extraction of the product into dichloromethane (3 ×). The combined extracts were washed with aqueous sodium hydrogen carbonate (2 ×) and water. After the solution had been dried (Na_2SO_4), the solvent was removed *in vacuo*. The crude product was purified by column chromatography using a chloroform/methanol (10:1) mixture. Yield: 0·25 g (20 per cent); m.p. 149°C. Elemental analysis. Found (calculated for $C_{35}H_{48}O_4N_4S_2$): C 64·10 (64·39), H 7·43 (7·41), N 8·30 (8·58), S 9·90 (9·82) per cent. IR, ν cm^{-1}, (nujol): 3090–3480 (OH), 1600 (C=N), 1510 C=C). ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, 6 H, CH_3), 1·27–1·43 (m, 16 H, $-CH_2-$), 1·72–1·83 (m, 4 H, $-CH_2-$), 2·73 (t, 2 H, –OH), 3·08 (t, 4 H, thiadiazole–CH_2-), 3·97 (d, 4 H, $-OCH_2-$), 4·19 (s, 4 H, $-OCH_2-$), 6·97 (d, 4 H, aromatic H), 7·82 (d, 4 H, aromatic H).

4.5.3. *1,3-Bis-{5-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)-phenoxy]pentanoyloxy}-2,2-bis-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)phenoxymethyl]propane* (**8**)

The compound was synthesized from **24** (0·15 g, 0·23 mmol), **21** (0·22 g, 0·57 mmol) and DCC (0·15 g, 0·57 mmol) using the procedure given for **7**. The crude product was purified by recrystallization from an ethanol/chloroform (1:2) mixture. Yield: 0·09 g (31 per cent); m.p. 158°C. ^{1}H NMR, δ ppm, $CDCl_3$: 0·85 (t, 12 H, CH_3), 1·26–1·33 (m, 32 H, $-CH_2-$), 1·74–1·76 (m, 16 H, $-CH_2-$), 2·39 (br t, 4 H, OOC–CH_2-), 3·02–3·11 (2t, 8 H, thiadiazole–CH_2-), 3·87 (br t, 4 H, $-CH_2O-$), 4·16 (s, 4 H, $-OCH_2-$, 4·39 (s, 4 H, $-OCH_2-$), 6·82–6·97 (m, 8 H, aromatic H), 7·76–7·84 (m, 8 H, aromatic H).

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References

[1] Allcock, H. R., and Kim, C., 1989, *Macromolecules*, **22**, 2596. Eidenschink, R., Kreutzer, F. H., and de Jeu, W. H., 1990, *Liq. Crystals*, **8**, 879. See also: Attard, G. S., Douglass, A. D., Imrie, C. T., and Taylor, L., 1992, *Liq. Crystals*, **11**, 779.

[2] Bach, V., Beck, K., Etzbach, K,. H., Siemensmeyer, K., and Wagenblast, G., (BASF), 1992, *21. Freiburger Arbeitstagung Flüssigkristalle*, P 40.

[3] Steglich, W., and Höfle, G., 1969, *Angew. Chem.*, **81**, 1001.

[4] Tschierske, C., and Girdziunaite, D., 1991, *J. prakt. Chem.*, **333**, 135.

[5] Allen, C. F. H., and Gates, J. W., Jr., 1955, *Org. Synth., Coll.*, **3**, 140.

[6] Mitsunobu, O., 1981, *Synthesis*, 1.

[7] Schmidt, O. Th., 1963, *Meth. Carbohydr. Chem.*, **II**, 318.

[8] De Belder, A. N., 1965, *Adv. Carbohydr. Chem.*, **20**, 19.

[9] Hough, L., Jones, J. K. N., and Magson, M. S., 1952, *J. chem. Soc.*, **2**, 1525.

[10] Furniss, B. S., Hannaford, A. J., Smith, P. W. G., and Tatchell, A. R. (editors), 1989, *Vogel's Textbook of Practical Organic Chemistry*, 5th edition (Longmann Scientific and Technical), p. 395.