Liquid crystalline 3-, 4- and 6-armed star molecules based on nitromethane-trispropanol or pentaerythritol without mesogen spacers

L. M. Wilson[a]

[a] Melville Laboratory for Polymer Synthesis, University of Cambridge, Cambridge, England

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Liquid crystalline 3-, 4- and 6-armed star molecules based on nitromethane-trispropanol or pentaerythritol without mesogen spacers

by L. M. WILSON

Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, England

Some molecules of unusual shape and apparently non-linear geometry, with mesogens tied directly to a central unit (for example, tetrahedral pentaerythritol), have been investigated for liquid crystalline behaviour. It was found that these three-, four- and six-armed 'star' molecules generated liquid crystalline mesophases, which were characterized by DSC, optical microscopy and X-ray diffraction. The temperature ranges of the fluid mesophases for the thermotropic compounds were above 158°C for the three-armed molecules and above 219°C for the four-and six-armed 'stars'. All the liquid crystalline compounds exhibited a smectic phase, which appears to be smectic A, with the molecules in their fully extended conformations within the layers. Some of the compounds also had a smectic phase of higher order or a nematic phase.

1. Introduction

Since the observation by Vorländer [1] early this century that the liquid crystalline state is observed with molecules of a linear shape, the most common and well-known liquid crystalline materials consist of small molecules that are linear rods or have axial symmetry, and are usually based on *para*-linked ring systems, for example, the cyanobiphenyls or phenylcyclohexyl compounds [2]. These have a rigid rod-like section with some terminal group, either a flexible alkyl or a polar group. Some compounds of more complex symmetry have also been investigated, such as the so-called twinned mesogens [3–5], which have two mesogenic rods connected together laterally via a single methylene or other bridging group.

But some molecules of apparent non-linear geometry, with four mesogenic groups tied to a central unit (tetrahedral pentaerythritol), with flexible links ($-[CH_2]_n-$) to the rigid mesogenic units, have shown liquid crystalline behaviour [6] and recently Percec [7] has shown that small dendrimer molecules with mesogen moieties attached via flexible spacers also show liquid crystalline properties. These flexible spacers have been thought necessary in order to 'decouple' the mesogenic units, allowing liquid crystalline ordering.

Here we report the synthesis of small 'star' molecules, consisting of three or more mesogenic groups tied to a small central core without further spacer units, but which still show liquid crystalline behaviour. These are based on nitromethane-trispropanoic acid or 'trispropanol and pentaerythritol or dipentaerythritol cores, directly bonded to the mesogenic units, to give 3-, 4- or 6-armed star molecules, as shown below. These molecules may appear at first not to be capable of giving anisotropic liquid crystalline phases, especially the tetrahedral pentaerythritol based molecules, since the connections to the arms become shorter and progressively more crowded around the central cores on going from compounds **1a, b** to compounds **4a, b, c**. The products were investigated for liquid crystalline behaviour by DSC, polarizing optical microscopy and X-ray diffraction.
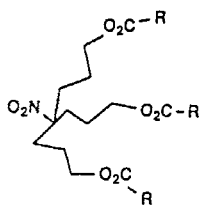
1a R = -PhPh-Pr
1b R = -PhPh
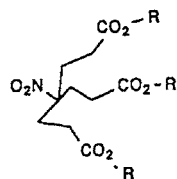
2 R = -Ph-O$_2$C-PhPh-Pr
Note, Ph = phenyl, Pr = Propyl
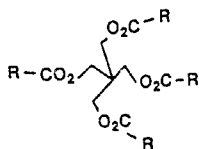
3a R = -Ph-O$_2$C-PhPh-Pr
3b R = -PhPh-Pr
3c R = -Ph-NHCO-PhPh-Pr

4a R = -Ph-O$_2$C-PhPh-Pr
4b R = -PhPh-Pr
4c R = -Ph-NHCO-PhPh-Pr

2. Experimental section

The reactions of nitromethane-trispropanol (**A**) with the corresponding mesogenic system (**B**),

$$O_2N-C(CH_2CH_2CH_2-OH)_3 + 3.HO_2C-PhPh-Pr \quad \text{or} \quad HO_2C-PhPh$$

to give **1a** and **1b** were performed using the Stupp method for ester formation [8], are described as follows: 5 mmol of **A** (calculated as the functional group equivalent) were stirred with a 10 per cent exces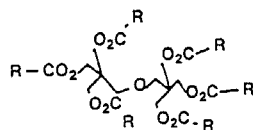s of **B** (5·5 mmol) in approximately 50 ml of CH$_2$Cl$_2$ and 15 ml of THF (all reagents were dried before use) and 0·63 g of p-toluene sulphonic acid (PTSA) and 0·40 g of dimethylaminopyridine (DMAP) were added together to the stirred solution under nitrogen to exclude moisture. 1·3 to 1·6 g of diisopropylcarbodiimide were then added. After a few hours, a white precipitate had formed. After 1 day the volume of the reaction mixture was reduced on a rotavaporator and the product was then precipitated out and washed by pouring the reaction mixture into a larger volume of methanol (approximately 100 ml). The product was collected by filtration and recrystallized twice from chloroform–methanol to remove PTSA/DMAP and diisopropylurea, and then dried. Yield, approximately 90 per cent **1a** and 90 per cent **1b**. IR for **1a**: aromatic ester visible; main peaks at 1710, 1285, 1112, 3050(w), 1609, 790 cm^{-1}, and nitro at 1540, 1360 cm^{-1}; for **1b**: 1711, 1278, 1112, 3050(w), 1609, 858, 747, 1536, 1360 cm^{-1}. NMR(δ), in CDCl$_3$, for **1a**: aromatic peaks at, 8·04 d 2 H, 7·64 d 2 H, 7·47 d 2 H, 7·21 d 2 H, CH peaks at, 4·35 t 2 H, 2·60 t 2 H, 2·17 m 2 H, 1·76 m 2 H, 1·65 q 2 H, 0·96 t 3 H. Elemental analysis: calculated: C, 77·25, H, 6·99, N, 1·55 per cent, found: C, 77·42, H 7·01, N, 1·39 per cent. NMR(δ), in CDCl$_3$, for **1b**, 8·13 d 2 H, 7·68 m 4 H, 7·49 m 3 H, 4·41 t 2 H, 2·17 m 2 H, 1·81 m 2 H. Elemental analysis: calculated: C, 75·87, H, 5·81, N, 1·81 per cent; found: C, 75·73, H, 5·89, N, 1·90 per cent; m.p., **1a**, KC 156°C (clearing point), S$_A$ 115·2°C (monotropic) on cooling, m.p., **1b**, 63°C.

The reactions of pentaerythritol or dipentaerythritol with 4′-n-propylbiphenyl-4-carboxylic acid, to give **3b** and **4b**, were performed as described above. Yield, 3b, approximately 86 per cent. IR for **3b**: aromatic ester visible; main peaks at 1727, 1713,

1266, 1104, 3050(w), 1607, 770 cm^{-1}. NMR (δ), in CDCl$_3$, for **3b**: aromatic peaks at, 8·04 d 2 H, 7·59 d 2 H, 7·49 d 2 H, 7·23 d 2 H with other peaks at 4·77 s 2 H, 2·64 t 2H, 1·68 m 2 H, 0·97 t 3 H. Elemental analysis: calculated: C, 80·86, H, 6·64 per cent; found: C, 81·00, H, 6·81 per cent. m.p., **3b**, 212°C. Yield, **4b**, approximately 85 per cent. IR for **4b**: aromatic ester visible; main peaks at 1715, 1265, 1104, 3050(w), 1608, 767 cm^{-1}. NMR (δ), in CDCl$_3$, for **4b**: aromatic peaks at 7·97 d 6 H, 7·50 d 6 H, 7·41 d 6 H, 7·18 d 6 H with other peaks at 4·66 s 6 H, 3·83 s 2 H, 2·62 t 6 H, 1·69 m 3 H, 0·98 t 9 H. Elemental analysis: calculated: C, 80·2, H, 6·68 per cent; found: C, 80·31, H, 6·73 per cent; m.p., **4b**, 261°C.

The preparations of **3a** and **4a** were carried out via the 4-benzyloxyphenyl esters, which were then deprotected to give the 4-hydroxyphenyl esters. Pentaerythritol or dipentaerythritol was reacted as described above with 4-benzyloxybenzoic acid to give the corresponding tetra- or hexa-4-benzyloxyphenyl ester. These esters were then deprotected to give the phenolic compounds in high yield by treatment with palladium on carbon (10 per cent) and ammonium formate in THF for approximately 6 h at approximately 65°C. The Pd/C and the excess of ammonium formate were removed by filtration using a glass filter paper and Büchner funnel. The solvent was removed from the filtrate on a rotavaporator to give a hygroscopic solid. For the pentaerythritol tetra-phenol: Yield approximately 87 per cent. IR: OH and aromatic ester visible; main peaks at 1688, 1716, 1607, 1273, 1161, 2900–3550 cm^{-1}. NMR (δ), in CD$_3$OD, aromatic peaks at 7·82 d 2 H, 6·74 d 2 H, OH at approximately 5·00 s (broad) 1 H, CH$_2$ peak at 4·62 s 2 H. ^{13}C NMR, 167·7, 163·7, 132·3, 121·68, 116·3, 64·8, 44·6 ppm. Elemental analysis: calculated: C, 64·28, H, 4·54 per cent; found: C, 64·18, H, 4·58 per cent. m.p., 185°C (gives a glass on cooling). For the dipentaerythritol hexa-phenol: Yield, approximately 85 per cent. IR: main peaks at 1694(br), 1609, 1266, 1165, 2900–3550 cm^{-1} NMR (δ), in CD$_3$OD, aromatic peaks at 7·76 d 6 H, 6·69 d 6 H, OH at approximately 4·92 s (broad) 3 H, CH$_2$ peaks at 4·49 s 6 H, 3·73 s 2 H. ^{13}C NMR, 167·2, 163·2, 132·5, 121·3, 115·8, 64, 44·8 ppm. Elemental analysis: calculated: C, 64·06, H, 4·72 per cent; found: C, 63·95, H, 4·83 per cent; m.p., 110°C (gives a glass on cooling).

These phenolic products were then esterified with 4'-*n*-propylbiphenyl-4-carboxylic acid, using the Stupp synthesis, and purified to give products **3a** and **4a**. Yield, **3a**, approximately 89 per cent. IR for **3a**: aromatic ester visible, main peaks at 1730, 1716, 1605, 1262, 1161, 764 cm^{-1}. NMR (δ), in CDCl$_3$, for **3a**: aromatic peaks at 8·17 d 2 H, 8·00 d 2 H, 7·63 d 2 H, 7·51 d 2H, 7·33 d 2 H, 7·25 d 2 H with other peaks at 4·77 s 2 H, 2·65 m 2 H, 1·69 m 2 H, 0·98 t 3 H. ^{13}C NMR, 1165·5, 164·6, 155·2, 146·5, 143·3, 137·1, 131·5, 130·9, 129·3, 127·6, 127·3, 127·1, 122·3, 64, 43·5, 37·9, 24·6, 14 ppm. Elemental analysis: calculated: C, 77·39, H, 5·58 per cent; found: C, 77·30, H, 5·62 per cent. m.p., **3a**, C (S$_B$?) 219°C S$_A$ 247·5°C (clearing point). Yield, **4a**, approximately 85 per cent. IR: for **4a**: aromatic ester visible, main peaks at 1729 (broad), 1606, 1263, 1161, 764 cm^{-1}. NMR (δ), in CDCl$_3$, for **4a**: aromatic peaks at 8·07 d 6H, 7·98 d 6 H, 7·56 d 6 H, 7·45 d 6 H, 7·22 d 6 H, 7·19 d 6 H with other peaks at 4·65 s 6 H, 3·81 s 2 H, 2·63 t 6 H, 1·67 m 6 H, 0·98 t 9 H. ^{13}C NMR, 165·4, 164·5, 155·1, 146·4, 143·3, 137·1, 131·4, 130·9, 130·6, 129·3, 127·6, 127·3, 127, 122·2, 64, 44·2, 37·9, 24·7, 14·1 ppm. Elemental analysis: calculated: C, 77·02, H, 5·63 per cent; found: C, 76·71, H, 5·64 per cent; m.p., **4a**, C 236°C S$_A$ 295°C (clearing point).

The amides **3c** and **4c** were made using the procedure above for **3a** and **4a**, but using the *p*-nitro instead of the benzyloxy compounds. The nitro compounds were reduced to the amines by palladium on carbon. Yield for the pentaerythritol tetra-amine, approximately 86 per cent. IR: aromatic ester visible, main peaks at 1694, 1621, 1601, 1270, 1173, 772, 3494, 3384 cm^{-1}. NMR (δ), in CDCl$_3$, aromatic peaks at 7·80 d 1H,

6·57 d 1 H, CH$_2$ peak at, 4·58 s 1 H, NH at 4·07 s (broad) 1 H. Elemental analysis: calculated: C, 64·70, H, 5·23, N, 9·15 per cent; found: C, 64·59, H, 5·50, N, 9·08 per cent. m.p., 116°C gives a glass on cooling). Yield for the dipentaerythritol hexa-amine, approximately 85 per cent. IR: aromatic ester visible, main peaks at 3462, 3365, 1694, 1601, 1266, 1171, 770 cm^{-1}. NMR (δ), in CD$_3$OD, aromatic peaks at 7·64 d 6 H, 6·52 d 6 H, NH at 4·91 s (broad) 3 H. CH$_2$ peaks at, 4·43 s 6 H, 3·68 s 2 H. Elemental analysis: calculated: C, 64·46, H, 5·37, N, 8·68 per cent; found: C, 64·16, H, 5·57, N, 8·31 per cent; m.p., 104·5°C (gives a glass on cooling).

Compounds **3c** and **4c** were then obtained from the amines and 4'-*n*-propylbiphenyl-4-carboxylic acid by the Stupp condensation. Recrystallization was from DMF/methanol. Yield, **3c**, approximately 90 per cent. IR for **3c**: aromatic ester and amide visible, main peaks at 1720, 1652, 1619, 1273, 3342 cm^{-1}. NMR (δ), in (CD$_3$)$_2$NCOD, for **3c**: 4 aromatic peaks at 8·15 d 2 H, 8·09 s 4 H, 7·84 d 2 H, 7·70 d 2 H, 7·34 d 2 H with other peaks at 4·90 s 2 H, 2·65 t 2 H, 1·67 m 2 H, 0·95 t 3 H, amide NH at 8·09 s 1 H. Elemental analysis: calculated: C, 77·60, H, 5·60, N, 3·73 per cent; found: C, 77·28, H, 5·81, N, 3·96 per cent; m.p., **3c**, C 291°C S$_A$ 335°C (some decomposition in air, clearing point). Yield, **4c**, approximately 90 per cent. IR for **4c**: aromatic ester visible, main peaks at 1718, 1651, 1620, 1272, 3342 cm^{-1}. NMR (δ), in (CD$_3$)$_2$NCOD, for **4c**: aromatic peaks at 8·13 d 6H, 8·07 s 12 H, 7·81 d 6 H, 7·72 d 6 H, 7·35 d 6H with other peaks at 4·79 s 6 H, 4·11 s 2 H, 2·69 t 6 H, 1·72 m 6 H, 1·01 t 9 H. Elemental analysis: calculated: C, 77·22, H, 5·65, N, 3·65 per cent; found: C, 76·98, H, 5·81, N, 3·67 per cent; m.p., **4c**, approximately C 355°C S$_A$ 371°C (decomposition, clearing point).

The trispropanoate **2** was prepared as for **1a** and **1b**, by reaction with HO–Ph–O2C–PhPh–Pr, the mono-ester of hydroquinone. This was prepared from 4'-*n*-propylbiphenyl-4-carboxylic acid by reaction with a 3-fold excess of hydroquinone (HO–Ph–OH), using the Stupp condensation, the 4'-*n*-propylbiphenyl-4-carboxylic acid dissolved in THF, being added slowly to the stirred mixture containing hydroquinone. Yield, of the hydroquinone mono-ester, 70–75 per cent. IR: aromatic ester visible, main peaks at 3150–3450, 3050, 3050(w), 1729, 1603, 1190, 1072 cm^{-1}. NMR (δ), in CD$_3$OD, aromatic peaks at 8·19 d 2 H, 7·77 d 2 H, 7·61 d 2 H, 7·30 d 2 H, 7·02 d 2 H, 6·82 d 2 H with other peaks at 2·64 s 2 H, 1·67 m 2 H, 0·97 t 3 H. ^{13}C NMR, 168, 156·5, 147·7, 145, 144·4, 138·4, 131·6, 130·2, 129·3, 128·1, 128, 123·5, 116·8, 38·7, 25·7, 14·1 ppm. Elemental analysis: calculated: C, 79·52, H, 6·02 per cent; found: C, 79·35, H, 6·08 per cent; m.p., C 180°C nematic, approximately 285°C (clearing point, decomposition) Yield for **2**, 82 per cent. IR for **2**; aromatic ester visible, main peaks at 1733, 1607, 1538, 1465, 1274, 1179, 764 cm^{-1}. NMR (δ), in CDCl$_3$, aromatic peaks at 8·15 d 2 H, 7·62 d 2 H, 7·52 d 2 H, 7·27 d 2 H, 7·24 d 2 H, 7·16 d 2 H with other peaks at 2·67 m 2 H, 2·61 t 2 H, 2·51 m 2 H, 1·67 m 2 H, 0·98 t 3 H. ^{13}C NMR, 170·6, 165·1, 148·8, 148, 146·5, 143·3, 137·3, 130·9, 129·3, 127·9, 127·3, 127·2, 123, 122·6, 92, 37·9, 30·2, 29, 24·7, 14·1 ppm. Elemental analysis: calculated: C, 73, H, 5·87, N, 1·49 per cent; found: C, 72·91, H, 5·92, N, 1·55 per cent; m.p., **2**, C 152°C S$_A$ 208°C nematic 280–290°C (clearing point with decomposition).

All reagents were obtained from Aldrich Chemical Co, except for 4'-*n*-propylbiphenyl-4-carboxylic acid which was obtained from TCI.

Measurements were performed using the following instruments: IR: Nicolet 510M spectrometer; NMR: Bruker WM250 MHz spectrometer; DSC: Perkin–Elmer DSC 7; Polarizing light microscopy: Leica Axioscope fitted with a Mettler FP 82 microfurnace. Elemental analyses were performed in the Department of Chemistry, University of Cambridge. The X-ray small angle powder diffraction measurements were made on a

Philips PW 1710 diffraction system. The samples were prepared by heating to obtain the isotropic and cooling down into the mesophase or by annealing at the mid-mesophase temperature for several minutes. The samples were then quenched in liquid nitrogen and ground to powders.

3. Results and discussion

The compounds **2**, **3a**, **4a**, **3c** and **4c** all show thermotropic smectic mesophases on heating and on cooling in the polarizing optical microscope. Compound **2** also showed a nematic phase at a higher temperature then the smectic. In **1a**, a mesophase was only observed on cooling (monotropic), and this was also a smectic A phase. Figure 1 (*a*)–(*d*) shows some of the textures observed for compounds **1a**, **2**, **3a** and **4a**. Focal-conic textures typical of smectic A phases were observed for all the liquid crystalline compounds except compounds **4a** and **4c**, which did not show clear focal-conics, but did show bâtonnets on cooling from the isotropic liquid [9, 10] with **4c** having a somewhat mosaic-like texture. Compound **4a** therefore has a smectic A (which is consistent with the X-ray diffraction results discussed below) or a higher order smectic phase, such as S_B. The smectic phase of **4c** looked very similar to **4a** under the microscope. The possibility of a discotic phase has also been suggested for these compounds (**4a** and **4c**), and they are being investigated further. The smectic phase of **2** looked similar to **3a** under the microscope, while the threaded nematic texture was seen for compound **2** above the smectic, although this was close to the decomposition temperature; the temperature of the nematic to isotropic transition cannot therefore be given with certainty, nor can the upper clearing point transition temperatures for compounds **3c**, **4a** and **4c**, which appear to be around 300°C or higher, but are close to the thermal decomposition or oxidation temperatures. The lower transitions, from solid to fluid mesophases can be given with certainty, since these are well below the decomposition temperatures. Compound **3a**, the pentaerythritol tetra (4′-propylbiphenyl-4-carboxybenzoate) ester may also have another more ordered phase with a very high viscosity below the smectic A phase; this may be a smectic B phase (which is consistent with the X-ray data quoted below). This phase is observed above about 130°C on heating, when the material begins to soften, and is seen in the DSC as a step transition similar to a glass transition, rather than a well-defined peak. On cooling the smectic phase is seen down to room temperature, with no visible change, except for the appearance of some cracks, but the sample slowly crystallized over several hours. The smectic texture of compound **3c** looked very similar to that of compound **3a**, but smectic A type bâtonnets were more prominent than focal-conics.

For the liquid crystalline compounds, second heating DSC measurements showed that the first (solid or crystalline to mesophase) transition has a smaller enthalpy than the final clearing transition. This indicates that the mesophase is highly ordered. The enthalpies are shown in table 1, together with the transition temperatures, but the clearing points for **2**, **3c** and **4c** are near the decomposition temperatures and therefore difficult to measure with precision; this is the case especially for **2** and **4c**, for which the clearing point can only be given as a lower estimate. The values of ΔH are fairly large, but consistent with the presence of 3, 4 or 6 mesogenic groups per molecule and the fairly high molecular mass values [10]. The corresponding enthalpies for the amides **3c** and **4c** are higher than for the esters.

In the case of **1b**, **3b** and **4b** no liquid crystalline behaviour was found. Presumably, for these molecules, the aromatic units are unable to stabilize a mesophase. **1b** is a glass, while **3b** and **4b** are crystalline at room temperature, and all show a single melting
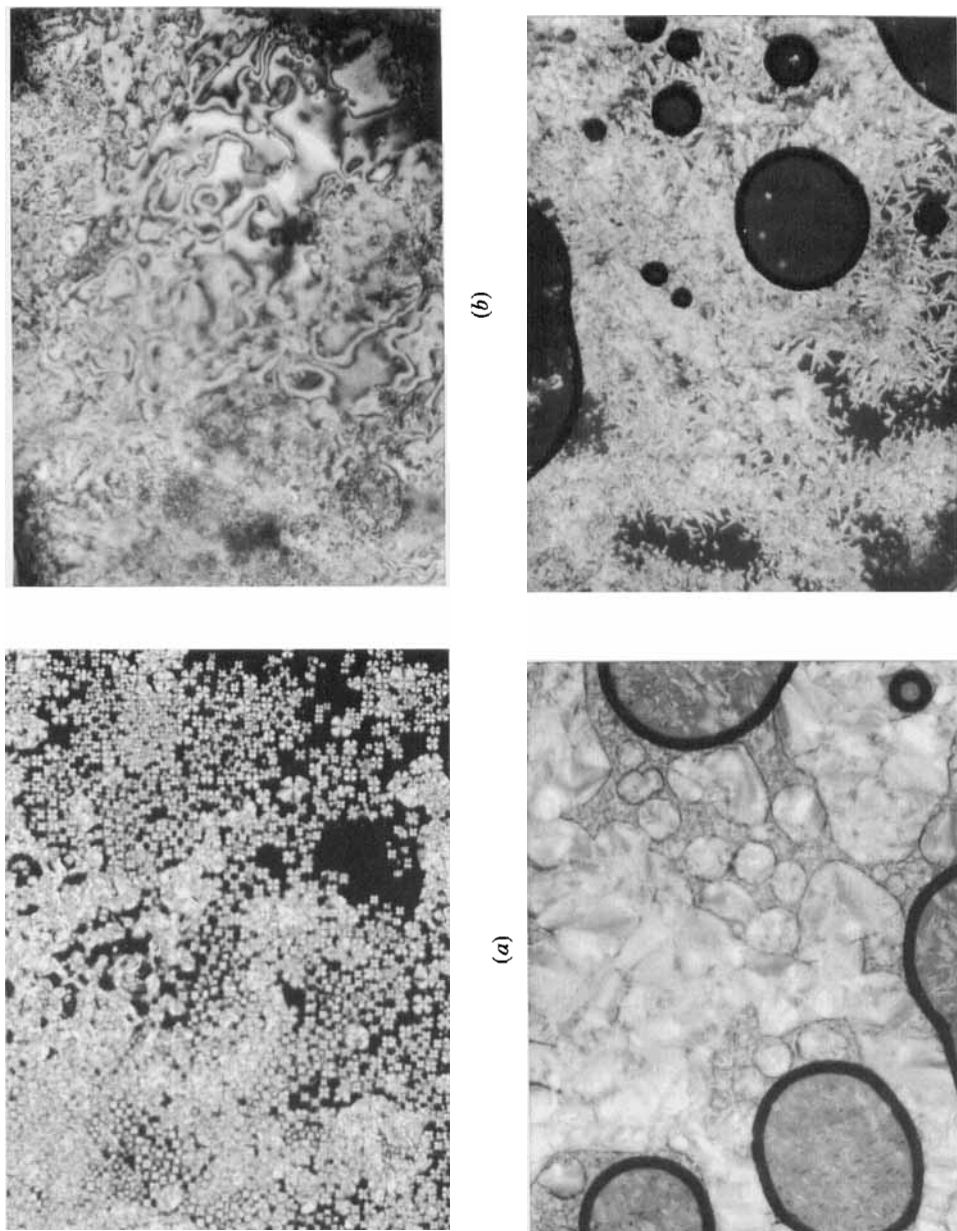
Figure 1. Polarizing optical micrograph of (a) compound **1a** at 100 × in the smectic phase at 112°C, (b) compound **2** at 100 × in the nematic phase at 228°C, (c) compound **3a** at 320 × in the smectic phase at 236°C, and (d) compound **4a** at 100 × in the smectic phase at 270°C.

Table 1. Thermal transition data for mesomorphic compounds.

Compound	Solid– mesophase 1/°C Enthalpy/kJ mol^{-1}	Mesophase 2–/°C Enthalpy/kJ mol^{-1}	Isotropic/°C Enthalpy/kJ mol^{-1}
1a	156–Isotropic 38·5	(Monotropic)	(115·2 S$_A$) (10·9)
2	158 S$_A$ 12·8	208 N 1·85	~280
3a	219 S$_A$ 11·5		247·5 40·6
3c	291 S$_A$ 35		~335 †
4a	236 S$_A$ 9·2		296 50·7
4c	355 S$_A$ (or S$_B$)18·8		~371 ~40
	Crystal m.p.		
1b	63 23·4		
3b	212 55·3		
4b	261 68·4		

† Sample sublimed in DSC.

endotherm by DSC. These data are also given in table 1 for comparison. Comparison of compound **1a** with **1b** shows that the addition of the propyl substituent is capable of giving liquid crystalline smectic behaviour. For **3b** and **4b** however, the same ester units are not enough to impose order on the pentaerythritol cores; the longer mesogenic units in **3a** and **4a** are however more strongly ordering, and smectic phases are observed. The corresponding amides, **3c** and **4c** are also smectic. The borderline between liquid crystalline and non-liquid crystalline behaviour for pentaerythritol is thus presumably between these two mesogenic units, while for the 3 armed star the borderline is near the shorter ester biphenyl-propyl unit.

These molecules can be considered to be similar to small sections of side-chain liquid crystalline polymers [6], such as polyacrylates which have a single methylene unit between the mesogenic sidechains. The packing of the mesogens could be similar to these, and it could also be similar to the ordering in the twinned mesogens described in the introduction which also show smectic A phases [4].

From space-filling models, it can be shown that smectic ordering of the mesogen is possible, because the connections of the mesogenic units to the core are flexible enough to allow rotation and therefore ordering of the units. The end to end fully extended molecule length can also be estimated and for **1a** it is ~43 Å. The X-ray smectic layer periodicity is then predicted to be ~43 Å, depending on the packing. Again for fully extended conformations, for **3a**, this is calculated to be about 53 Å, and for **4a**, 57–58 Å. Extended conformations are assumed to be much more likely for compounds **3** and **4**, because the molecules are then sterically less crowded about the core. However it is not impossible, especially for compound **1**, for the molecule to be otherwise arranged.

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Table 2. X-Ray diffraction data for mesomorphic compounds.

| Compound	Angle/$^{\circ}2\theta$ (intensity)	d-spacing/Å	Diffraction peak width/$^{\circ}2\theta$
1A	4·44 (w)	20·0	0·30
	6·35 (v.w)	13·70	0·40
	19·4 (m)	4·60	2·00
	21·5 (w)	4·15	1·60
3a	3·77 (m)	24·0	0·40
	510 (w)	17·4	0·30
	20·0 (m)	4·50	1·40
4a	3·55 (m)	26·0	0·25
	4·90 (w)	18·0	0·30
	19·7 (w)	4·55	2·50

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Powder X-ray diffraction measurements were made to check these predictions of the layer spacing periodicity and to investigate the liquid crystalline mesophase structure in quenched samples. The resulting patterns are relatively simple and informative. The Bragg angles and spacings are given in table 2 and diffraction intensity versus angle (2θ) diagrams are shown in figure 2 for compounds 3a and 4a. They all show sharp peaks at low angles indicating ordering into layers and a peak at high angles which is broad or diffuse.

For compound 1a, two low angle peaks are observed, corresponding to 20 Å and 13·70 Å. These are in the ratio 1·5:1, indicating 002 and 003 indexing. The X-ray layer periodicity is thus about 40 Å which agrees with the fully extended molecular length and indicates a fully extended molecular arrangement in the smectic layers. The high angle peak corresponding to 4·6 Å is rather broad and also has a shoulder at 4·15 Å. This is consistent with smectic A ordering, as observed by microscopy. For compound 3a, again two peaks are seen at low angles. This is shown in figure 2 (a). The peaks correspond to 24 and 17·4 Å and are in the ratio 1:1·5, so the layer periodicity is about 48 Å. From molecular models the fully extended molecular length is about 52–53 Å. Therefore the molecules in the layers are in a fully extended conformation. The single, rather broad, but not diffuse, high angle peak indicates a hexagonal arrangement with good ordering within the layers and this suggests a smectic B phase. This may indeed be the high viscosity smectic phase that is observed below about 219°C by DSC and which was identified as an ordered phase by optical microscopy; this is consistent with the DSC because the sample may quench from the isotropic into the more highly ordered phase (see Experimental). However, a smectic A phase is observed at higher temperature, up to the clearing point, 247·5°C. This high angle peak corresponds to approximately 4·5 Å and is the expected lateral spacing between the mesogens in the layers.

Compound 4a shows two peaks at low angles; the ratio of the spacings corresponding to these peaks is 1·5:1, again probably indicating 002 and 003 indexing due to periodic layer spacings in a smectic phase. This is shown in figure 2 (b). At high angles there is one main peak which is quite diffuse. This indicates a fairly liquid ordering in the layers and thus appears to indicate a smectic A phase. The X-ray diffraction data give the layer periodicity (001 index) as 52–53 Å, again showing there is
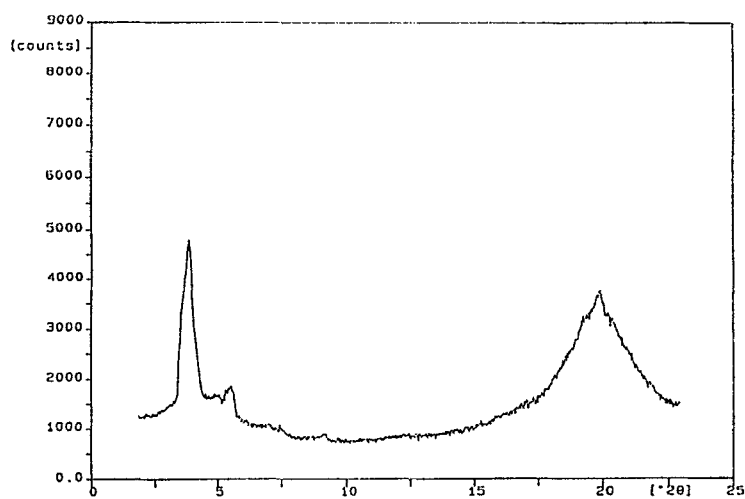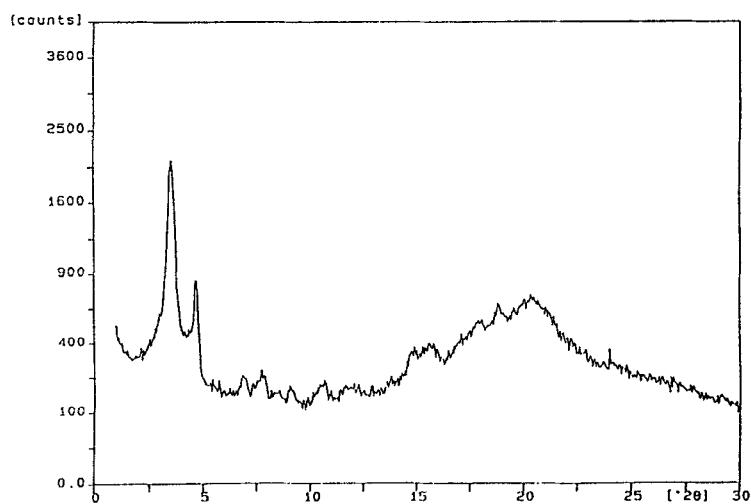
Figure 2. X-ray diffraction spectrum, intensity versus angle(2theta), for *a*) compound **3a**, and (*b*) compound **4a**.
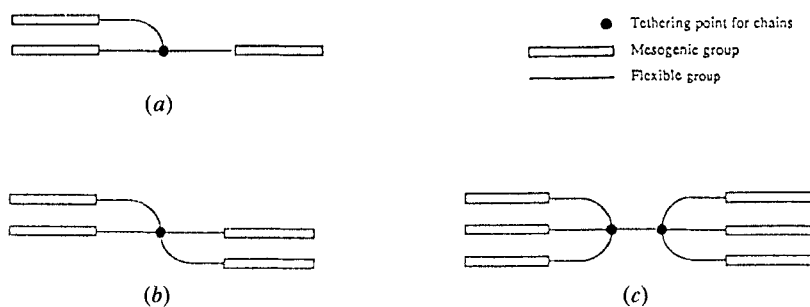

Figure 3. The fully extended molecular arrangements for these materials.

an almost fully extended molecular ordering in the layers of the mesophase. The high angle diffraction corresponds to 4·4 Å, which is typical for the lateral spacing between mesogens.

The fully extended molecular arrangements (see figure 3 (*a*), (*b*) and (*c*)) found for these 3-, 4- and 6-armed molecules are similar to the situation for some analogous tetrahedral molecules, as found by Eidenschink [6] and show that Vorländer's rule [1] is still valid, even for such apparently non-linear molecules.

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