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Tethered Mesogens; 3-Armed Liquid Crystal Molecules

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Some molecules of unusual shape and apparently non-linear geometry, with three mesogenic arms tied directly to a central unit have been investigated for liquid-crystalline behaviour. They showed smectic liquid-crystalline mesophases, which were characterised by DSC, optical microscopy and X-ray diffraction. The temperature ranges of the fluid mesophases for the monotropic compounds were below 87.6°C and for the thermotropic compound was above 142.1°C. The phase for 1 appears to be smectic A.

INTRODUCTION

Structure-property relationships in liquid crystalline systems are particularly attractive subjects for study due to the extreme sensitivity of mesophase properties to small changes in chemical structure. We are interested in examining the limits of structure that are compatible with liquid crystallinity. One such area is *Twinned Mesogens*, in which independent mesogenic molecules are twinned or joined to produce a new molecular species which may or may not be mesogenic.[2–5] The nematic dendrimer molecules of Percec[6] are a dramatic example of mesogens tied to a central (globular) unit. The resulting dendrimers show nematic ordering. Also, Eidenschink[10] has made liquid-crystalline molecules based on pentaerythritol with some additional flexible hydrocarbon spacers. These adopt an extended calamitic conformation giving rise to the mesophase.

It has been suggested[7] that tethered structures with three mesogenic arms be investigated; by tethered we mean there is a common point connecting three or more mesogenic units. We therefore wished to determine how the mesogenic units self-assemble in such a crowded molecular geometry, and whether the mesogenic field is a sufficiently strong driving force to alter chain conformations to produce a mesogenic assembly of the molecules. Here we describe the synthesis and characterisation of three molecules containing linear mesogens linked together. Schematic representations of

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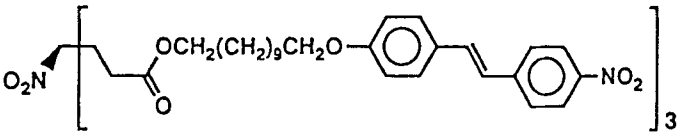
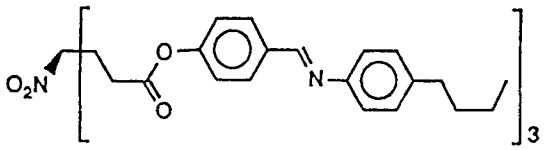
the compounds are shown below.

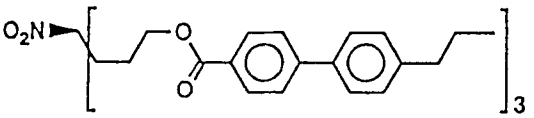
Compound 1



Compound 2



Compound 3.



EXPERIMENTAL

Compound 1

This was prepared from 4-(11-hydroxyundecyloxy) 4′-nitrostilbene. The 4-hydroxy-4′-nitrostilbene precursor of this compound was synthesised as described in reference 9, and was converted to the aliphatic alcohol by reaction with 11-bromoundecanol. Then this was reacted with nitromethane-tris(propanoic acid), using the carbodiimide activating method[8] of ester formation to give 1.

IR, 1734 (C=O, *s*), 1250 (C—O, *s*), 1175 (C—O, *s*), 1540 (N=O, *m*), 1340 (N=O, *m*), 3100 (C—H Ar, *s*), 1590 (Ar, *m*), 1107 (Ar, *m*), 841 (Ar, *m*) cm.$^{-1}$

NMR ($CDCl_3$, TMS), δ ppm; 8.18 (*AX*, $J = 8.75$, 2H), 7.57 (*AX*, $J = 8.75$, 2H), 7.46 (*AX*, $J = 8.75$, 2H), 6.89 (*AX*, $J = 8.75$, 2H), 7.20 (*AB*, $J = 16.35$, 1H), 6.97 (*AB*, $J = 16.35$, 1H), 4.05 (*t*, $J = 6.75$, 2H), 3.95 (*t*, $J = 6.5$, 2H), 2.28 (*m* 2H), 1.79 (*m* 2H), 1.60 (*m* 2H), 1.41 (*m* 2H), 1.28 (*m* 14H).

Elemental analysis, Calculated %C 70.05, %H 7.4, %N 3.9

Found %C 70.0, %H 7.5, %N 3.8,

Yield, Approximately 90%. Melting Point K 100°C S_A 87.6°C I.

Compound 2

Nitromethane-tris(propanoic acid) and 4-hydroxybenzaldehyde were reacted using the carbodiimide method as above to give the intermediate tris(benzaldehyde) ester. This product was then reacted with 4-butylaniline (15% excess) to give the imine product, 2, in the usual way.

IR, 1755 (C=O, *s*) 1206 (C—O, *s*), 1542 (N=O, *m*), 1360 (N=O, *m*), 1167, 1146 (Ar, *m*), 1625 (C=N, *m*), 3050–3100 (C—H Ar, *w*), 1594 (Ar, *m*) cm.$^{-1}$

NMR ($CDCl_3$, TMS), δ ppm; 7.89 (*AX*, $J = 8.5$, 2H), 7.15 (*m* 6H, three overlapping doublets), 8.45 (*s* 1H), 2.70 (*m*, 2H), 2.62 (*t*, $J = 7.5$, 2H), 2.50 (*m*, 2H), 1.51 (*m* 2H), 1.18 (*m* 2H), 0.91 (*t*, $J = 7.25$, 3H).

Elemental analysis, Calculated %C 74.5, %H 6.7, %N 5.7

Found %C 74.5, %H 6.8, %N 5.6

Yield, Approximately 90%. Melting Point K 142.1°C S_B 149.6°C I

Compound 3

4-propylphenyl-4′-benzoic acid was reached with nitromethane-tris(propanol) using the carbodiimide method, as above.

IR, 1710 (C=O, *s*) 1285 (C—O, *s*), 1540 (N=O, *m*), 1360 (N=O, *m*), 3050 (C—H Ar, *s*), 1609 (Ar, *m*), 790 (Ar, *m*) $cm.^{-1}$

NMR ($CDCl_3$, TMS), δ ppm; 8.04 (*AX*, $J = 7.75$, 2H), 7.64 (*AX*, $J = 7.75$, 2H), 7.47 (*AB*, $J = 7.75$, 2H), 7.21 (*AB*, $J = 7.75$, 2H), 4.35 (*t*, $J = 6.6$, 2H), 2.60 (*t*, $J = 7.5$, 2H), 2.17 (*m* 2H), 1.76 (*m* 2H), 1.65 (*m* 2H), 0.96 (*t*, $J = 7.25$, 3H).

Elemental analysis, Calculated %C 77.3, %H 7.0, %N 1.6

Found %C 77.4, %H 7.0, %N 1.4

Yield, Approximately 90%. Melting Point 156°C (S_A 115.2°C) I

All reagents were obtained from Aldrich Chemical co, except 4-propylphenyl-4′-benzoic acid which was obtained from TCI (Tokyo Kasei Organic Chemicals). Measurements were performed on the following instruments: IR, on Nicolet 510 M spectrometer; NMR, on Bruker WM 250 MHz spectrometer; DSC, on Perkin Elmer Series 7; Polarizing light microscopy, on a Leica Axioscope fitted with a Mettler FP82 microfurnace. The X-ray diffraction measurements were performed on a Philips PW 1710 diffraction system. The samples were prepared by heating to the isotropic and cooling down into the mesophase then quenched in liquid nitrogen and ground to powders for the X-ray measurements. Elemental analyses were performed in the Department of Chemistry, University of Cambridge.

RESULTS AND DISCUSSION

The mesophase transition temperatures are given in the experimental section above. All three compounds examined showed liquid crystalline behaviour. Compound 2 showing bâtonnets on heating and on cooling in the polarising optical microscope (POM) as shown in Figure 1 below, with the total enthalpy change for the two transitions on cooling being approximately equal to that on heating. Compounds 1 and 3 showed monotropic smectic phases on cooling only, having smectic A type fans and 'maltese crosses'. The compounds crystallised on cooling to room temperature. In each case the mesophase observed in the POM was smectic implying a lamellar layered structure. This is confirmed by the powder X-ray diffraction discussed below.

The DSC scans and enthalpies of the transitions are in line with the optical identification of the phases, the smectic- to-isotropic transition for compound 2 having

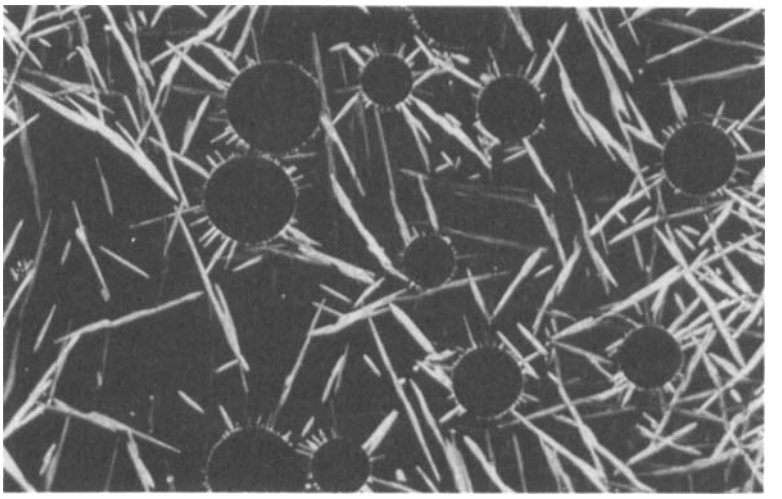


FIGURE 1 Polarising optical micrograph of compound 2 at 100X in the smectic phase.

an enthalpy change at least three times that of the other compounds (34 kJ/mol vs. 8.2 for compound 1 and 10.9 for compound 3), implying a more highly ordered mesophase.

The DSC of compound 3 is shown in Figure 2, below.

The analogue of compound 3 without the 4-propyl group was not liquid crystalline, having a melting point of 63°C, but this was unsurprising as the unsubstituted biphenyl ester group itself is not a typical mesogenic group. In this small series of materials, the

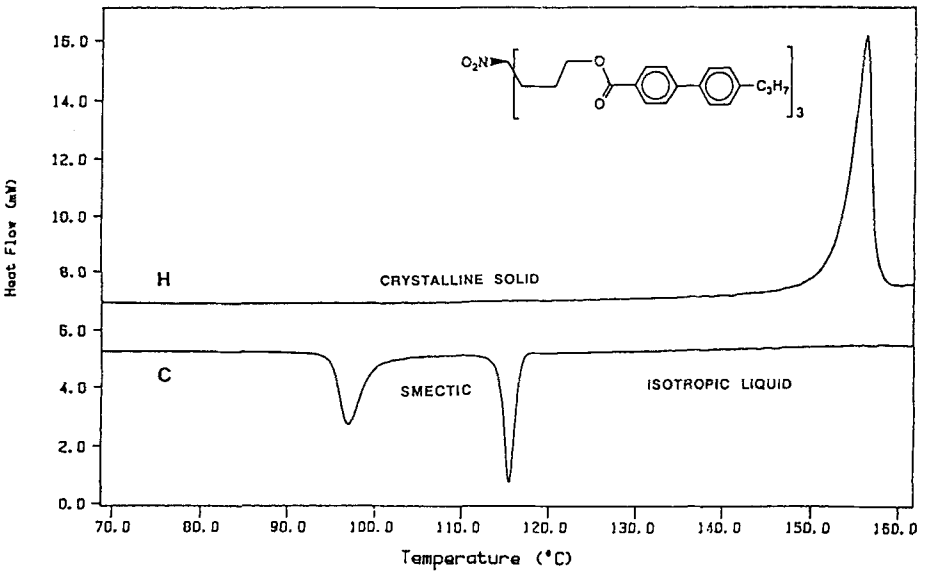
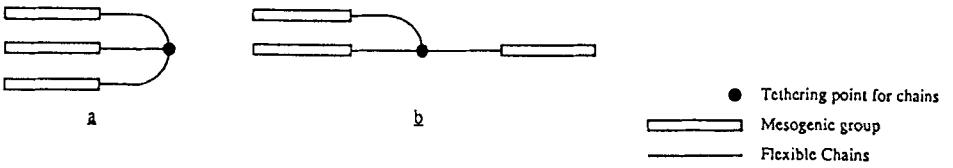


FIGURE 2 DSC thermogram for compound 3, showing second heating and cooling.

ones having typical mesogenic calamitic groups showed a mesophase. Therefore tethering, in this case, is not detrimental to liquid crystallinity even with relatively short tethering chains. In compound 1 the mesophase is stabilised due to the greater decoupling from the tetrahedral tethering point and the mesogenic groups can act more independently. The clearing point of compound 1 is also lower than 2 and 3, presumably again due to the long aliphatic chain.

There are two possibilities for the conformations of these molecules, as shown below and since the compounds exhibit mesophases, a supramolecular assembly of many of these molecules must form an anisotropic array. Therefore either *a* and *b* is possible. Eidenschink has prepared tethered compounds based on the tetrahedral pentaerythritol core,[10] which are compared with small segments of side chain liquid crystalline polymers and in which the fully extended conformation *b* is proposed.



Powder X-ray diffraction measurements were made to investigate the liquid-crystalline mesophase structure on quenched samples. Compounds 2 and 3 showed evidence of cold crystallisation, but still had low angle peaks. The diffraction data for 1 are given in Table 1.

The higher angle peak was diffuse for compound 1 and rather broad for 3. For compound 1, there is only one very weak peak at low angle, corresponding to a layer spacing of 21.2 Å, which is probably a second or third order peak. It was normally not possible to observe peaks below 2–2.5 degrees (2θ) with this equipment and the first order peak may therefore be hidden. From molecular models it can be calculated that the fully extended length of one arm, to the end of the nitro group, is 32 Å and the fully extended molecular length is about 60 Å. Therefore it is most likely that this is in fact a third order peak and the layer periodicity is approximately 63 Å, assuming the molecules have a fully extended molecular layer arrangement (they could be tilted, but this was not observed optically, or have a bilayer type ordering due to the polar nitro groups, see below). The diffuse high angle peak indicates a liquid structure within the layers and this suggests a smectic A phase. The centre of this peak corresponds to approximately 4.1 Å and is the lateral spacing between the mesogens in the layers. This spacing is a little smaller than the other compounds (2 and 3) because this molecule is mostly composed of a methylene chain, which is slightly narrower than the phenylene

TABLE I

X-Ray diffraction data for mesomorphic compound 1

Compound	Angle (Deg. 2theta) (intensity)	*d*-value (Ångstroms)	Diffraction peak width (Deg. 2theta)
1	4.17 (v.w)	21.20	0.60
	21.60 (m)	4.10	5.00

units. The calculated length of each arm to the nitro group for 2 is approximately 22 Å while for the fully extended molecule the end to end length is about 43 Å. The X-ray diffraction shows the lowest angle peak at about 41–42 Å, although for the reasons mentioned this value is not reliable. At high angle there is one main peak which was narrower than for the other compounds 1 and 3, (which again may be due to crystallisation), corresponding to 4.5 Å. Note that the mesophase for compound 2 was quite fluid (in the POM). In compound 3, two low angle peaks are observed. The extended molecular length is approximately 40 Å, and the lower angle peak corresponded to about 40 Å. The high angle peak corresponding to 4.6 Å is rather broad but also has a shoulder at 4.15 Å.

The fact that the X-ray layer spacings (if not first order) are about twice the length of one arm of these molecules does not necessarily imply an extended conformation as shown in *b* above. There is the possibility of bilayer formation, facilitated by the polar nitro groups, with the molecules in the conformation shown in *a*, leading to the same (double) layer spacing. However, while this is quite possible in 1, it is less likely in 2 and 3 due to steric repulsions between the three arms (with shorter spacers) and crowding about the central nitro-methane carbon atom. The fully extended arrangement (b) of these molecules is similar to the situation observed in the analogous tetrahedral molecules, found by Eidenschink.[10] Although these molecules are similar in structure to the interdigitated 'biforked' mesogens with smectic A phases,[11] no evidence for interdigitation has been found.

Acknowledgement

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