Cyclopalladated acac and cp liquid crystals: a comparative study

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The cyclopalladation of mesogenic Schiff bases yields two series of novel metallomesogens. The flat acetylacetonate derivatives show both nematic and smectic A phases with extended mesogenic ranges. In contrast, the non-planar cyclopentadienyl complexes show nematic phases at much lower temperatures than those of the acetylacetonate complexes.

There is currently much interest in the synthesis of metal-containing liquid crystals owing to the perceived advantages of combining the properties of liquid crystal systems with those of transition metals. The area has been well reviewed recently,[1–5] with excellent new work appearing constantly.[6–11] Cyclopalladated compounds have proved to be a particularly fertile area of research, with many different examples from many different groups.[10,12–22]

We have been studying a number of cyclopalladated Schiff base compounds with two very different co-ligands and present our results here.

Synthesis

The synthesis of the new compounds described here, **3** and **5**, is summarised in Scheme 1. The synthesis of the 4-alkyloxy-*N*-(4′-alkyloxybiphenyl)benzylidene ligands **1** *via* a simple condensation of the appropriate aldehyde and aniline proceeded in high yield. The cyclopalladation step to give the intermediate **2** was essentially quantitative, and **2** was used without further purification. The synthesis of the acetylacetonate (acac) derivatives **3** from **2** proceeded in good yield, and these complexes were purified by column chromatography. The synthesis of the cyclopentadienyl (cp) complexes **5** from **2** *via* **4** gave a poor yield overall, after purification. All homologues of compounds **1**, **3** and **5** were analysed by ^{1}H and ^{13}C NMR and gave good elemental analyses (see Table 2, later).

Thermal properties

The thermal behaviour of the ligands **1** is listed in Table 1 and summarised in Fig. 1. Thus, all the ligands showed smectic F, smectic C and nematic phases before clearing. The phases were identified on the basis of their optical texture, the nematic and smectic C phases exhibiting schlieren textures, the nematic showing both four- and two-point brushes, the smectic C only four-point brushes. The smectic F phase showed a schlieren-mosaic type texture on cooling from the smectic C phase. The absence of any point disclinations allowed us to distinguish it from the smectic I phase.

The thermal behaviour of the acac complexes **3** is listed in Table 1 and summarised in Fig. 1. Thus, all the complexes showed a smectic A phase and, with the exception of **3d**, a nematic phase before clearing. The phases were identified on the basis of their optical texture. The smectic A phase appeared as a focal-conic fan texture which separated on cooling from the isotropic as batonnets which consisted of growing focal-conic domains. The melting and clearing points of complexes **3** neatly mirror those of the ligands from which they are derived: the melting points of complexes **3** are *ca.* 10 K lower, and the clearing points are essentially the same. The fact that acac complexes do not exhibit the more ordered smectic phases shown by the ligands is not surprising when one considers that the shape of the complexes will be distorted away from the calamitic shape of the ligand by the presence of the Pd(acac) moiety on the side. Presumably this group disrupts the packing of the molecule within the crystal, resulting in the lower melting point of the complexes compared with the ligands. The absence of a nematic phase for compound **3d** is not unexpected given the presence of the two long chains (seven carbons) at either end of the molecule, which presumably stabilise the smectic phase. It is interesting to note that the clearing points of complexes **3a** and **3b**, which both have four carbons on the biphenyl group, are very similar, as are those of **3c** and **3d**, which both have seven carbons. It is also interesting to note that the stability of the smectic phase seems to be related to the length of the chain on the cyclopalladated ring. Thus, complexes **3b** and **3d**, which both have seven carbons on the cyclopalladated ring, locating the bulky Pd(acac) moiety more towards the centre of the molecule. have the most stable smectic A phases.

The thermal behaviour of the cp complexes **5** is listed in Table 1 and summarised in Fig. 1. Thus, all the complexes showed only a nematic phase, with the exception of **5d**, which exhibits a smectic A phase too. The phases were identified on the basis of their optical texture, the nematic and smectic A phases exhibiting classic textures. The melting and clearing points of complexes **5** are much lower than those of both the ligands **1** and the acac complexes **3**. The fact that cp complexes do not exhibit the more ordered smectic phases is not surprising when one considers the shape of the complexes. Whilst both the ligands and the acac complexes can be thought of as essentially planar, the cp ring is perpendicular to the plane of the ligand. Clearly this group disrupts the packing of the molecule within the crystal, resulting in the reduced melting and clearing points of the complexes and the destabilisation of the smectic phases. The presence of a smectic phase for compound **5d** is not surprising given the presence of the two long chains (seven carbons) at either end of the molecule, and this mirrors the behaviour of the acac complex **3d**. It is interesting to note that the melting points of complexes **5a** and **5c**, which both have four carbons on the cyclopalladated ring, are very similar, as are those of **5b** and **5d**, which both have seven, and thus the bulky Pd(cp) moiety located more towards the centre of the molecule.

Compounds **5** decompose at *ca.* 180 °C on transition to the isotropic liquid, whereas compounds **3** do not decompose at temperatures almost 100 K higher. Chemically, the major difference between the two complexes is the electron count on the palladium: the cp complex has a formal count of $18e^{-}$, whereas the acac complex has one of $16e^{-}$. The geometry of the cp complex is formally trigonal bipyramidal, whilst that of the acac complex is square planar. The chemistry of pal-

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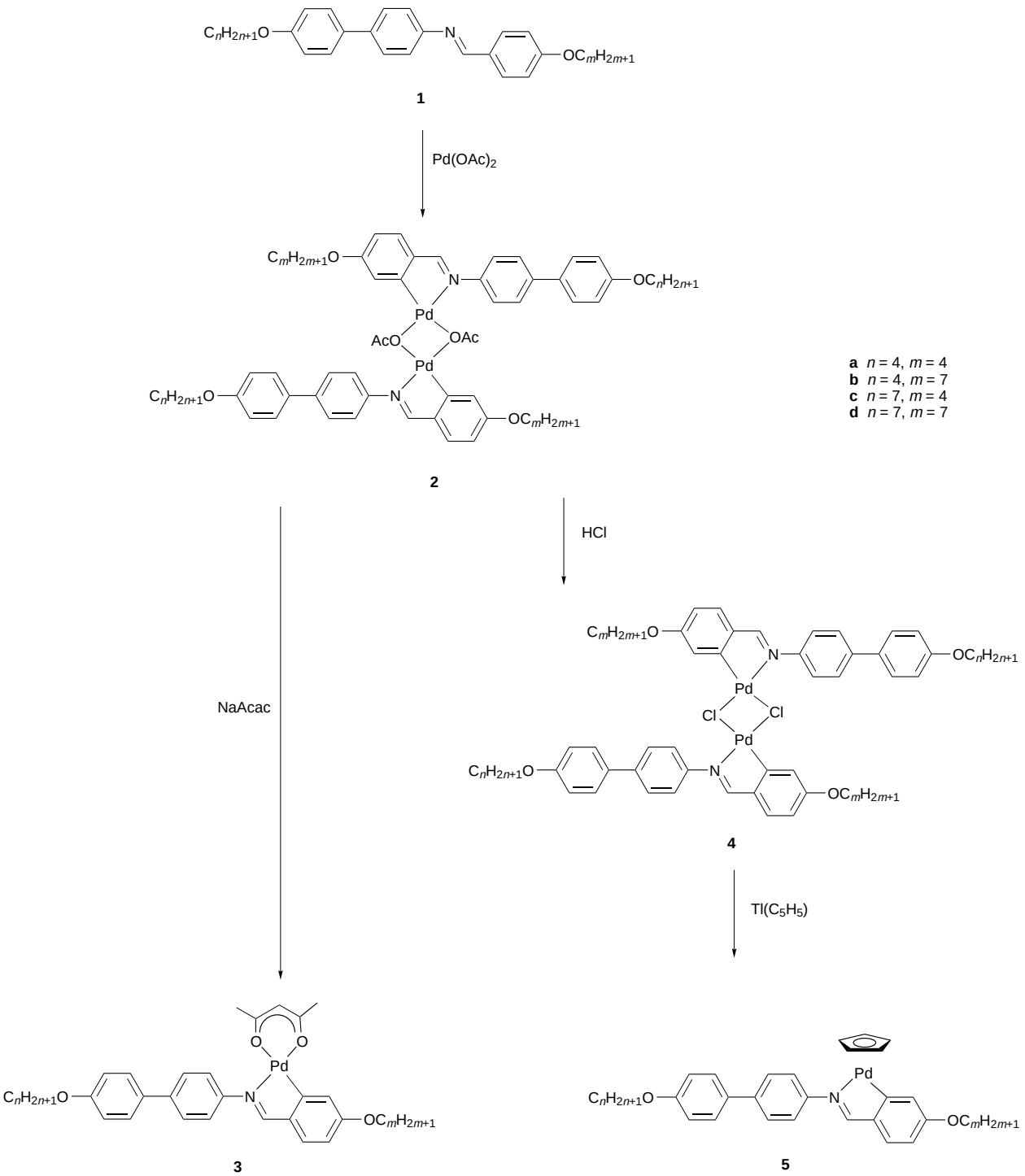


Scheme 1

ladium(II) is dominated by square-planar $16e^-$ species, with very few examples of $18e^-$ complexes. Thus the observed thermal stabilities of our compounds are entirely reasonable.

Compounds **5** represent the only isomerically pure half-sandwich liquid crystals ever reported. The only other half-sandwich liquid crystals known are those reported by Ghedini *et al.*,[10] where an azobenzene cyclometallates to give two isomeric products. Ghedini's compounds, which like ours contain three aromatic rings, only exhibited nematic phases and at very similar temperatures to ours. Ghedini *et al.* also synthesised a couple of compounds with only two aromatic rings, but observed no mesogenic behaviour for these cp derivatives. In contrast, some earlier work by Espinet *et al.*[14] had shown that the acac derivatives of a two-ring system did exhibit mesogenic behaviour, with both smectic A and nematic phases being observed.

Thus it can be seen that our results are consistent with established precedent: compared with the acac group, the cp group brings down both the melting and clearing points of the complexes and shows a strong preference for the nematic phase. It is clear that the cp group will become a popular motif in metallomesogen chemistry.

Experimental

General

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on either a Bruker AC250 or

Table 1 Mesogenic behaviour of compounds **1**, **3** and **5**

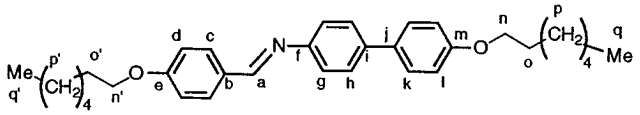
compd.	trans.	T/°C	trans.	T/°C	trans.	T/°C	trans.	T/°C
1a	$C–S_F$	191	$S_F–S_C$	197	$S_C–N$	201	N–I	272
1b	$C–S_F$	160	$S_F–S_C$	171	$S_C–N$	216	N–I	252
1c	$C–S_F$	171	$S_F–S_C$	178	$S_C–N$	215	N–I	255
1d	$C–S_F$	157	$S_F–S_C$	161	$S_C–N$	217	N–I	254
3a	$C–S_A$	184	$S_A–N$	209	N–I	260		
3b	$C–S_A$	162	$S_A–N$	241	N–I	261		
3c	$C–S_A$	155	$S_A–N$	225	N–I	249		
3d	$C–S_A$	141	$S_A–I$	245				
5a	C–N	125	N–I	182[a]				
5b	C–N	101	N–I	145				
5c	C–N	125	N–I	179[a]				
5d	$C–S_A$	92	$S_A–N$	165	N–I	178[a]		

*Some decomposition.

on an AC400 in $CDCl_3$ and are referenced to external $SiMe_4$, assignments being made with the use of decoupling, NOE and the DEPT and COSY pulse sequences. Thermal analyses were performed on an Olympus BH2 microscope equipped with a Linkam HFS 91 heating stage and a TMS90 controller, at a heating rate of 10 K min^{-1}. All elemental analyses were performed by Warwick Microanalytical Service.

Preparation of 4-heptyloxy-*N*-(4′-heptyloxybiphenyl)benzylidene, 1d

Compound **1d** is described in detail, all other homologues were prepared similarly. 4-Heptyloxybenzaldehyde (1.61 g, 7.10×10^{-3} mol) was added to a solution of 4′-heptyloxy-4-aminobiphenyl (2.00 g, 7.10×10^{-3} mol) in toluene (200 ml). The mixture was heated at reflux for 2 h using a Dean Stark trap and in the presence of molecular sieves. The solvent was removed and the product recrystallised from chloroform. Yield 2.47 g (72%, 5.1×10^{-3} mol).



NMR data: δ_H: 8.44 (1 H, s, H_a), 7.87 (2 H, AA′XX′, H_c), 7.57 (2 H, AA′XX′, H_h), 7.55 (2 H, AA′XX′, H_k), 7.28 (2 H, AA′XX′, H_g), 6.96 (2 H, AA′XX′, H_d), 6.95 (2 H, AA′XX′, H_l), 4.03 [2 H, t, ^3J(HH) 7.0 Hz, $H_{n'}$], 4.01 [2 H, t, ^3J(HH) 7.0 Hz, H_n], 1.81 (4 H, m, $H_{o,o'}$), 1.40 (16 H, m, $H_{p,p'}$), 0.89 [6 H, t, ^3J(HH) 7.0 Hz, $H_{q,q'}$]; δ_C: 159.2 (C_a), 158.5 ($C_{e,m}$), 138.1 (C_i), 132.9 ($C_{b/j}$), 130.5 (C_c), 127.7 (C_h), 127.2 (C_k), 121.2 (C_g), 114.7 ($C_{d/l}$), 114.6 ($C_{d/l}$), 68.0 (C_n), 67.8 ($C_{n'}$), 31.7 ($C_{p,p'}$), 29.1 ($C_{o,o'}$), 28.9 ($C_{p,p'}$), 25.9 ($C_{p,p'}$), 19.2 ($C_{p,p'}$), 14.0 ($C_{q,q'}$).

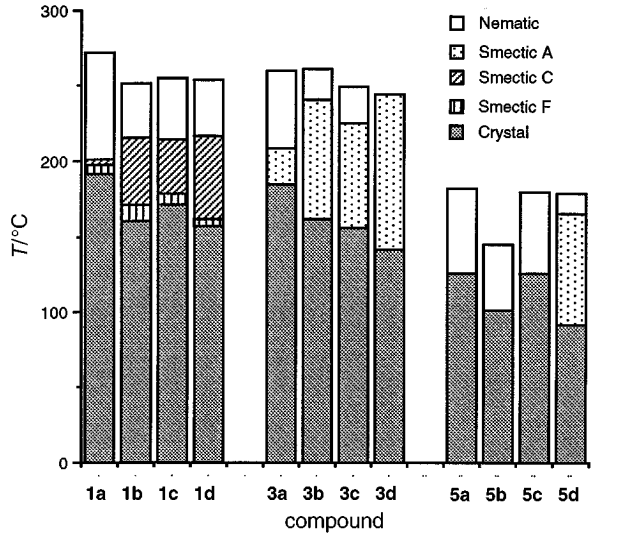
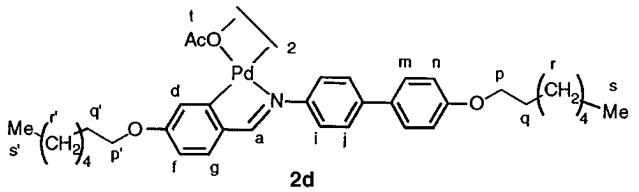


Fig. 1 Phase behaviour of compounds **1**, **3** and **5**

The mesogenic behaviour of all homologues is summarised in Fig. 1 and detailed in Table 1. Elemental analyses are detailed in Table 2.

Preparation of orthometallated palladium acetate complex, 2d

Compound **2d** is described in detail, all other homologues were prepared similarly. Ligand **1d**, (0.41 g, 8.5×10^{-4} mol) and palladium acetate (0.191 g, 8.5×10^{-4} mol) were dissolved in acetic acid (250 ml) at 60 °C, and stirred (20 h). The solvent was removed, the crude product dissolved in chloroform, filtered to remove traces of palladium black and the yellow solution evaporated to dryness. Yield 0.55 g (98%, 4.2×10^{-4} mol).



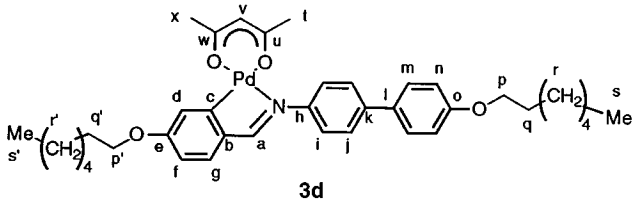
NMR data: δ_H: 7.59 (1 H, s, H_a), 7.51 (2 H, AA′XX′, H_m), 7.35 (2 H, AA′XX′, H_j), 7.18 [1 H, d, ^3J(HH) 8.4 Hz, H_g], 6.95 (2 H, AA′XX′, H_n), 6.78 (2 H, AA′XX′, H_i), 6.59 [1 H, dd, ^3J(HH) 8.4 Hz, ^4J(HH) 2.3 Hz, H_f], 6.03 [1 H, d, ^4J(HH) 2.3 Hz, H_d], 4.05 [2 H, t, ^3J(HH) 6.4 Hz, $H_{p'}$], 4.00 [2 H, t, ^3J(HH) 6.7 Hz, H_p], 1.90 (3H, s, H_t), 1.81 (4 H, m, $H_{q,q'}$), 1.40 (16 H, m, $H_{r,r'}$), 0.88 [6 H, t, ^3J(HH) 7.1 Hz, $H_{s,s'}$].

Table 2 Elemental analysis data for compounds **1**, **3** and **5**

			found (expected)		
compd.	n	m	C (%)	H (%)	N (%)
1a	4	4	80.9 (80.8)	7.8 (7.8)	3.4 (3.5)
1b	4	7	81.2 (81.2)	8.4 (8.4)	3.1 (3.2)
1c	7	4	81.6 (81.2)	8.4 (8.4)	3.2 (3.2)
1d	7	7	81.3 (81.6)	8.7 (8.9)	3.0 (2.9)
3a	4	4	63.4 (63.4)	6.2 (6.2)	2.3 (2.3)
3b	4	7	64.5 (64.9)	6.6 (6.7)	2.0 (2.2)
3c	7	4	64.7 (64.9)	6.7 (6.7)	2.3 (2.2)
3d	7	7	66.3 (66.0)	7.2 (7.3)	1.9 (2.0)
5a	4	4	69.9 (67.2)	6.2 (6.2)	2.4 (2.5)
5b	4	7	68.1 (68.5)	6.6 (6.7)	2.1 (2.3)
5c	7	4	68.2 (68.5)	6.9 (6.7)	2.2 (2.3)
5d	7	7	69.5 (69.6)	7.6 (7.2)	2.2 (2.1)

Preparation of palladium acetylacetonate complex, 3d

Compound **3d** is described in detail, all other homologues were prepared similarly. Sodium acetylacetonate (0.038 g, 3.08×10^{-4} mol) was added to a solution of the acetate bridged palladium complex **2d** (0.200 g, 1.54×10^{-4} mol) in acetone (150 ml) at room temperature and stirred (2 h). The solvent was removed and the product was purified by column chromatography on silica, eluting with a 50 : 50 mixture of dichloromethane and hexane. Yield 0.135 g (64%, 1.96×10^{-4} mol).



3d

NMR data: δ_H: 8.03 (1 H, s, H_a), 7.58 (2 H, AA′XX′, H_j), 7.51 (2 H, AA′XX′, H_m), 7.46 (2 H, AA′XX′, H_i), 7.31 [1 H, m, ^3J(HH) 8.1 Hz, H_g], 7.14 [1 H, d, ^4J(HH) 2.3 Hz, H_d], 6.97 [2 H, AA′XX′, ^3J(HH) 8.4 Hz, H_n], 6.60 [1 H, dd, ^3J(HH) 8.3 Hz, ^4J(HH) 2.3 Hz, H_f], 5.36 (1 H, s, H_v), 4.08 [2 H, t, ^3J(HH) 6.5 Hz, $H_{p'}$], 4.02 [2 H, t, ^3J(HH) 6.5 Hz, H_p], 2.10 (3H, s, H_x), 1.91 (3H, s, H_t), 1.84 (4 H, m, $H_{q,q'}$), 1.40 (16 H, m, $H_{r,r'}$), 0.90 [6 H, t, ^3J(HH) 8.2 Hz, $H_{s,s'}$]; δ_C: 188.3 ($C_{u/w}$), 185.7 ($C_{u/w}$), 172.4 (C_a), 160.4 (C_e), 158.7 (C_o), 146.3 (C_h), 139.7 ($C_{b/c}$), 138.8 ($C_{b/c}$), 132.6 (C_k), 129.5 (C_g), 127.9 (C_m), 127.6 (C_l), 126.5 (C_j), 123.6 (C_i), 115.7 (C_d), 114.7 (C_n), 111.4 (C_f), 100.1 (C_v), 67.7 (C_p), 67.5 ($C_{p'}$), 31.2 ($C_{q,q'}$), 31.1 ($C_{q,q'}$), 29.2 ($C_{r,r'}$), 27.8 (C_t), 27.4 (C_x), 25.9 ($C_{r,r'}$), 19.1 ($C_{r,r'}$), 13.8 ($C_{s,s'}$).

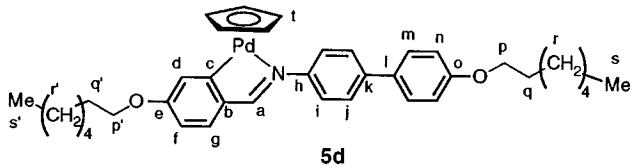
The mesogenic behaviour of all homologues is summarised in Fig. 1 and detailed in Table 1. Elemental analyses are detailed in Table 2.

Preparation of chloro-bridged palladium complex, 4d

Compound **4d** is described in detail, all other homologues were prepared similarly. One equivalent of 0.4 mol dm^{-3} methanolic hydrogen chloride was added to the acetato bridged palladium complex **2d**, (0.356 g, 3.1×10^{-4} mol) dissolved in chloroform (250 ml) at room temperature causing the clear yellow solution to become cloudy. The solvent was removed and the crude product was washed with acetone (15 ml) and filtered to collect the product. Yield 0.21 g (54%, 1.72×10^{-4} mol).

Preparation of palladium cyclopentadienyl complex, 5d

Compound **5d** is described in detail, all other homologues were prepared similarly. Thallium cyclopentadienide (0.200 g, 7.64×10^{-4} mol, 4 equiv.) was added to a solution of the chloro-bridged palladium complex **4d** (0.239 g, 1.91×10^{-4} mol) in THF (250 ml) and heated at reflux (1 h). The mixture was filtered and the solvent removed. The crude product was purified by column chromatography on silica, eluting with chloroform to yield a red solid. Yield 0.040 g (28%, 5.16×10^{-5} mol).



5d

NMR data: δ_H: 7.86 (1 H, s, H_a), 7.54 (4 H, m, $H_{i,m}$), 7.52 [1 H, d, ^3J(HH) 8.4 Hz, H_g], 7.35 (2 H, AA′XX′, H_j), 7.24 [1 H, d, ^4J(HH) 2.3 Hz, H_d], 6.97 (2 H, AA′XX′, H_n), 6.59 [1 H, dd, ^3J(HH) 8.4 Hz, ^4J(HH) 2.3 Hz, H_f], 5.80 (5 H, s, H_t), 4.02 [2 H, t, ^3J(HH) 6.9 Hz, $H_{p'}$], 4.01 [2 H, t, ^3J(HH) 6.9 Hz, H_p], 1.84 (4 H, m, $H_{q,q'}$), 1.40 (16 H, m, $H_{r,r'}$), 0.90 [6 H, t, ^3J(HH) 8.2 Hz, $H_{s,s'}$]; δ_C: 164.3 (C_a), 158.9 (C_e), 157.7 (C_o), 139.6 ($C_{b/c/h}$), 138.9 ($C_{b/c/h}$), 138.4 ($C_{b/c/h}$), 138.1 ($C_{b/c/h}$), 132.4 (C_k), 131.8 (C_g), 130.5 (C_l), 128.0 ($C_{j/m}$), 127.9 ($C_{j/m}$), 125.6 (C_d), 123.0 (C_i), 114.8 (C_n), 110.5 (C_f), 95.8 (C_t), 68.0 (C_p), 67.8 ($C_{p'}$), 31.8 (C_q), 31.3 ($C_{q'}$), 29.2 ($C_{r,r'}$), 26.0 (C_r), 19.2 ($C_{r,r'}$), 14.1 ($C_{s/s'}$), 13.9 ($C_{s/s'}$).

The mesogenic behaviour of all homologues is summarised in Fig. 1 and detailed in Table 1. Elemental analyses are detailed in Table 2.

We thank the University of Warwick for financial support (D.P.L.), and Johnson-Matthey for loan of chemicals.

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Paper 6/05791H; *Received* 20*th August*, 1996