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# Synthesis and mesogenic properties of novel board-like liquid crystals†

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The syntheses of novel octa- and tetra-substituted systems based on tetrabenz[*a*,*c*,*h*,*j*]anthracene are reported. The disc-shaped octa-substituted material exhibits a columnar mesophase, whereas the tetra-substituted material exhibits a lamellar phase. Binary mixtures of the two materials were examined in order to explore the change over from discotic to calamitic behaviour as a function of concentration. At the crossover point, the possibility of the formation of a biaxial phase was investigated.

## 1. Introduction

Molecular shape determines to a large extent the type of mesophase observed for thermotropic liquid crystals. For example, in general, rod-like molecules give rise to smectic and/or nematic mesophases, whereas disc-like molecules self-organise to give columnar mesophases. Columnar phases are also observed when a flat core is replaced by a pyramidal or conical shaped unit[1] or even when the central core is absent.[2]

Since the theoretical prediction in 1970 of the possibility of the existence of a biaxial nematic phase for thermotropic liquid crystals,[3] much effort has been directed towards designing novel molecules, which in some way combine the features of rods and discs. Several different approaches have been utilised thus far in attempting to obtain low-molecular-weight thermotropic biaxial nematic materials. In the course of these investigations, board-like molecules (sanidic),[4] polycatenar compounds derived from calamitic compounds modified with several terminal chains,[5,6] disc-like molecules where the number of substituents was reduced,[7] rod–disc dimers,[8] disc–disc dimers,[9] different combinations of disc–rod–disc and rod–half-disc dimers[10] were prepared. Theoreticians have suggested an alternative route to producing a thermotropic biaxial nematic phase, which involves mixing rod-like with disc-like molecules rather than specifically linking rods and discs. However, the main drawback of this approach with respect to biaxial nematics is the tendency of both components to phase separate, because of their very different structural features. The design of the above mentioned novel dimeric structures by covalently linking geometrically different units[9–10] was used with the intention of overcoming issues of phase-separation.

The aim of our work was to explore the borderline, as described by theory,[11] between calamitic and discotic systems by studying novel board-like molecules in the hope of observing a nematic biaxial phase either for individual materials or in binary mixtures between calamitic and discotic systems. The targeted compounds (**I**) were based on the tetrabenz[*a*,*c*,*h*,*j*]anthracene structure. Triphenylene is an excellent core unit for generating disc-like molecules that give columnar mesophases[12] and the tetrabenz[*a*,*c*,*h*,*j*]anthracene unit is formally related to a triphenylene structure but is more elongated and board-like because of the fusion of a phenanthrene unit at its 9,10-bond with the 2,3-bond of triphenylene. This new architecture therefore gave us the opportunity to study both rod-like (*via* tetra-substituted) and disc-like (*via* octa-substituted) systems.

## 2. Experimental

### 2.1. Materials and characterisation techniques

Starting materials were purchased from Aldrich or Lancaster and used without further purification; 2-bromooctane was of technical grade. Column chromatography was performed over silica gel (35–75 μm particle size, 200 to 400 mesh, Merck). Analytical TLC was performed on Kieselgel F-254 precoated silica gel plates (Merck).

The structures of the compounds prepared were confirmed by spectroscopic methods. $^1$H NMR spectra were recorded using either a JEOL JNM-GX (270 MHz) or a JEOL JNM-LA (400 MHz) spectrometer with tetramethylsilane (TMS) as an internal standard; *J* values are given in Hz. IR spectra were recorded on a Perkin–Elmer 882 infrared spectrophotometer. Mass spectra were measured with a Finnigan-MAT 1020 GC/MS. Elemental analyses were performed on a Fisons Instruments Carlo Erba EA 1108 CHN analyser using acetanilide as the reference standard. A Perkin–Elmer DSC 7 Differential Scanning Calorimeter was used for determining the transition temperatures and transition enthalpies; heating and cooling rates were 10 °C min$^{-1}$ and the transition temperatures reported are the onset values. The calorimeter was calibrated against pure indium metal (mp = 156.6 °C, enthalpy change = 28.5 J g$^{-1}$). An Olympus BH-2 polarizing microscope equipped with a Mettler FP82 HT hot-stage and a Mettler FP90 central processor was used to determine melting points, examine the thermal transitions and observe the defect textures of the liquid crystal phases. XRD measurements were performed with a Pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-Kα beam. The sample was held in Lindemann glass capillaries (1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The patterns were collected on flat photographic film.

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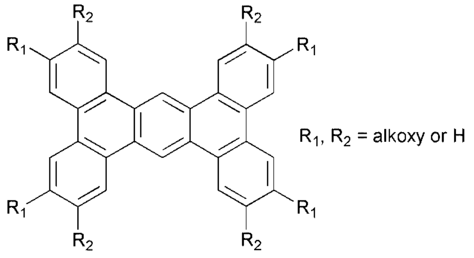

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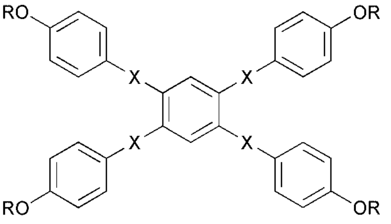
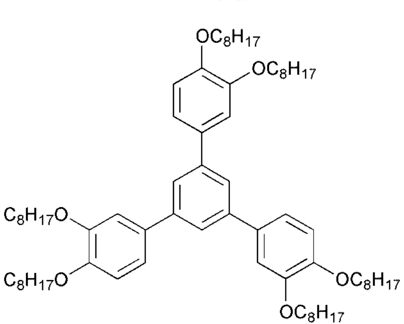


II X =C≡C, R = $OC_{13}H_{27}$: K 96 (N 74.2) °C Iso Liq
III X = (central ring)-OOC, R = $OC_8H_{17}$: K 109.9 (N 105.4) °C Iso Liq
IV X = (central ring)-OOC, R = $OC_{12}H_{25}$: K 102.2 (SmC 88.5 N 100.20) °C Iso Liq



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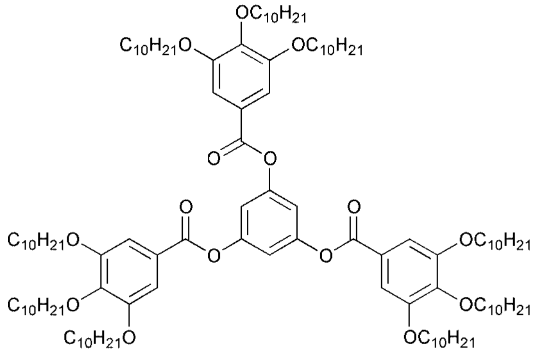


VI

K (N 27.3) 46.8 °C Iso Liq

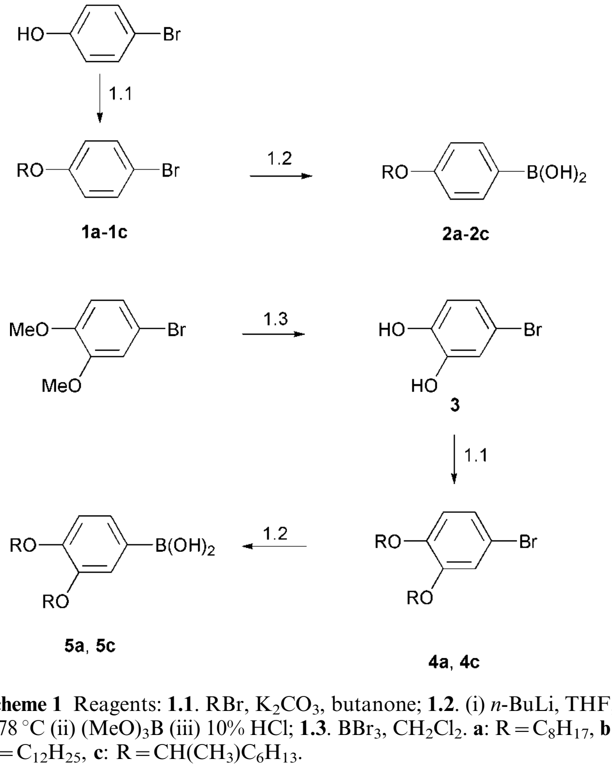
Molecular modelling studies were performed on a Silicon Graphics workstation (Indigo XS24, 4000) using the programs Quanta and CHARMm. Within CHARMm, the Adopted Basis Newton Raphson (ABNR) algorithm was used to locate the molecular conformation with the lowest potential energy. The minimisation calculations were performed until the root mean square (RMS) force reached 4.184 kJ $mol^{-1}$ $Å^{-1}$, which is close to the resolution limit. The RMS force is a direct measure of the tolerance applied to the energy gradient (*i.e.*, the rate of change of potential energy with step number) during each cycle of minimisation. The calculation was terminated in cases where the average energy gradient was less than the specified value. The results of the molecular mechanics calculations were generated using the programs QUANTA V4.0 and CHARMm V22.2. The programs were developed and integrated by Molecular Simulations Inc. The modelling packages assume the molecules to be a collection of hard particles held together by elastic forces, in the gas phase, at absolute zero, in an ideal motionless state, and the force fields used are those described in CHARMm V22.2. In addition to Quanta and CHARMm, molecular simulations were generated using an Apple MacIntosh G3 computer and *ChemDraw3D$^{TM}$* as part of a *ChemDraw Ultra 6.0* programme.

## 2.2. Synthesis of materials

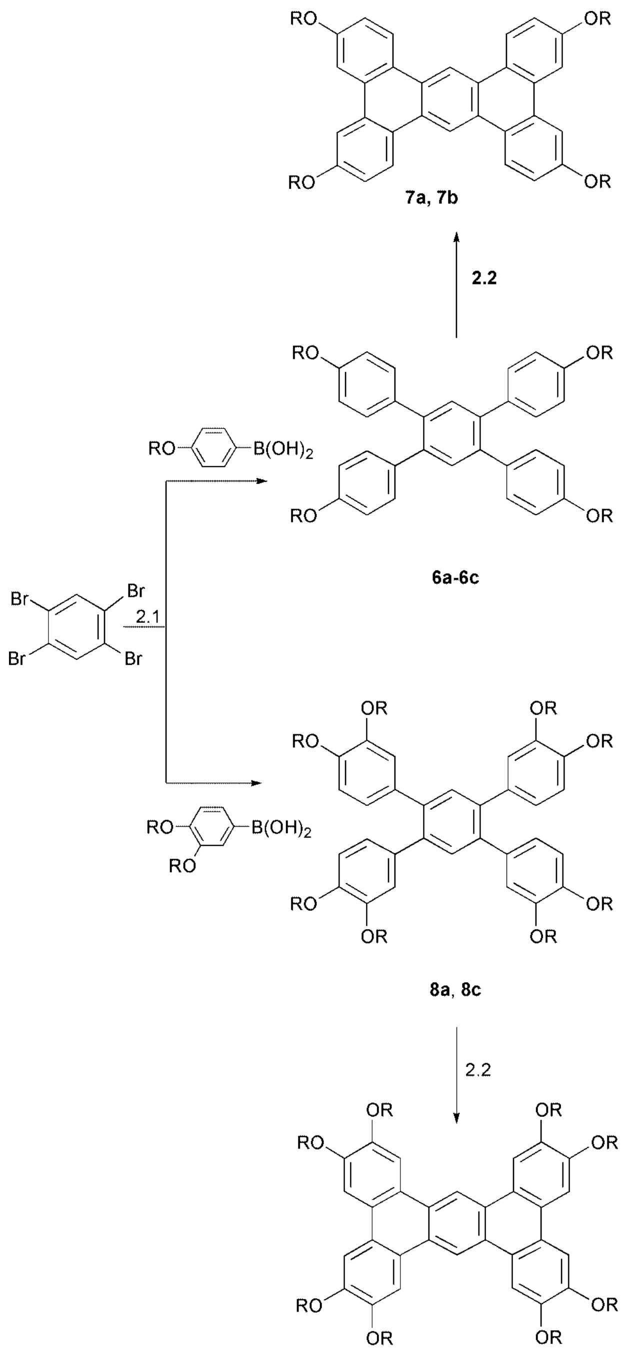
The preparation of tetrabenz[*a*,*c*,*h*,*j*]anthracene and some related derivatives have been achieved using extreme reaction conditions involving pyrolysis at temperatures up to 400 °C.[13] Furthermore, none of the compounds reported so far have lateral alkoxy substituents. We have developed an unambiguous and efficient route to these substituted derivatives, which have more flexible regions and are therefore conducive to the formation of liquid-crystalline materials. The synthetic pathways used in the preparation of the targeted compounds are shown in Schemes 1 and 2.

Alkylation of 4-bromophenol and 4-bromo-1,2-dihydroxybenzene with the appropriate bromoalkane, following standard procedures yielded compounds **1a–1c**, **4a** and **4c**. Boronic acids **2a–2c**, **5a** and **5c** were prepared by the reaction of the alkoxybromo derivatives with *n*-butyllithium and subsequent treatment with trimethyl borate followed by *in situ* hydrolysis using hydrochloric acid.[14] Demethylation of 4-bromo-1,2-dimethoxybenzene using boron tribromide afforded the required starting material 4-bromo-1,2-dihydroxybenzene **3**.[15]

Compounds **6a–c**, **8a** and **8c** were prepared by the tetrakis(triphenylphosphine)palladium(0)-catalysed coupling of commercially available 1,2,4,5-tetrabromobenzene with the boronic acids, according to the procedure described by Hird *et al.*[16] Nearly quantitative conversions were achieved in spite of the steric hindrance arising from the *ortho*-substituents and the presence of four reactive sites in the molecule. The key step in the synthesis was the oxidative cyclodehydrogenation[17] of the 1,2,4,5-tetrasubstituted intermediates using $FeCl_3$ as the Lewis acid, to afford the final compounds. In the case of compound **8a**, with disubstituted peripheral aromatic rings, the cyclisation reaction proceeded regioselectively affording only the desired compound **9a**. The presence of a single reaction product was confirmed by the $^1H$ NMR spectra, which showed only singlets for the aromatic protons. It has been reported previously that



**Scheme 1** Reagents: **1.1**. RBr, $K_2CO_3$, butanone; **1.2**. (i) *n*-BuLi, THF, −78 °C (ii) $(MeO)_3B$ (iii) 10% HCl; **1.3**. $BBr_3$, $CH_2Cl_2$. **a**: $R = C_8H_{17}$, **b**: $R = C_{12}H_{25}$, **c**: $R = CH(CH_3)C_6H_{13}$.



**Scheme 2** Reagents: **2.1**. Pd(PPh$_3$)$_4$, DME, 20% Na$_2$CO$_3$; **2.2**. FeCl$_3$, dichloromethane, CH$_3$NO$_2$. **a**: R = C$_8$H$_{17}$, **b**: R = C$_{12}$H$_{25}$, **c**: R = CH(CH$_3$)C$_6$H$_{13}$.

compounds with alkoxy substituents undergo oxidative dealkylation in the presence of Lewis acids, which involves ether cleavage and oxidation to quinonoid aromatic structures.[18] It is remarkable that in the work reported here for compounds with *n*-alkoxy substituents, only the cyclised compounds **7a**, **7b** and **9a** were obtained and in 80% yield, and there was no evidence of quinone derivatives being formed. However, when the substituents in the aromatic ring were branched alkoxy chains (compound **6c**), only decomposition of the starting material was observed.

## General synthetic procedures

***1-Bromo-4-octyloxybenzene 1a*** was prepared as described in ref. 14. Yield 95%, bp 76 °C at 0.05 mmHg. $^1$H-NMR (CDCl$_3$) $\delta$ 0.89 (3H, t), 1.25–1.50 (10H, m), 1.76 (2H, quint), 3.91 (2H, t), 6.77 (2H, d), 7.35 (2H, d). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2933, 1492, 1288, 1246, 822, 641.

***1-Bromo-4-dodecyloxybenzene 1b*** was prepared as described for compound **9** in ref. 14. The excess of 1-bromododecane was removed by distillation and the residual oil crystallised at room temperature. The compound was used without further purification in the next step. Yield 90%, mp 34 °C. $^1$H-NMR (CDCl$_3$) $\delta$ 0.88 (3H, t), 1.25–1.50 (18H, m), 1.76 (2H, quint), 3.91 (2H, t), 6.77 (2H, d), 7.36 (2H, d). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2931, 1492, 1287, 1245, 822, 640.

***1-Bromo-4-(1-methylheptyloxy)benzene 1c*** was prepared as described for compound **9** in ref. 14. Yield 77%, bp 130 °C at 0.05 mmHg. $^1$H-NMR (CDCl$_3$) $\delta$ 0.87 (3H, t), 1.25–1.80 (13H, m), 4.29 (1H, sext), 6.76 (2H, d), 7.35 (2H, d). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2937, 1483, 1244, 823, 641.

***4-Octyloxyphenylboronic acid 2a*** was prepared as described for compound **53** in ref. 14. Yield 91%. $^1$H-NMR (CDCl$_3$) $\delta$ 0.89 (3H, t), 1.25–1.55 (10H, m), 1.72–1.88 (2H, m), 4.05 (2H, t), 7.00 (2H, d), 8.14 (2H, d).

***4-Dodecyloxyphenylboronic acid 2b*** was prepared as described for compound **53** in ref. 14. Yield 65%. $^1$H-NMR (CDCl$_3$) $\delta$ 0.88 (3H, t), 1.20–1.50 (18H, m), 1.75–1.90 (2H, m), 4.40 (2H, t), 7.00 (2H, d), 8.15 (2H, d).

***4-(1-Methylheptyloxy)phenylboronic acid 2c*** was prepared as described for compound **53** in ref. 14. Yield 95%. $^1$H-NMR (CDCl$_3$) $\delta$ 0.89 (3H, t), 1.25–1.80 (13H, m), 4.48 (1H, sext), 6.98 (2H, d), 8.14 (2H, d).

***4-Bromo-1,2-dihydroxybenzene 3*** was prepared as described in ref. 15. Yield 98%, mp 85 °C (lit. 85–86 °C).[15] $^1$H-NMR (CDCl$_3$) $\delta$ 5.25 (s, 1H), 5.40 (s, 1H), 6.74 (d, 1H), 6.93 (dd, 1H), 7.02 (d, 1H). IR (KBr) $\nu_{max}$/cm$^{-1}$ 3600–3000, 1616, 1502, 1277, 1181, 1111, 887, 803, 777.

***4-Bromo-1,2-bis(octyloxy)benzene 4a*** was prepared as described for compound **9** in ref. 14. Yield 95% (liquid; crystallises at room temperature but melts below 30 °C). $^1$H-NMR (CDCl$_3$) $\delta$ 0.86–0.90 (6H, m), 1.25–1.50 (20H, m), 1.75–1.85 (4H, m), 3.95 (2H, t), 3.96 (2H, t), 6.73 (1H, d), 6.97–7.00 (2H, m). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2932, 2861, 1503, 1471, 1255, 1222, 1024, 797.

***4-Bromo-1,2-bis(1-methylheptyloxy)benzene 4c*** was prepared as described for compound **9** in ref. 14. Yield 79%, bp 180 °C at 0.02 mmHg, $^1$H-NMR (CDCl$_3$) $\delta$ 0.88 (6H, t), 1.20–1.80 (26H, m), 4.20–4.30 (2H, m), 6.75 (1H, dd), 6.95–7.02 (2H, m). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2935, 2862, 1491, 1379, 1256, 1213, 1134, 1059, 942.

***3,4-Bis(octyloxyphenyl)boronic acid 5a*** was prepared as described for compound **53** in ref. 14. Yield 80%. $^1$H-NMR (CDCl$_3$) $\delta$ 0.40–0.70 (6H, m), 1.25–1.55 (20H, m), 1.82–1.90 (4H, m), 4.08 (2H, t), 4.13 (2H, t), 7.00 (1H, d), 7.68 (1H, d), 7.81 (1H, dd).

***3,4-Bis(1-methylheptyloxy)phenylboronic acid 5c*** was prepared as described for compound **53** in ref. 14. Yield 75%. $^1$H-NMR (CDCl$_3$) $\delta$ 0.85–0.90 (6H, m), 1.25–1.88 (26H, m), 4.40–4.50 (2H, m), 7.00 (1H, d), 7.72 (1H, s), 7.80 (1H, d).

***1,2,4,5-Tetrakis(4-octyloxyphenyl)benzene 6a***: Column chromatography: eluent, hexane–dichloromethane (4 : 1). Recrystallised from ethanol. Yield 65%, mp 103.2 °C. $^1$H-NMR (CDCl$_3$) $\delta$ 0.89 (12H, t, *J* 7.0), 1.28–1.48 (40H, m), 1.73–1.80 (8H, m), 3.92 (8H, t, *J* 6.6), 6.77 (8H, d, *J* 8.8), 7.12 (8H, d, *J* 8.8), 7.42 (2H, s). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2933, 2860, 1612, 1519, 1478, 1246, 1176, 831. MS *m*/*z* 895 (M$^+$), 354, 186, 120, 94, 66 (100%). Calc. for C$_{62}$H$_{86}$O$_4$: C, 83.17; H, 9.68%; found: C, 83.28; H, 9.89%.

***1,2,4,5-Tetrakis(4-dodecyloxyphenyl)benzene 6b***: Column chromatography: eluent, hexane–dichloromethane (4 : 1). Recrystallised from ethanol with drops of toluene. Yield 60%, mp 82.7 °C. $^1$H-NMR (CDCl$_3$) $\delta$ 0.88 (12H, t, *J* 6.8), 1.25–1.45 (72H, m), 1.72–1.80 (8H, m), 3.92 (8H, t, *J* 6.6), 6.76 (8H, d, *J* 8.8), 7.12 (8H, d, *J* 8.8), 7.42 (2H, s). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2927, 2858, 1612, 1521, 1476, 1245, 1177, 1032, 831. Calc. for C$_{78}$H$_{118}$O$_4$: C, 83.66; H, 10.62%; found: C, 83.70; H, 10.71%.

***1,2,4,5-Tetrakis[4-(1-methylheptyloxy)phenyl]benzene 6c***:

Column chromatography: eluent, hexane–dichloromethane (4 : 1). Recrystallised from ethanol. Yield 50%, mp 66.5 °C. $^1$H-NMR ($CDCl_3$) δ 0.88 (12H, t, *J* 6.8), 1.25–1.75 (52H, m), 4.28–4.35 (4H, m), 6.75 (8H, d, *J* 8.2), 7.11 (8H, d, *J* 8.2), 7.44 (2H, s). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2953, 2862, 1611, 1516, 1482, 1246, 1177, 833. MS *m*/*z* 897, 446, 427, 352, 267, 71 (100%). Calc. for $C_{62}H_{86}O_4$: C, 83.17; H, 9.68%; found: C, 83.29; H, 9.75%.

***3,6,12,15-Tetrakis(octyloxy)tetrabenz[a,c,h,j]anthracene 7a***: Recrystallised from ethanol–toluene (2 : 1). Yield 80%, mp 132.3 °C. $^1$H-NMR ($CDCl_3$) δ 0.92 (12H, t, *J* 6.8), 1.34–1.46 (32H, m), 1.53–1.61 (8H, m), 1.88–1.95 (8H, m), 4.19 (8H, m), 7.28 (4H, dd, *J* 2.3 and 9.0), 7.91 (4H, d, *J* 2.3), 8.71 (4H, d, *J* 9.0), 9.48 (2H, s). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2927, 2859, 1618, 1472, 1425, 1232, 1203, 1038, 834, 804. MS *m*/*z* 286, 174, 143, 110, 93, 76, 65. Calc. for $C_{62}H_{82}O_4$: C, 83.55; H, 9.27%; found: C, 83.46; H, 9.33%.

***3,6,12,15-Tetrakis(dodecyloxy)tetrabenz[a,c,h,j]anthracene 7b***: Recrystallised from ethanol–toluene (1 : 1). Yield 80%, mp 112.0 °C. $^1$H-NMR ($CDCl_3$) δ 0.88 (12H, t, *J* 8.8), 1.25–1.50 (64H, m), 1.52–1.62 (8H, m), 1.87–1.95 (8H, m), 4.19 (8H, t, *J* 6.0), 7.29 (4H, dd, *J* 1.9 and 8.5), 7.93 (4H, d, *J* 1.9), 8.73 (4H, d, *J* 8.5), 9.50 (2H, s). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2927, 2856, 1617, 1425, 1233, 1202, 1038, 861, 806. Calc. for $C_{78}H_{114}O_4$: C, 83.97; H, 10.30%; found: C, 83.80; H, 10.64%.

***1,2,4,5-Tetrakis[3,4-bis(octyloxy)phenyl]benzene 8a***: Column chromatography: eluent, hexane–dichloromethane (3 : 1). Recrystallised from ethanol with drops of toluene. Yield 91%, mp 64.9 °C. $^1$H-NMR ($CD_2Cl_2$) δ 0.87–0.91 (24H, m), 1.29–1.49 (80H, m), 1.59–1.66 (8H, m), 1.74–1.81 (8H, m), 3.69 (8H, t, *J* 6.6), 3.94 (8H, t, *J* 6.7), 6.67 (4H, s), 6.79 (8H, s), 7.47 (2H, s). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2931, 2860, 1523, 1472, 1251, 1140, 1020, 817, 727. MS *m*/*z* 1408 ($M^+$, 100%), 1297, 1185, 1073. Calc. for $C_{94}H_{150}O_8$: C, 80.17; H, 10.74%; found: C, 80.15; H, 10.69%.

***1,2,4,5-Tetrakis[3,4-bis(1-methylheptyloxy)phenyl]benzene 8c***: Column chromatography: eluent, hexane–dichloromethane (4 : 1). Yield 40% (liquid). $^1$H-NMR ($CDCl_3$) δ 0.85–0.90 (24H, m), 1.25–1.80 (104H, m), 3.90–4.00 (4H, m), 4.17–4.27 (4H, m), 6.69 (4H, s), 6.75–6.88 (8H, m), 7.47 (2H, s). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2935, 2863, 1516, 1480, 1255, 1136.

***2,3,6,7,11,12,15,16-Octakis(octyloxy)tetrabenz[a,c,h,j]anthracene 9a***: Recrystallised from toluene. Yield 80%, mp 164.6 °C. $^1$H-NMR ($C_6D_5CD_3$, 70 °C) δ 0.90–1.00 (24H, m), 1.30–1.50 (80H, m), 1.56–1.70 (8H, m), 1.87–2.02 (8H, m), 4.20 (8H, t, *J* 6.4), 4.26 (8H, t, *J* 6.5), 8.09 (4H, s), 8.44 (4H, s), 9.69 (2H, s). IR (KBr) $\nu_{max}$/cm$^{-1}$ 2929, 2858, 1524, 1443, 1262, 1173, 1070, 838. MS *m*/*z* 1404 ($M^+$, 100%). Calc. for $C_{94}H_{146}O_8$: C, 80.40; H, 10.48%; found: C, 80.00; H 10.61%.

***Synthesis of 1,2,4,5-tetraphenylbenzene derivatives (compounds 6a–c, 8a and 8c)***: A mixture of 1,2,4,5-tetrabromobenzene (1 mmol) in DME (1,2-dimethoxyethane) (8 ml) and 20% aq. $Na_2CO_3$ (10 ml) was stirred under a positive pressure of nitrogen. Tetrakis(triphenylphosphine)palladium(0) (0.10 mmol) was added followed by the boronic acid (6 mmol) dissolved in DME (5 ml). The resulting mixture was heated under reflux for 24 h and allowed to cool to room temperature. The organic phase was separated and the aqueous phase was washed with diethyl ether (×2). The combined organic layers were washed with water, brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography and recrystallisation.

***Synthesis of final compounds (compounds 7a, 7b and 9a)***: The 1,2,4,5-tetraphenylbenzene derivative (1 mmol) was stirred in dry dichloromethane (100 ml) under nitrogen. A solution of $FeCl_3$ (10 mmol) in nitromethane (2 ml) was then added dropwise *via* a syringe. After 1 h the mixture was quenched with methanol and the precipitate was filtered off and purified by recrystallisation.

***Preparation of binary mixtures of 7a and 9a***: The preparation of binary mixtures of compounds **7a** and **9a** in the isotropic phase was not possible due to the high clearing temperature of compound **9a**. Mixtures were therefore prepared by dissolving specific amounts of two materials in toluene (Aldrich, 99.8%, HPLC grade). The solvent was evaporated by heating the samples at atmospheric pressure and traces of remaining solvent were removed by keeping the samples under reduced pressure (0.05 mmHg) at 60 °C for several hours. Toluene was used because of the insolubility of compound **9a** in the other solvents that were tested.

**Table 1** Phase transitions and transition enthalpy changes for **7a**, **7b**, **8a** and **9a**

| Compound | Transition temperatures (°C) and enthalpy changes (kJ mol$^{-1}$ in [ ]) | | | | |
|---|---|---|---|---|---|
| **7a** | Iso | 179.1 [36.91] | Cryst B-Cr | | |
| **7b** | Iso | 145.2 [39.53] | Cryst B-Cr | | |
| **8a** | Iso | 74.4 [24.28] | Col$_h$ | −29.9 | Glass |
| **9a** | Iso | 251.8 [7.05] | Col$_h$ | 154.6 [57.83] | Cr |

## 3. Results and discussion

The liquid crystal properties of the synthesised compounds were investigated by polarized light optical microscopy and differential scanning calorimetry (DSC). The results obtained are summarised in Table 1.

For compounds **7a** and **7b**, the DSC first heating scan showed two major peaks, but further heating and cooling scans showed only several low enthalpy peaks after the isotropic liquid to mesophase transition (Fig. 1). By X-ray diffraction experiments these materials only showed a crystalline structure over the whole temperature range studied (from room temperature to isotropization). In particular, for compound **7a** this was revealed by the complexity of the patterns, which contained numerous sharp rings in all the angular regions. However, upon annealing at the clearing point and further cooling a defect texture typical of a crystal B texture was observed by optical microscopy (see Fig. 2). When cooling at 10 °C min$^{-1}$, a rapid transition from the isotropic liquid occurred, that gave rise to a defect texture which was typical of a crystal. The formation of the crystal state was nucleated *via* an intermediary crystal B phase which was present at the growing edges of the crystal. This is not inconsistent with the X-ray measurements, that need exposure times of, at least, several minutes to obtain sufficiently exposed photographs. Therefore, the X-ray patterns taken at high temperatures, even very close to the transition to/from the isotropic liquid, contain the reflections from the crystal phase and not totally from the thermodynamically unstable crystal B. Furthermore, this hypothesis is consistent with the results obtained by DSC where the exotherm associated with the process of nucleation exhibits a high temperature shoulder which would correspond to the

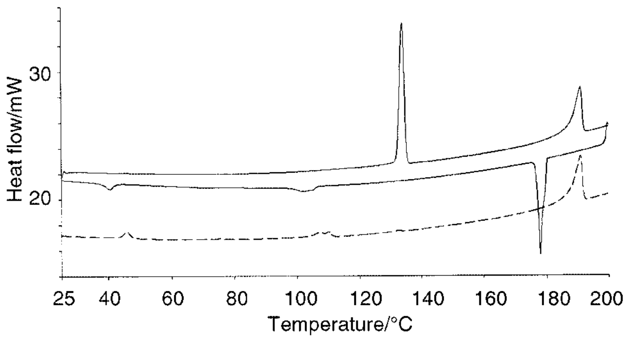


**Fig. 1** DSC traces of compound **7a** (rate 10 °C min$^{-1}$). The solid line corresponds to the first scan; the dashed line corresponds to the second scan.

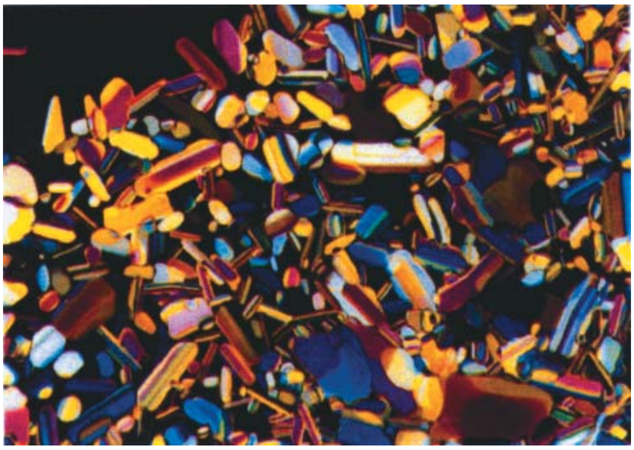


**Fig. 2** Optical texture of the crystal B phase exhibited by compound **7a** under crossed polarizers at 189.4 °C (on heating).

isotropic liquid to crystal B transition, which occurs just before recrystallisation.

An increase in the number of peripheral alkoxy substituents attached to the aromatic core from four to eight induced a change from calamitic to discotic nature. Compound **9a** exhibited a columnar hexagonal phase for which the texture observed under crossed polarizers (Fig. 3) was a combination of mosaics with linear birefringent defects and homeotropic digitated stars; both are typical features for columnar hexagonal phases.[19] X-Ray diffraction studies confirmed the mesophase assignment made by optical microscopy and DSC (Fig. 4). The patterns taken above 155 °C show a strong maximum in the low-angle region, that corresponds to the (1 0) reflection from a two-dimensional hexagonal lattice with a lattice constant $a = 26$ Å. Although, in principle, other low-angle reflections should be observed to unambiguously assign the mesophase symmetry, the optical textures are unequivocally characteristic of a hexagonal columnar mesophase. Moreover, the absence of other reflections at low angles apart from the (1 0) reflection is frequent in diffraction patterns of hexagonal columnar mesophases, and it is due to a minimum in the form factor, which precludes the observation of peaks in this angle region.[20] Molecular modelling gives the approximate diameter of the molecular disc as 31 Å which corresponds to an inter-columnar distance of 26.8 Å.

At high angles, two diffuse scattering maxima are observed corresponding to distances of about 4.6 and 3.8 Å. The first of them is common in all kinds of mesomorphic phases and arises from short-range correlations between the conformationally-disordered hydrocarbon chains. The 3.8 Å maximum is due to

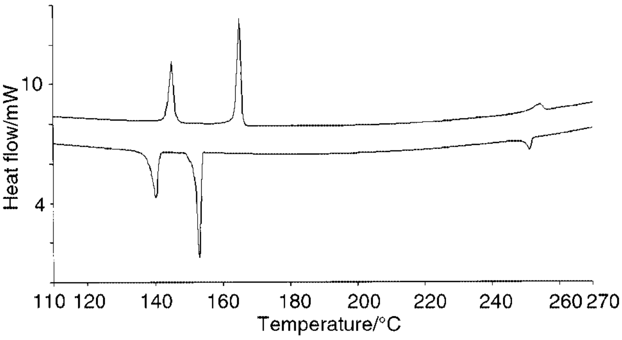


**Fig. 4** DSC traces of compound **9a** (rate 10 °C min$^{-1}$), showing both the heating and cooling cycles.

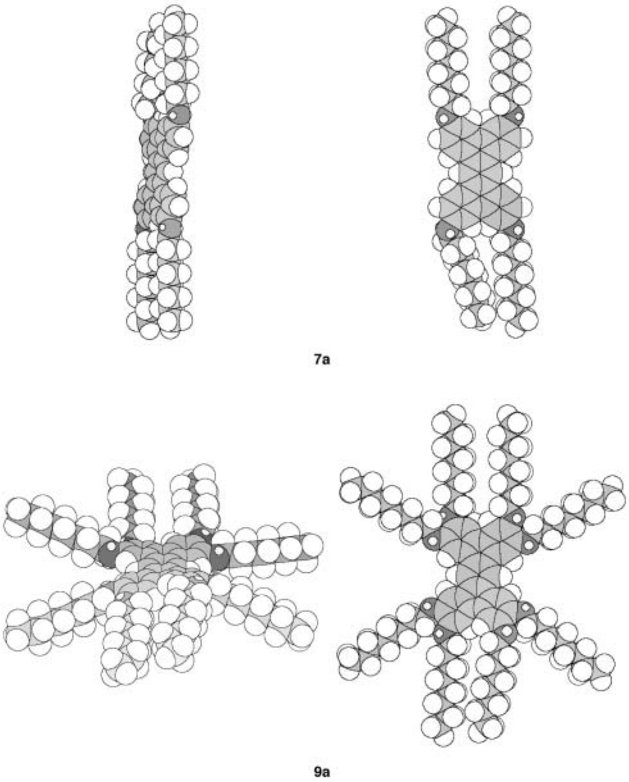


**Fig. 5** Molecular models to show the shape of (a) compound **7a** and (b) compound **9a**.

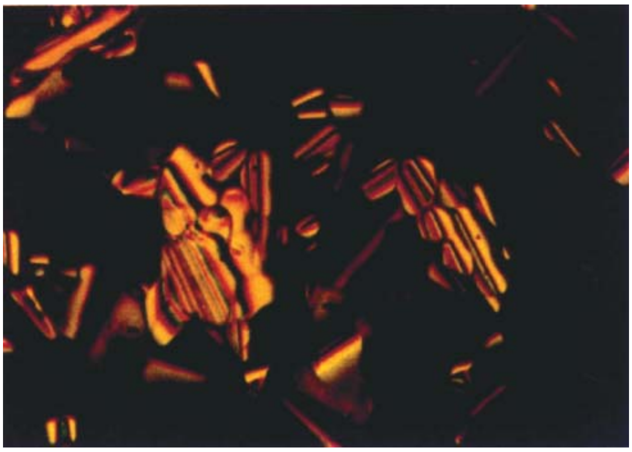


**Fig. 3** Optical texture of the Col$_h$ phase exhibited by compound **9a** under crossed polarizers at 224.0 °C (on cooling).

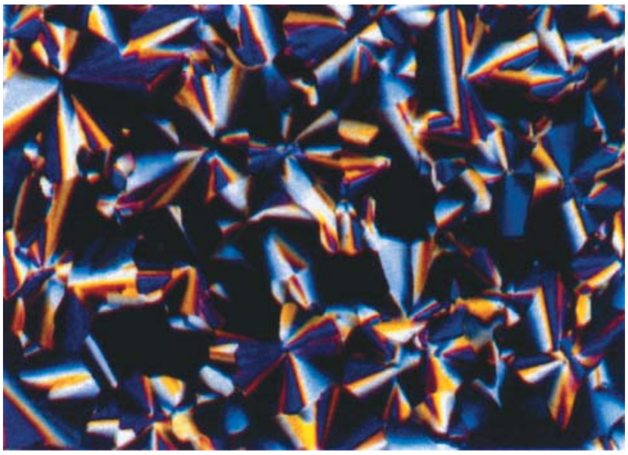


**Fig. 6** Optical texture of the Col$_h$ phase exhibited by compound **8a** under crossed polarizers at 67.0 °C (on cooling).

the intra-columnar order and corresponds to the average stacking distance of the aromatic cores.

Molecular models of compounds **7a** and **9a** (Fig. 5) show planar extended aromatic cores. The eight alkoxy chains in compound **9a** can be arranged to provide a substantial covering of the peripheral region of the molecule, a condition which is required in molecular design in order to form a columnar phase.[21] However, for compounds of type **7**, incomplete filling of the space around the core results, thereby giving rise to an overall calamitic or lath-like molecular shape.

Surprising results were found when studying compound **8a**. In the cooling process this compound exhibited a dendritic growth from the isotropic liquid, which is typical for the formation of a hexagonal columnar phase. Upon annealing, the mesophase defects changed to give a fan-like texture typical of a discotic hexagonal disordered phase ($\mathrm{Col_h}$) (Fig. 6). The material did not crystallise on further cooling, and only showed a transition to the isotropic liquid upon subsequent heating. By DSC, the first heating scan showed two major transitions; the first peak corresponds to the transition from the crystal to the columnar mesophase and the second one corresponds to the transition to the isotropic liquid. On cooling, crystallisation did not occur but a glass transition at −29.9 °C was detected and only the peak related to the isotropization was observed on further heating scans. However, when the DSC scan was repeated after one week, the peak corresponding to the melting of the material was again observed, showing that crystallisation of the compound takes place when it is left for a long period of time. The slowness in its crystallisation allowed the X-ray diffraction study of the mesophase at room temperature on a sample of **8a** cooled from the isotropic liquid. The low-angle region of the pattern contained a set of four rings in a reciprocal spacing ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{9}$. These maxima are indexed, respectively, as the (1 0), (1 1), (2 0) and (3 0) reflections from the two-dimensional hexagonal lattice and give a lattice constant $a = 27.5$ Å. The occurrence of a higher number of low-angle reflections for this compound compared to compound **9a** is probably related to the different temperature of the experiments. At higher temperatures, the mobility of the molecules increases, thus reducing the degree of order. In fact, in the X-ray patterns of **8a** taken at temperatures close to the clearing point, the intensity of the low-angle maxima (excepting the (1 0) reflection) diminishes and the (1 1) and (3 0) reflections practically vanish. However, the hexagonal lattice constant $a$ does not change at high temperature and its value remains equal to 27.5 Å. In the high-angle region only a diffuse halo at 4.4 Å characteristic of the molten chains is observed. The absence of scattering related to the molecular stacking distance along the column axes, even at room temperature, means that the intra-columnar order is poorer for **8a** than for **9a**.

Structures of type **6** and **8** are related to compounds previously reported where the linkage between the central 1,2,4,5-tetrasubstituted benzene ring and the outer aromatic rings was an alkyne[4b] or ester group.[22] In these cases the greater length of the alkyne (**II**) or ester linking group (**III** and **IV**) allowed intramolecular interactions between adjacent peripheral rings which resulted in the generation of calamitic behaviour. For the shorter direct C–C bond connection, it appears that intermolecular interactions dominate leading to a columnar arrangement of the molecules. In these cases the number of substituents, and the small free volume between the core and the peripheral chains, play a decisive role in the mesogenic character of the systems, since no liquid-crystalline behaviour was detected when only four chains were present (compounds **6a–c**).

Furthermore, the mesogenic behaviour of **9a** can be compared to some reported 1,3,5-trisubstituted benzene derivatives. The hexaalkoxy-substituted structure **V**, where the linkage between the central and the peripheral rings is a direct C–C bond, have been reported not to show any mesogenic properties.[23] However, trialkoxy-substituted benzene rings linked to a central 1,3,5-trisubstituted benzene *via* an ester group exhibit discotic liquid-crystalline behaviour (**VI**).[24] Since compound **9a** displays discotic behaviour, it appears that the number of substituents providing an efficient filling of the space around the central ring has a stronger influence than the nature of the linking group between the peripheral ring and the central ones.[21]

Molecular modelling of compound **8a** shows that the peripheral aromatic rings are twisted out of the plane defined by the central aromatic ring by between 40 and 50° (54.3° has been calculated to be the value for the interannular twist in a molecule of *o*-terphenyl).[25] This is in agreement with previous results showing that structural planarity is not a prerequisite to observe a columnar arrangement[21] (*cf.* structure **VI**, cyclohexane derivatives,[26] sugar-based liquid crystals[27]).

The main effect induced by the planarity of the structure induced by cyclisation is to promote mesophase formation. Compounds of type **7** derived from compounds **6a** and **6b** exhibit mesomorphic behaviour, whereas the parent compounds are non-mesomorphic. In comparison with the structures bearing eight alkoxy chains (compounds **8a** and **9a**), the stronger interaction between the molecules for compound **9a** causes a change from a hexagonal disordered phase exhibited by the parent compound **8a** to a hexagonal ordered phase, as well as increasing the transition temperatures.

None of the compounds prepared exhibited a nematic phase, and so, to study in more detail the border-line between discotic and calamitic behaviour, we prepared binary mixtures of compound **9a** (with a hexagonal columnar phase) and compound **7a** (with a crystal B phase). The usual problem of poor miscibility and ready phase separation in mixtures of calamitic and discotics[28] was expected to be minimised for these two components since they have identical core structures which would be expected to enhance the interactions between the rod-like and disc-like molecules.

Binary mixtures of compounds **7a** and **9a** were studied by DSC and polarized light optical microscopy and the resulting binary phase diagram is shown in Fig. 7.

The first point to note about these results is that the mixtures of the compounds were homogeneous across the whole phase diagram and no immiscibility or phase separation was observed in any of the individual binary mixtures that was tested. No additional mesophases were induced for any of the mixtures

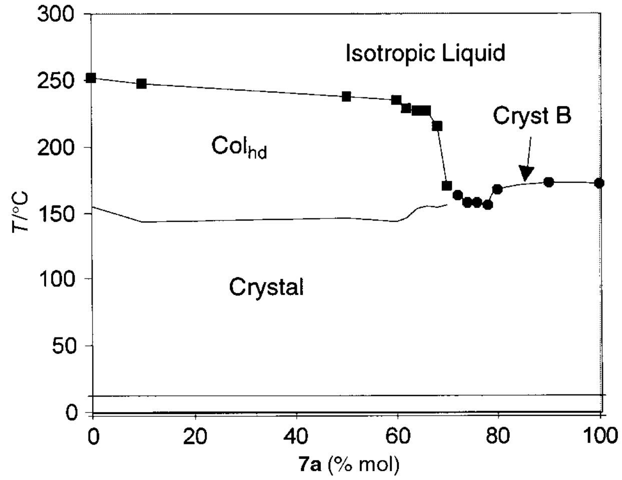


**Fig. 7** Phase diagram of binary mixtures (mol %) between **7a** and **9a** taken on cooling. The crystal B region exists over a small temperature range to the right of the figure. Key: ■ the isotropic to columnar phase transition, ● the isotropic liquid to crystal B transition, the columnar to solid phase transition is shown as a continuous line, the crystal B to solid phase transition could not be detected by microscopy because of either rapid crystallisation or the formation of a glass.

and it is remarkable that the columnar phase exists even with a high concentration of the calamitic compound **7a** present. It seems that molecules of **7a** can be accommodated within the columnar structure without disturbing the packing of compound **9a**. In a complementary fashion, adding the discotic compound **9a** to calamitic compound **7a** simply gives a crystal B phase that has an almost constant thermal stability with respect to change in concentration. However, there is a sudden change in the nature of the mesophase shown by the mixtures of about 30% molar of the discotic component. The discotic mesophase for mixtures at 32% content of component **9a** then change to a crystal B mesophase at 30% of component **9a**; *i.e.* over a 2% difference in concentration the nature of the liquid crystal morphology is totally changed. Thus, our attempts to generate a biaxial smectic phase were unsuccessful, as with nematic phases there appears to be an immiscibility gap between the two uniaxial systems which extends only over a percent in change in concentration.

## 4. Conclusions

Novel board-like liquid-crystalline materials based on tetrabenz[*a*,*c*,*h*,*j*]anthracene have been synthesised and characterised. A change from lamellar to discotic mesomorphic behaviour was observed when increasing the number of pheripheral alkoxy substituents from four (compounds **7a** and **7b** showed a crystal B phase) to eight (the material **9a** exhibited a $\mathrm{Col_h}$ phase). The non-planar tetra-substituted benzene intermediate **8a** bearing eight alkoxy chains also showed columnar liquid-crystalline behaviour ($\mathrm{Col_h}$ phase). Binary mixtures of the structurally related compounds **7a** (calamitic) and **9a** (discotic) were mesogenic and did not show any evidence of phase-separation across the whole phase diagram, although no additional mesophases were induced.

Theory suggests[11] that the packing restrictions which could promote biaxiality in the nematic binary mixture of rod-like and plate-like molecules may at some time cause demixing of the phase. Calculations show[11] that the thermodynamic stabilisation against demixing can be achieved by introducing selective rod–plate interactions. Attempts to chemically incorporate such interactions by hydrogen bonding lead, however, to strong distortions of the board-like structures.

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