

Hierarchical Organisation in Shape-Amphiphilic Liquid Crystals

Paul H. J. Kouwer,* Georg H. Mehl

University of Hull, Department of Chemistry, Cottingham Road, Hull HU6 7RX, UK.

E-mail: p.kouwer@science.ru.nl; g.h.mehl@hull.ac.uk.

Supporting Information

Experimental

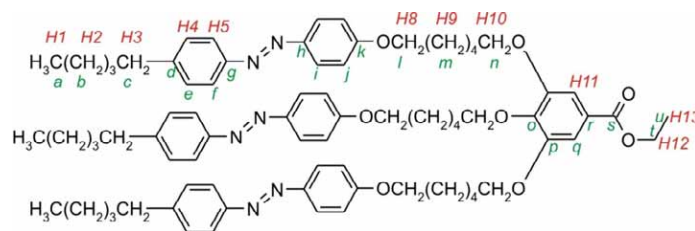
Materials. Mesogens **14** and **15** were prepared according to procedures we have described previously.^{S1,S2} The other materials were used as purchased unless stated otherwise. Tetrahydrofuran (THF) was distilled from sodium.

Instrumental. NMR spectra were recorded on a Jeol JNM-ECP 400 FT-IR spectrometer (400 MHz). Chemical shifts are reported in ppm relative to TMS. Phase transitions were determined using a Perkin Elmer DSC 7 in nitrogen atmosphere calibrated against an indium standard (reported transition temperatures are the onset of the endotherm). The mesophases were studied on an Olympus BH-2 optical polarizing microscope, equipped with a Mettler FP82 HT hot stage with a Mettler FP90 central processor and a JVC digital video camera for picture capturing. X-ray diffraction experiments were performed on a MAR345 diffractometer with a 2D image plate detector (CuK α radiation, graphite monochromator, $\lambda = 1.54 \text{ \AA}$). The samples were heated in the presence of a magnetic field using a home-built capillary furnace. Molecular modelling experiments (molecular mechanics and semi-empirical (PM3 force field) models on Cambridge Soft Chem3D Pro version 1999), were carried out on final and partial structures to determine the (sub)molecular dimensions. Although, by all means, we do not claim to find minimised equilibrium structures by these simple procedures, the results allow us to estimate the molecular dimensions rather accurately.

Synthesis. 4-(4-Pentylphenylazo)phenol (5). A solution of 4-pentylaniline (8.15 g, 50 mmol) and conc. HCl (15 ml) in water (100 ml) was chilled at 0 °C and sodium nitrite (3.45 g, 50 mmol) was added in small portions, keeping the temperature below 5 °C. After stirring

for 2 hours at low temperatures the solution of the diazonium salt was slowly added to a chilled (0 °C) solution of phenol (4.7 g, 50 mmol) and NaOH (2.5 g, 63 mmol) in water (25 mL), again keeping the temperature below 5 °C. The red product separated from the solution and was filtered off. Compound **7** was purified by two crystallisations from ethanol, yielding red crystals (10.8 g, 43 mmol, 86 %). Analysis: ¹H NMR (400 MHz, CDCl₃): δ = 7.85, 7.82, 7.30, 6.93 (4×dd, 8H, CH aromatic); 2.67 (t, 2H, CH₂Ph); 1.71-1.61, 1.42-1.30 (2×m, 6H, CH₂ aliphatic); 0.91 (t, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ = 158.76, 150.42, 146.67, 146.12 (4×C aromatic); 129.11, 125.04, 122.47, 115.97 (4×CH aromatic); 35.78 (CH₂Ph); 31.41, 30.93, 22.48 (CH₂ aliphatic); 13.98 (CH₃).

4-(6-Bromohexyloxy)phenyl-(4-pentylphenyl)diazene (6). A mixture of **5** (5.0 g, 20 mmol), 1,6-dibromohexane (24.4 g, 100 mmol), K₂CO₃ (5.9 g, 36 mmol), KI (0.5 g, 3 mmol) and butanone (100 mL) was stirred and heated to reflux overnight. The mixture was allowed to cool to room temperature, the solids were filtered off, washed with acetone and the solvents were evaporated under reduced pressure. The oily residue was diluted with CH₂Cl₂ (5 mL) precipitated in methanol (50 mL) and the crude product was filtered. Pure **6** was obtained after crystallisation from MeOH:acetone as yellow-orange crystals (6.4 g, 15 mmol, 74%). Analysis: ¹H NMR (400 MHz, CDCl₃): δ 7.89, 7.77, 7.29, 6.97 (4×dd, 8H, *H6*, *H5*, *H4* and *H7*); 4.02 (t, 2H, *H8*); 3.42 (t, 2H, CH₂Br); 2.65 (t, 2H, *H3*); 1.91-1.25 (m, 14H, *H2* and *H9*); 0.91 (t, 3H, *H1*). ¹³C NMR (100 MHz, CDCl₃): δ 161.32, 150.98, 146.95, 145.81 (4×C aromatic); 129.02, 124.55, 122.49, 114.62 (4×CH aromatic); 68.01 (CH₂O); 35.80 (CH₂Ph); 32.63 (CH₂Br); 33.75, 29.00, 27.89, 25.26 (CH₂ spacer); 31.44, 30.99, 22.51 (CH₂ tail); 14.01 (CH₃).



3,4,5-tris[6-(4-(4-pentylphenylazo)phenoxy)hexyloxy]benzoic acid ethyl ester (7), ^1H and ^{13}C NMR assignment, see above). A mixture of **6** (4.29 g, 10.0 mmol), ethyl gallate (0.60 g, 3.0 mmol), K_2CO_3 (2.10 g, 15.2 mmol), KI (0.20 g, 1.2 mmol) and butanone (50 mL) was heated to reflux overnight. The mixture was allowed to cool to room temperature, the solids were filtered off, washed thoroughly with warm acetone and the solvents were evaporated under reduced pressure. The residue was diluted with CH_2Cl_2 (10 mL) and precipitated in methanol (50 mL) and the product (and excess starting material) was filtered off. Pure **7** was obtained after multiple crystallisations from both acetone and CH_2Cl_2 /hexane mixtures, yielding 2.31 g (1.86 mmol, 62 %) of a yellow-orange powder. Analysis: ^1H NMR (400 MHz, CDCl_3): δ 7.88-7.79, 7.75-7.68, 7.29-7.21, 6.98-6.89 (4×m, 24H, *H6*, *H5*, *H4* and *H7*); 7.27 (s, 2H, *H11*); 4.33 (t, 2H, *H12*); 4.05, 4.04-4.01 (3×t, 12H, *H10*, *H10'* and *H8*); 2.64 (t, 6H, *H3*); 1.91-1.25 (m, 42H, *H2* and *H9*); 1.37 (t, 3H, *H13*); 0.88 (t, 9H, *H1*). ^{13}C NMR (100 MHz, CDCl_3): δ 166.45 (*s*); 161.42, 161.40 (*k*); 152.76 (*p*); 151.02 (*g*); 146.97, 146.94 (*d*); 145.82, 145.80 (*h*); 142.16 (*o*); 129.05 (*e*); 125.26 (*q*); 124.61 (*i*); 122.54 (*f*); 114.68 (*j*); 108.01 (*r*); 73.70 (*n*); 68.99 (*n'*); 68.23, 68.13 (*l*); 61.08 (*t*); 35.84 (*c*); 29.26, 29.21, 25.92, 25.84 (*m*); 31.50, 31.03, 22.56 (*b*); 14.45 (*u*); 14.08 (*a*).

3,4,5-tris[6-(4-(4-pentylphenylazo)phenoxy)hexyloxy]benzoic acid (8). A mixture of **7** (2.0 g, 1.6 mmol), ethanol (50 ml) and aqueous KOH (5 ml, 4N) was stirred and heated under reflux for 2 hours, until TLC indicated complete consumption of the starting material. The reaction mixture was neutralised with conc. HCl, cooled and the precipitated product was filtered from the mixture and washed with water. Due to its very low solubility, this mesogen was not further isolated, but the product was directly used for the esterification with the disc-shaped mesogens.

1,2-Bis(11-hydroxyundecyloxy)benzene (10). A mixture of catechol (2.5 g, 20 mmol), 11-bromoundecan-1-ol (14.4 g, 57 mmol), K_2CO_3 (15.0 g, 109 mmol), KI (1.5 g, 0.9 mmol) and dimethylformamide (DMF, 150 mL) was stirred at 100 °C for 16 hours. The mixture was allowed to cool to room temperature and the reaction mixture was precipitated into a diluted HCl solution. The crude product was filtered off, recrystallised from a methanol/acetone mixture and dried. The product was esterified without further purification. Analysis: ^1H NMR

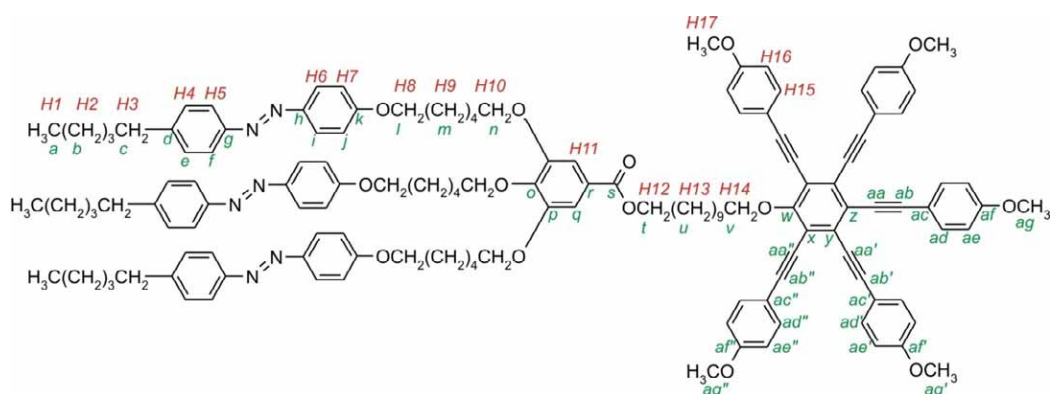
(400 MHz, CDCl₃): δ 6.81 (s, 4H, CH aromatic); 3.91 (t, 4H, CH₂OPh); 3.56 (t, 4H, CH₂OH); 1.80-1.18 (m, 36H, CH₂ spacer).

1,2-Bis(11-acetyl undecyloxy)benzene (11). To a solution of **10** (all from the previous step) and triethylamine (10 g, 100 mmol) in dry CH₂Cl₂ (100 mL) was added drop-wise a solution of acetyl chloride (10 g, 120 mmol) in dry ether (100 mL). The reaction mixture was stirred until TLC indicated complete conversion to the double esterified product. The solids were filtered off, the solvents were removed under reduced pressure and the product was crystallised from a methanol/aceton mixture. Pure **11** was obtained after column chromatography (SiO₂, eluent CH₂Cl₂/hexane), yielding 7.1 gram (13.4 mmol, 67 % over 2 steps) of a clear oil. ¹H NMR (400 MHz, CDCl₃): δ 6.86 (s, 4H, CH aromatic); 4.03 (t, 4H, CH₂OAc); 3.97 (t, 4H, CH₂OPh); 2.02 (s, 6H, COCH₃); 1.80-1.18 (m, 36H, CH₂ spacer).

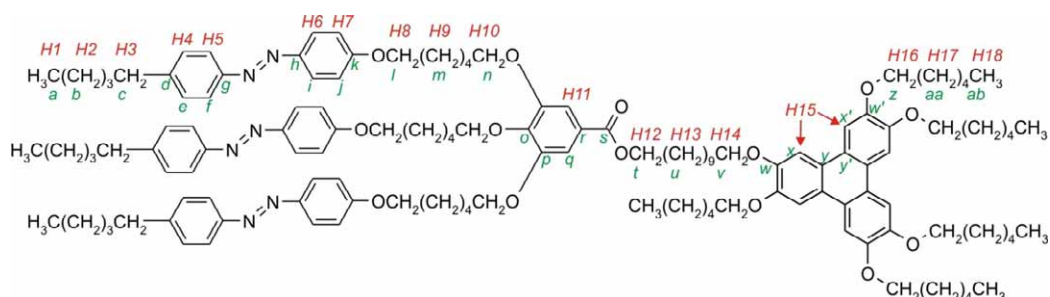
2,3-Bis(11-hydroxyundecyloxy)-6,7,10,11-tetrakis(hexyloxy)triphenylene (13) (For ¹H and ¹³C NMR assignment, see Figure for compound **3**). To mixture of **12** (0.73 g, 1.32 mmol), **11** (1.35 g, 2.53 mmol) and CH₂Cl₂ (20 mL) was added FeCl₃ (1.1 g, 6.8 mmol). The reaction mixture was stirred overnight at room temperature and precipitated into chilled methanol (*T* = -20 °C) and the crude product was filtered off. The pure diester was isolated after column chromatography (SiO₂, eluent: CH₂Cl₂/hexane (3:1) to CH₂Cl₂) as a off-white waxy solid, yield: 0.89 gram (0.82 mmol, 62 %). ¹H NMR (400 MHz, CDCl₃): δ 7.85 (s, 6H, *H15*); 4.25 (t, 4H, *H12*); 4.06 (t, 12H, *H14* and *H16*); 2.05 (s, 6H, COCH₃); 1.91-1.20 (m, 68H, *H13* and *H17*); 0.90 (t, 12H, *H18*).

The diol **11** was obtained after refluxing the ester with *para*-toluenesulphonic acid (*p*TSA, 0.2 g, 1.2 mmol) in ethanol (30 mL). The solvent was evaporated and the residue was subjected to a column for chromatography (SiO₂, eluent: CH₂Cl₂ to CH₂Cl₂:ethyl acetate (3:1)), yielding **13** as a white solid, yield 0.81 gram (0.80 mmol, 98 %). ¹H NMR (400 MHz, CDCl₃): δ 7.76 (s, 6H, *H15*); 4.16 (t, 12H, *H14* and *H16*); 3.55 (t, 4H, *H12*); 1.95-1.15 (m, 68H, *H13* and *H17*); 0.86 (t, 12H, *H18*). ¹³C NMR (100 MHz, CDCl₃): δ 148.95, 148.92 (*w*, *w'*); 123.58, 123.56 (*y*, *y'*); 107.31, 107.29 (*x*, *x'*); 69.70 (*z*); 69.67 (*v*); 68.96 (*n'*); 63.04 (*t*); 31.67, 29.41, 25.84, 22.64 (*aa*); 32.78, 29.64, 29.58, 29.50, 29.45, 26.18, 25.76 (*u*); 14.04 (*ab*).

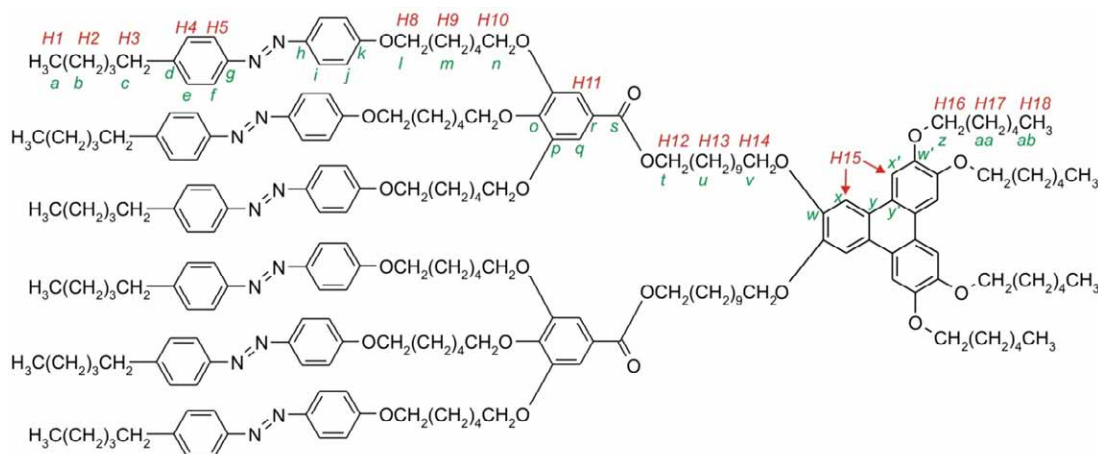
General procedure esterification reactions of the calamitic trimer and the discotic mesogens. A mixture of benzoic acid **8** (1.2 eq., 100–200 mg) discotic mesogen **13** (1 eq.), **14** (1 eq.) or **15** (0.5 eq.), *N,N*-dicyclohexylcarbodiimide (DCC, 4 eq.), 4-(dimethylamino)pyridine (DMAP, 1 eq.), *para*-toluenesulphonic acid (*p*TSA, 0.5 eq.) in dry CH₂Cl₂ or dry THF (5–10 mL) was stirred for 5 days at room temperature in inert atmosphere. The solvent was removed under reduced pressure and the reaction mixture was applied to a silica column for purification. Crystallisation from MeOH/CH₂Cl₂ yielded the materials as yellow-orange powders.



3,4,5-Tris[6-{4-(4-pentylphenylazo)phenoxy}hexyloxy]benzoic acid 11-[pentakis(4-methoxyphenyletynyl)phenoxy]undecyl ester (1, ¹H and ¹³C NMR assignment, see above). Synthesis according to the general procedure, starting with 92 mg (0.1 mmol) of **13**. Purification using column chromatography (SiO₂, eluent CH₂Cl₂:hexane (2:1) to CH₂Cl₂) and crystallisation from MeOH/CH₂Cl₂. Yield: 116 mg (0.055 mmol, 55 %) of a yellow-orange powder. Analysis: ¹H NMR (400 MHz, CDCl₃): δ 7.85-7.75 (m, 12H, *H5* and *H6*); 7.56-7.48 (m, 10H, *H15*); 7.29-7.22 (m, 8H, *H4* and *H11*); 6.95-6.89 (m, 6H, *H7*); 6.88-6.81 (m, 10H, *H16*); 4.31 (t, 2H, *H12*); 4.25 (t, 2H, *H14*); 4.03, 4.00 (2×t, 12H, *H8* and *H10*); 3.81, 3.80 (2×s, 15H, *H17*); 2.63 (t, 2H, *H3*); 1.91-1.21 (m, 60H, *H2*, *H9* and *H13*); 0.87 (t, 9H, *H1*). ¹³C NMR (400 MHz, CDCl₃): δ 166.32 (*s*); 161.22 (*k*); 159.89, 159.79, 159.70 (*af*, *af'*, *af''*); 159.77 (*w*); 152.60 (*p*); 150.87 (*g*); 146.79, 146.76 (*d*, *d'*); 145.62, 145.60 (*h*, *h'*); 142.00 (*o*); 133.15, 133.02, 132.99 (*ad*, *ad'*, *ad''*); 128.88 (*e*); 128.28 (*y*); 125.11 (*q*); 124.42 (*i*); 123.73 (*z*); 122.38 (*f*); 119.74 (*x*); 115.61, 115.44, 115.37 (*ac*, *ac'*, *ac''*); 114.48 (*j*); 114.00, 113.96 (*ac*, *ac'*, *ac''*); 107.84 (*r*); 99.05, 98.88, 96.82 (*aa*, *aa'*, *aa''*); 86.51, 85.98, 83.45 (*ab*, *ab'*, *ab''*); 74.50 (*v*); 73.15 (*n*); 68.83 (*n'*); 68.06, 67.97 (*l'*, *l*); 65.11 (*t*); 55.21 (*ag*); 35.80 (*c*); 31.45, 30.99, 22.52 (*b*); 29.23, 29.17, 25.90, 25.81 (*m*); 30.58, 30.22, 29.64, 29.61, 29.56, 29.29, 28.72, 26.37, 26.02 (*u*); 14.02 (*a*).



3,4,5-Tris[6-{4-(4-pentylphenylazo)phenoxy}hexyloxy]benzoic acid 11-{3,6,7,10,11-pentakis(hexyloxy)triphenylene-2-yloxy}undecyl ester (2, ¹H and ¹³C NMR assignment, see above). Synthesis according to the general procedure, starting with 137 mg (0.15 mmol) of **14. Purification using column chromatography (SiO₂, eluent CH₂Cl₂:hexane (1:1) to CH₂Cl₂) and crystallisation from MeOH/CH₂Cl₂. Yield: 208 mg (98 μmol, 65%) of a yellow-orange powder. Analysis: ¹H NMR (400 MHz, CDCl₃): δ 7.87-7.83, 7.78-7.74, 7.28-7.23, 6.96-6.91 (4×m, 24H, H6, H5, H4 and H7); 7.82 (s, 6H, H15); 7.26 (s, 4H, H11); 4.28 (t, 2H, H12); 4.21 (t, 12H, H14 and H16); 4.04, 4.02, 3.99 (3×t, 24H, H10, H10' and H8); 2.64 (t, 6H, H3); 1.95-1.20 (m, 100H, H2, H9, H13 and H17); 0.91 (t, 15H, H18); 0.89 (t, 9H, H1). ¹³C NMR (100 MHz, CDCl₃): δ 166.40 (s); 161.35 (k); 152.71 (p); 150.99 (g); 148.96, 148.94 (w, w'); 146.93 (d); 145.76 (h); 142.21 (o); 129.01 (e); 125.24 (q); 124.54 (i); 123.62, 123.59 (y, y'); 122.50 (f); 114.60 (j); 108.00 (r); 107.37, 107.31 (x, x'); 73.27 (n); 69.72 (v); 69.67 (z); 68.96 (n'); 68.18, 68.08 (l', l); 65.22 (t); 35.81 (c); 31.68, 29.41, 25.84, 22.64 (aa); 31.45, 31.00, 22.52 (b); 30.21, 29.67, 29.60, 29.54, 29.46, 29.33, 28.75, 26.17, 26.00 (u); 29.22, 29.16, 25.90, 25.81 (m); 14.05 (ab); 14.02 (a).**



3,4,5-Tris[6-{4-(4-pentylphenylazo)phenoxy}hexyloxy]benzoic acid 11-(3-(11-{3,4,5-tris[6-{4-(4-pentylphenylazo)phenoxy}hexyloxy]benzoyloxy}undecyloxy)-6,7,10,11-tetrais(hexyloxy)triphenylene-2-yloxy)undecyl ester (3, ¹H and ¹³C NMR assignment, see above). Synthesis according to the general procedure, starting with 73 mg (0.073 mmol) of 15. Purification using column chromatography (SiO₂, eluent CH₂Cl₂:hexane (3:1) to CH₂Cl₂) and crystallisation from MeOH:CH₂Cl₂. Yield: 105 mg (0.031 mmol, 42 %) of a yellow-orange powder. Analysis: ¹H NMR (400 MHz, CDCl₃): δ 7.88-7.78, 7.74-7.65, 7.29-7.21, 6.98-6.89 (4×m, 48H, *H6*, *H5*, *H4* and *H7*); 7.86 (s, 6H, *H15*); 7.27 (s, 4H, *H11*); 4.29 (t, 2H, *H12*); 4.23 and 4.22 (2×t, 12H, *H14* and *H16*); 4.05, 4.03, 4.01 (3×t, 48H, *H10*, *H10'* and *H8*); 2.66 (t, 12H, *H3*); 1.95-1.20 (m, 156H, *H2*, *H9*, *H13* and *H17*); 0.89 (m, 30H, *H1* and *H18*). ¹³C NMR (100 MHz, CDCl₃): δ 166.44 (*s*); 161.34 (*k*); 152.71 (*p*); 150.98 (*g*); 148.97, 148.94, 148.90 (*w*, *w'*, *w''*); 146.91 (*d*); 145.74 (*h*); 142.09 (*o*); 128.99 (*e*); 125.21 (*q*); 124.54 (*i*); 123.60, 123.57, 123.55 (*y*, *y'*, *y''*); 122.49 (*f*); 114.58 (*j*); 107.97 (*r*); 107.36, 107.29, 107.27 (*x*, *x'*, *x''*); 73.25 (*n*); 69.72 (*v*); 69.65 (*z*); 68.95 (*n'*); 68.17, 68.06 (*l'*, *l*); 65.20 (*t*); 35.79 (*c*); 31.67, 29.40, 25.85, 22.64 (*aa*); 31.45, 30.99, 22.51 (*b*); 30.22, 29.67, 29.61, 29.56, 29.50, 29.33, 28.76, 26.21, 26.01 (*u*); 29.23, 29.17, 25.90, 25.81 (*m*); 14.08 (*ab*); 14.04 (*a*).

References:

- (S1) Kouwer, P. H. J.; Pourzand, J.; Mehl, G. H. *Chem. Commun.* 2004, 66-67
 (S2) Kouwer, P. H. J.; Jager, W. F.; Mijs, W. J.; Picken, S. J. *Macromolecules* 2002, **35**, 4322-4329.