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Synthesis and properties of novel columnar liquid crystals based on symmetrical and non-symmetrical 1,3,5-trisubstituted benzene derivatives

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Synthesis and properties of novel columnar liquid crystals based on symmetrical and non-symmetrical 1,3,5-trisubstituted benzene derivatives

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In this structure–property correlation study we have investigated a number of novel disc-shaped compounds incorporating a 1,3,5-trisubstituted benzene at the central core. All the materials with peripheral arms attached through an ester linkage exhibited a columnar phase (Col_r or Col_h). The sole use of core–OOC–arm ester linkages resulted in a Col_r phase, whereas any inclusion of a core–COO–arm linkage caused a Col_h phase. We suggest that columnar mesophases are being generated due to space being occupied in the peripheral regions by the gradual offset stacking of individual molecules in the self-organised phase structure.

Keywords: synthesis; columnar; liquid crystals; discotic

1. Introduction

Following their discovery in 1977 research into discotic liquid crystals (LCs) is now more than 30 years old. This is however relatively recent compared with the well-established area of calamitic liquid crystal research which dates back more than a century [1–4]. In recent times discotic LC materials have received a great deal of attention due to their technological importance in low-dimensional conductivity [5], optical compensation films for electro-optical display devices [6, 7], holographic data storage [8] and photovoltaic cells [9]. Much of this research has been focused on the triphenylene structure, due to its relative ease of synthesis [10–12] and its strong tendency to form columnar mesophases [10]. However, compounds based on a single benzene ring as the central core have increased in importance since 1977 following the pioneering work of Chandrasekhar [1].

The mesomorphism and other physical properties of the various alternative structures are of course driven by their molecular architecture [10]. One of the most important structural features which determines LC formation is the proportion of free space around the central core of the molecule [11]. In the majority of discotic LC materials incorporating a single aromatic ring at the central core, hexa-substitution of the aromatic ring is employed [12]. Indeed, in most discotic LC materials the degree of free space around the central core is kept to a minimum [10–12].

During the present investigation of discotic LC materials incorporating a central 1,3,5-trisubstituted benzene as core, we have come across novel materials that depart from the traditional principle of discotic LC structures which rely on a molecular structure having the minimum of free space around the central core. On the other hand, stable columnar phases are produced by these materials due to efficient packing of the molecules within the columnar stacks, and free space around the central core becomes available on the macroscopic scale.

2. Results and discussion

The synthesis of the six novel 1,3,5-trisubstituted disc-shaped compounds (**1**–**6**) is illustrated in Schemes 1–7, and their molecular structures and transition temperatures are indicated in Schemes 2–7.

In view of the large amount of free space around the central core, these materials might not be expected to exhibit columnar mesomorphism. Indeed, a previously known compound of similar structure [13] (**7,** Figure 1) has very low liquid crystal phase stability in the form of a monotropic nematic discotic (N_D) phase.

Compound **1** (see Scheme 2) was designed to have bent peripheral arms in order to allow these to be positioned close to the core, and thus to fill the space better than the conventional linear arms in **7**, and this in turn should enhance columnar phase stability. Compound **1** did indeed exhibit a columnar phase, albeit monotropic, to 96°C, which by optical polarising microscopy was identified as a Col_h phase. Differential scanning calorimetry (DSC) showed a clear reversible enthalpy change, supporting the results obtained by optical polarising microscopy. A possible model which accounts for the columnar phase morphology of **1** is shown in Figure 2. It is suggested that the molecules are stacked in a gradually offset manner throughout the columns, which effectively fills the space and gives a columnar mesophase. The high degree of space filling

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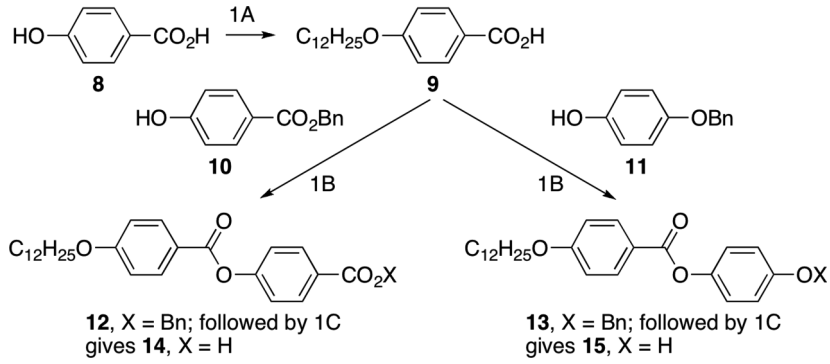
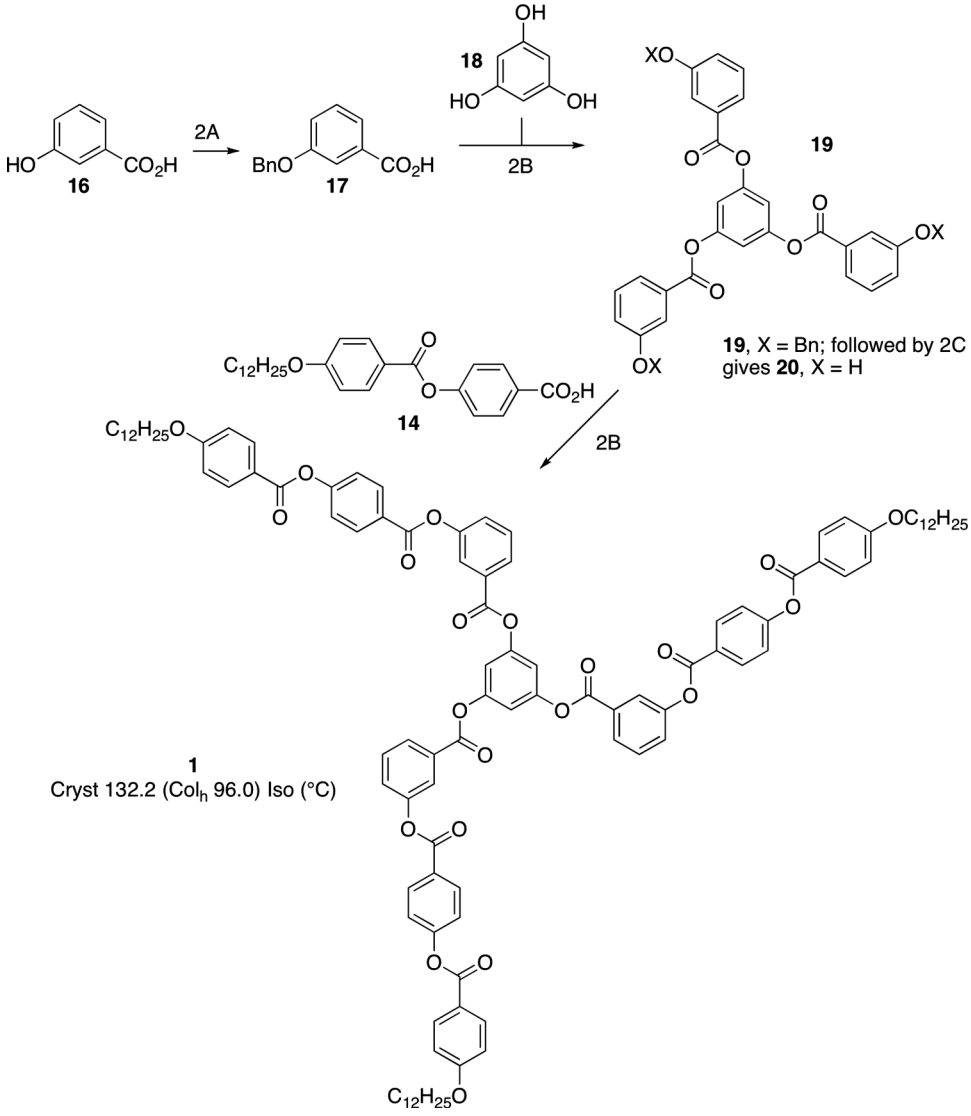
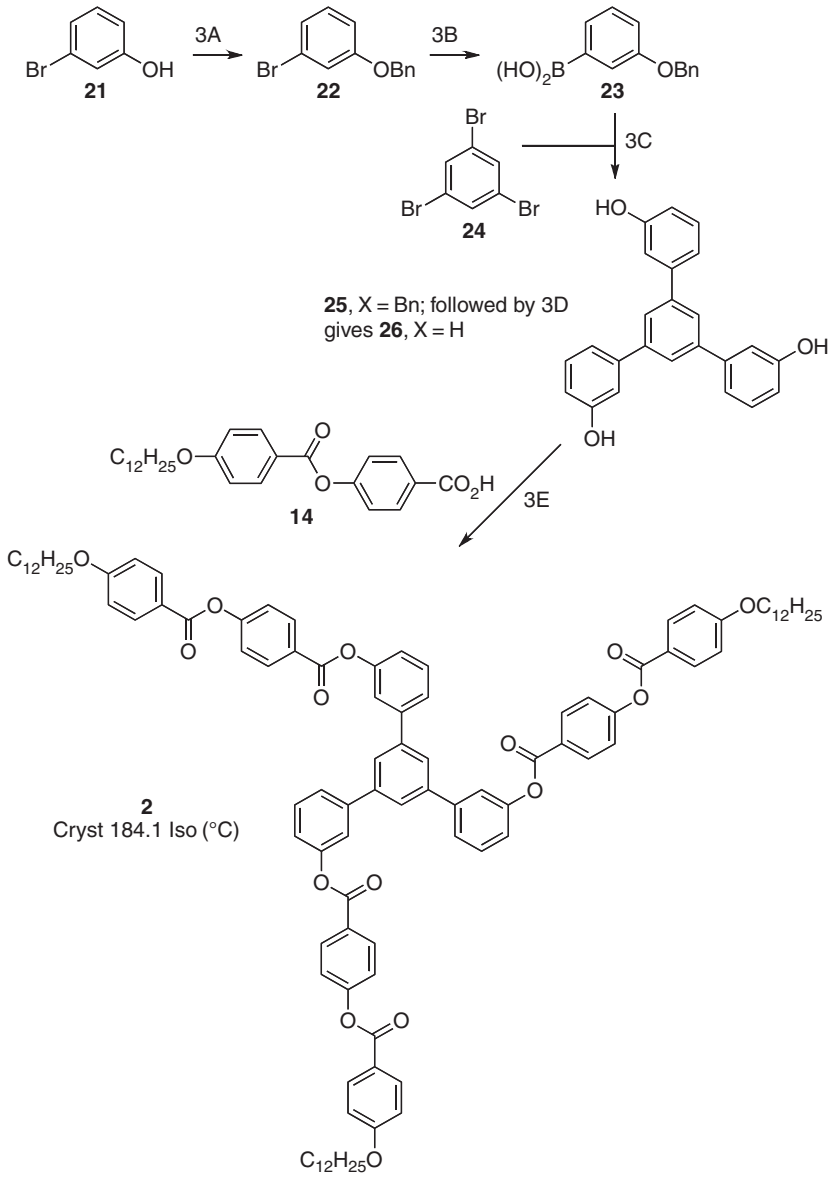


Note. 1A: (i) $C_{12}H_{25}Br$, NaOH; (ii) 36% HCI; 1B: DCC DMAP; 1C: H_2, 10% Pd/C.
Scheme 1.



Note. 2A: (i) BnBr, KOH; (ii) 36% HCI; 2B: DCC DMAP; 2C: H_2, 10 % Pd/C.
Scheme 2.

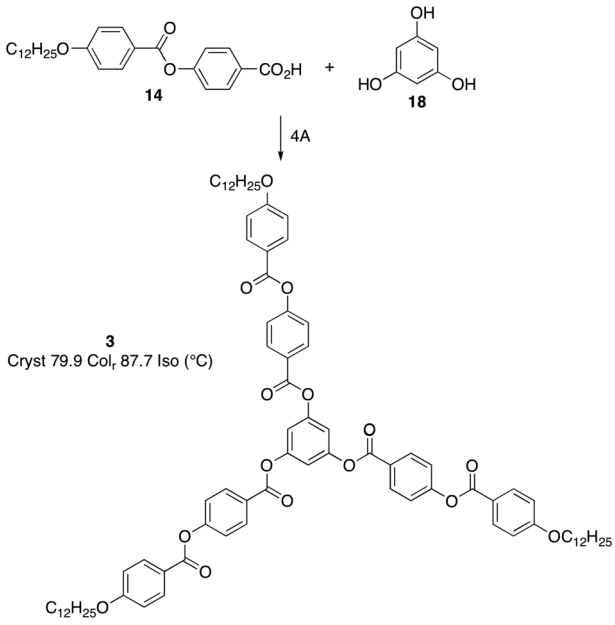


Note. 3A: (i) BnBr, K_2CO_3; 3B: (i) Mg; (ii) $(MeO)_3B$; 10% HCI; 3C: $Pd(PPh_3)_4$, Na_2CO_3; 3D: H_2, 10% Pd/C; 3E: DCC DMAP.
Scheme 3.

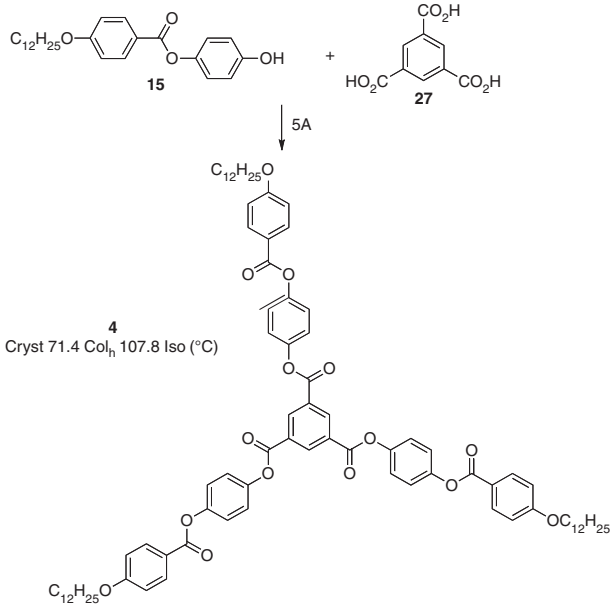
also confers a high melting point, which is clearly not favourable for the generation of liquid crystal phases. However, in line with previous observations the flexible peripheral units impede crystallisation, which enables the generation of a monotropic mesophase [11, 12].

Compound **2** (Scheme 3) is similar to **1**, apart from the absence of ester linkages at the central benzene core, and this gives a larger 4-ringed aromatic core. As might be expected, **2** does not exhibit mesophase behaviour, probably due to the steric bulk of the closely packed peripheral benzene rings which are linked directly to the central benzene core, causing inter-annular twisting at the points of attachment. The non-planar nature of the structure at the central core makes it unlikely that this material will exhibit columnar mesophase morphology. In addition, the lack of flexibility at the core attachment also reduces the possibility that calamitic or banana mesomorphism might be exhibited.

Encouraged by the generation of the columnar mesophase exhibited by **1** (Scheme 2), analogous compounds having conventional linear arms with ester linkages to the central benzene core have been prepared (**3**–**6**). Compound **3** (Scheme 4) has a similar style of ester linkage with a trioxybenzene core as has **1**, whereas **4** (Scheme 5) is an isomeric compound with an alternative arrangement, comprising ester linkages attached to a tricarboxylate central core. It is clear from optical polarising microscopy that **3** exhibits a



Note. 4A: DCC DMAP.
Scheme 4.



Note. 5A: DCC DMAP.
Scheme 5.

columnar phase (see Figure 3), which from the presence of rectilinear lines is likely to have rectangular symmetry. However, several different types of Col_r phase exist, and the precise classification of its symmetry needs to be confirmed by X-ray diffraction. The more ordered Col_r phase of **3** in comparison to the Col_h phase of **1** may be attributed to its more ordered nature, due to the presence of linear peripheral arms. The columnar phase of **3** is enantiotropic, but has lower phase thermal stability (87.7°C) than that of **1** (96.0°C), which would suggest that our conclusion that bent peripheral arms fill the space more effectively than a linear system is correct.

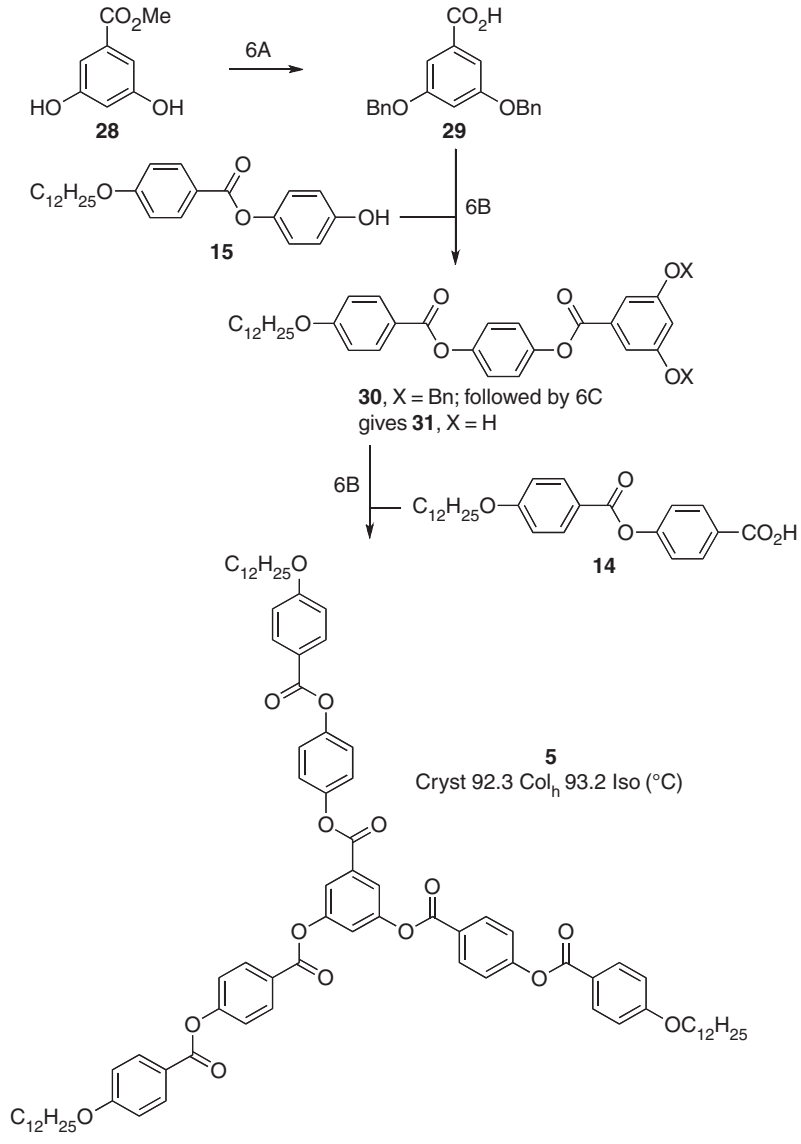
The tricarboxylate nature at the centre of **4** (Scheme 5) provides a larger and more polarisable core (Figure 4), since the carbonyl groups are conjugated with the central benzene nucleus [14]. It is therefore no surprise that **4** exhibits a columnar phase, and that its thermal stability (107.8°C) is greater by 20°C than that of **3** (87.7°C). However, the columnar phase of **4** is of the more usual Col_h type (see Figure 5), which is to be expected from its larger and more polarisable core.

Bearing in mind the significant differences in mesophase type and phase stability between **2** and **4,** it was of interest to synthesise and evaluate two non-symmetrical isomeric materials containing one and two reverse ester linkages, **5** and **6,** respectively (Schemes 6 and 7). Compound **5** (Scheme 6) contains two oxycarbonyl linkages and only a single carbonyloxy linkage, which makes its core size larger (see Figure 4) and more polarisable than in **3**, and a Col_h phase is thus exhibited, as is the case with **4**. The phase thermal stability of **5** (93.2°C) is intermediate between that of **3** (87.7°C) and **4** (107.8°C), but somewhat closer to **3,** which reflects its hybrid structural nature (see Figure 4). On the other hand, **6** (Scheme 7) has two carbonyloxy linkages and one oxycarbonyl linkage, which brings its structure closer in size and character to that of **4**. Similarly, **6** exhibits a Col_h phase, and its phase thermal stability (99.8°C) is greater than that of **5**. It is perhaps unusual that the two non-symmetrical compounds (**5** and **6**) have such a high melting point in comparison to their symmetrical analogues (**3** and **4**), but melting points tend to be much less predictable than mesophase morphology and thermal stability.

3. Summary

All the novel compounds investigated were based on a 1,3,5-trisubstituted benzene core, and thus had a considerable amount of free space in the peripheral regions. It is therefore surprising that all the ester-linked materials exhibited a columnar phase (Col_r or Col_h), although the compound with peripheral arms linked directly to the benzene core (**2**) is non-mesogenic, owing to its lack of conformational flexibility.

However, we offer the logical explanation that the free space is occupied in the bulk mesophase structure as the molecules self-organise in the columnar phase, due to the gradual offset location of the peripheral arms as the molecules stack on top of one other (see Figure 2, for example). Such an offset arrangement of the molecules in the columns is facilitated by the conformationally flexible ester linkages.



Note. 6A: (i) BnBr, K_2CO_3; (ii) KOH; (iii) 36% HCI; 6B: DCC DMAP; 6C: H_2, 10% Pd/C.
Scheme 6.

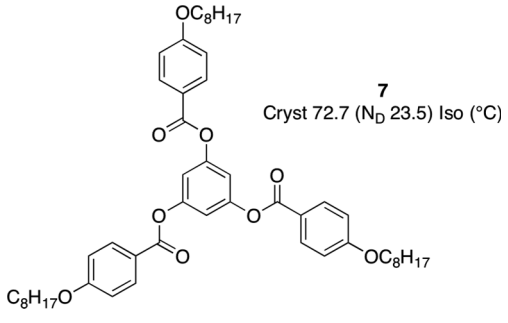


Figure 1. Structure of **7.**

When the three peripheral arms had a bent-core construction (**1**), offsetting was particularly favoured, and hence the columnar phase stability of **1** was shown to be higher than that of **3**, which had three linear peripheral arms. Both **1** and **3** have all three peripheral arms linked through an oxycarbonyl linkage. The isomer (**4**) of **1,** with all three ester linkages reversed (carbonyloxy), had a much higher columnar phase stability due to its larger and more polarisable central core unit, which includes the carbonyl moiety (see Figure 4). Predictably, the two compounds (**5** and **6**) with non-symmetrical linking groups at the central core had columnar phase

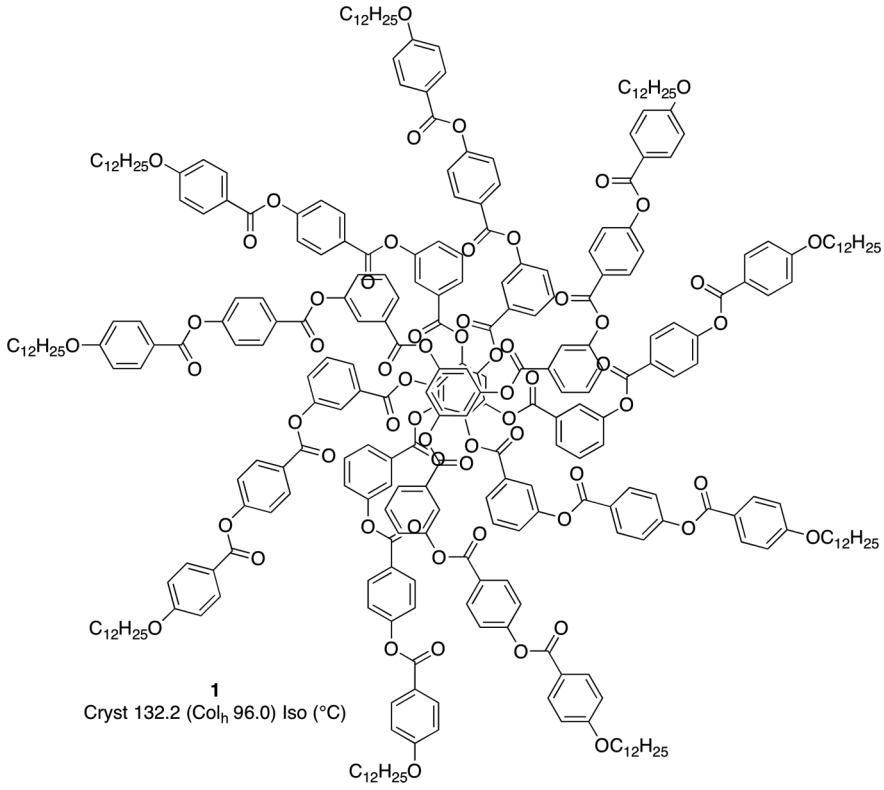


Figure 2. The suggested gradual offset molecular self-organization in the columnar phase structure of **1**.

stability falling between those of its symmetrical isomers, **1** and **4**. Also as predicted on the basis of core size and polarisability, **6**, with two carbonyloxy linkages and only one oxycarbonyl linkage, had higher columnar phase stability than **5**, with just one carbonyloxy linkage and two oxycarbonyl linkages.

4. Experimental

All starting materials and solvents were used as purchased without further purification. The syntheses of the majority of the materials used are detailed below. In the remaining cases the materials were commercially available.

Tetrakis(triphenylphosphine)palladium(0) was prepared according to the procedure in the literature [15]. All the final products were filtered through Schleicher and Schuell filter papers to remove particulates, in addition to the purification techniques described.

A range of techniques were employed to characterise the materials. The structure of all the compounds was confirmed by nuclear magnetic resonance (NMR) spectroscopy using a JEOL JNM ECP400 spectrometer. All proton ^{1}H–NMR and 13C–NMR spectra were recorded at 400 MHz and 100.5 MHz, respectively, using tetramethylsilane ($\delta_H = 0$ ppm) as internal standard. Infrared spectra were recorded on a Perkin–Elmer FTIR Spectrum RX1, using Perkin–Elmer Spectrum software (version 5.0.1). Mass spectra were recorded using one of the following techniques. Solid probe electronic ionisation spectra were recorded using a Shimadzu QP5050A quadrupole GC–MS at 70 eV with the probe at 350°C, in conjunction with Shimadzu Class–5000 processing software. Matrix-assisted laser desorption ionisation (MALDI) spectra were recorded using a Bruker Reflex IV MALDI–TOF mass spectrometer operating in reflection mode, with accelerating voltage in the range 20–25 kV. The nitrogen laser provided photons at 337 nm, and typically 100–150 laser shots were accumulated and averaged. MALDI mass spectra were processed using Bruker Compass software comprising FlexControl and FlexAnalysis packages.

Elemental analysis was performed on all final products using a Fisons EA 1108 CHN analyser. All results obtained were within ±0.30% of the expected value for hydrogen and ±0.50% of that for carbon. High performance liquid chromatography was used to determine the purity of all final products, and all were found >99%. The system comprised a Gilson 233XL autosampler, 321 binary solvent pump, Hewlett Packard 1100 series diode array detector, and a Phenomenex Luna 5 μm C18(2) column, utilising (typically) 30% dichloromethane (DCM) / 70% acetonitrile as eluent.

Melting points, liquid crystal transition temperatures and mesophase morphologies were all determined by

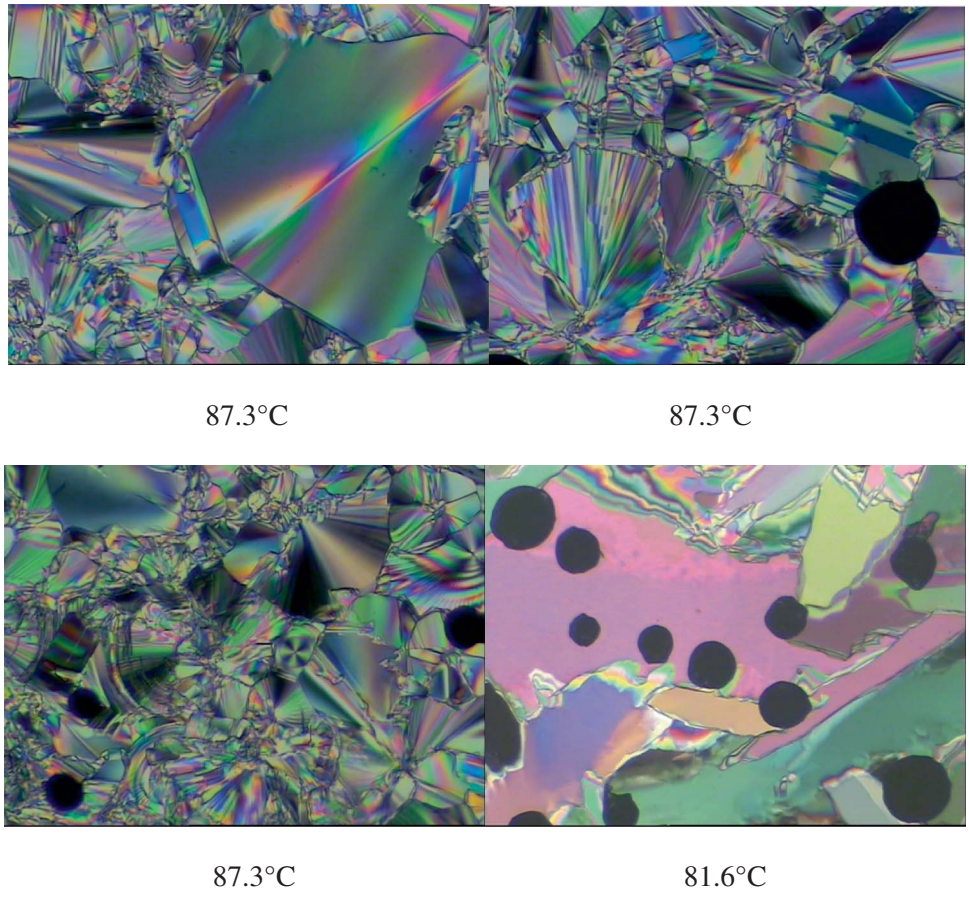


Figure 3. Photomicrographs of the Col_r phase exhibited by **3**, taken at the stated temperature.

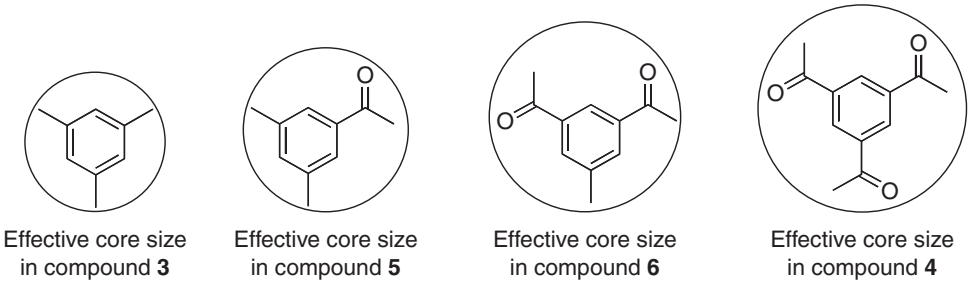


Figure 4. Relative size of the core units in **3**–**6**.

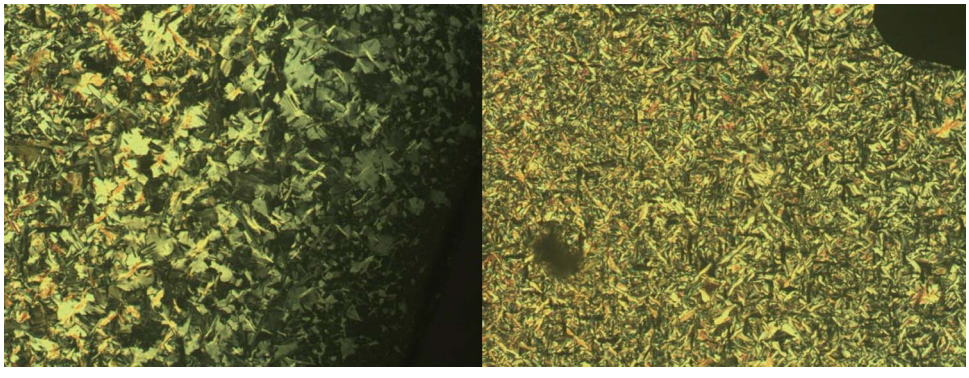
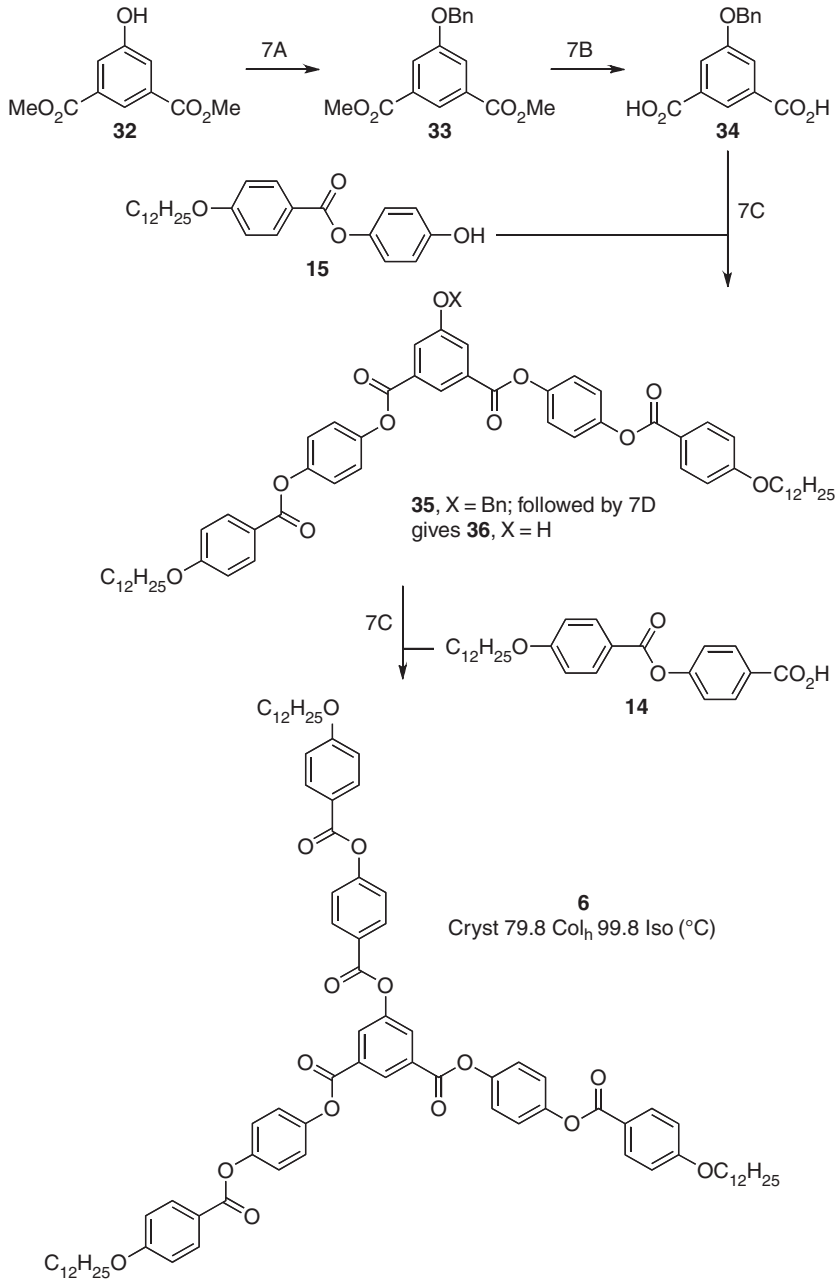


Figure 5. Photomicrographs of the Col_h phase exhibited by **4** at 94.7°C.



Note. 7A: (i) BnBr, K_2CO_3; 7B: (i) NaOH; (ii) 36% HCI; 7C: DCC DMAP; 7D: H_2, 10% Pd/C.
Scheme 7.

polarised optical microscopy using an Olympus BH2 polarising optical microscope, Mettler FP52 heating stage and and FP82 controller. Polarised optical micrographs were obtained using a JVC TK–C1481 colour video camera in conjunction with Mettler Studio Capture software and the polarised microscopy setup. Liquid crystal transition and isotropisation temperatures and melting points of all final products were confirmed by DSC, and all temperatures quoted are onset values from the transitions. DSC results were obtained using a Mettler DSC822e with STARe software, calibrated using indium (melting point onset 156.6°C, enthalpy 28.45 J g^{-1}) and zinc (melting point onset 419.47°C). The calibration of the DSC was checked daily using the indium standard, allowing ±0.3°C and ±0.3 J g^{-1} experimental error. Aluminium pans were used as the standard reference.

4.1 4-Dodecyloxybenzoic acid (9)

1-Bromododecane (32.60 g, 0.131 mol) was added drop-wise to a stirred heated mixture of **8** (9.03 g,

0.0654 mol), sodium hydroxide (5.23 g, 0.131 mol), water (100 ml) and ethanol (400 ml), which was heated under reflux for 24 h. The mixture was cooled to room temperature and a second portion of sodium hydroxide (5.23 g, 0.131 mol) and water (500 ml) added, and the mixture was heated under reflux for a further 2 h. After cooling to room temperature the mixture was poured on to ice and acidified (Congo Red) with 20% hydrochloric acid. The resulting precipitate was filtered off and recrystallised from ethanol / ethyl acetate (5:1) to yield colourless needle-like crystals.

Yield 16.81 g (84%). Transitions (°C) Cryst 92.4 SmC 131.5 N 142.0 Iso (lit. Cryst 88 SmC 130 N 137 Iso) [16]. ^{1}H–NMR ($CDCl_3$) δ_H 0.88 (3H, t), 1.21–1.37 (16H, m), 1.47 (2H, quint), 1.81 (2H, quint), 4.01 (2H, t), 6.93 (2H, d, $J = 7.8$ Hz), 8.05 (2H, d, $J = 7.8$ Hz). MS *m/z* 306 (M^+).

4.2 Benzyl 4-(4-dodecyloxyphenylcarbonyloxy) benzoate (12)

To a stirred solution of **9** (10.00 g, 32.68 mmol), **10** (7.50 g, 32.89 mmol) and *N*,*N*-dicyclohexylcarbodiimide (DCC) (6.80 g, 33.00 mmol) in dry dichloromethane (DCM) (200 ml), 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.60 g, 4.91 mmol) was added and the reaction mixture stirred at room temperature under an atmosphere of dry nitrogen for 24 h. The DCM was removed *in vacuo*, and the crude product purified by column chromatography (silica gel, DCM) to give a white crystalline solid.

Yield 13.40 g (78%). mp = 61–62°C (lit. 62–63°C).[16] ^{1}H–NMR ($CDCl_3$) δ_H 0.88 (3H, t), 1.28–1.38 (16H, m), 1.81 (2H, quint), 4.04 (2H, t), 5.38 (2H, s), 6.97 (2H, d, $J = 7.8$ Hz), 7.27 (2H, m), 7.41 (5H, m), 8.13 (4H, m). MS *m/z* 516 (M^+).

4.3 4-Benzyloxyphenyl 4-dodecyloxybenzoate (13)

Compound **13** was prepared using a similar procedure to that for **2**, but using the following reagents and quantities: **9** (10.00 g, 32.80 mmol), **11** (6.60 g, 33.00 mmol), DCC (6.80 g, 33.00 mmol), dry DCM (200 ml) and DMAP (0.60 g, 4.91 mmol). The crude product was purified by column chromatography (silica gel, DCM) to give a white crystalline solid.

Yield 12.90 g (80%). mp = 98–99°C. ^{1}H–NMR ($CDCl_3$) δ_H 0.88 (3H, t), 1.22–1.44 (16H, m), 1.47 (2H, quint), 1.81 (2H, quint), 4.04 (2H, t), 5.28 (2H, s), 6.97 (4H, 2 × d, $J = 7.8$ Hz), 7.10 (2H, 2 × d, $J = 7.8$ Hz), 7.40 (5H, m), 8.13 (2H, d, $J = 7.8$ Hz). MS *m/z* 488 (M^+).

4.4 4-(4-Dodecyloxyphenylcarbonyloxy)benzoic acid (14)

To a stirred solution of **12** (4.30 g, 8.33 mmol) in tetrahydrofuran (THF) (500 ml) was added palladium on charcoal (10%, 1.00 g). The reaction mixture was stirred in an atmosphere of dry hydrogen at room temperature over 8 h. The palladium on charcoal was filtered off and the THF removed *in vacuo*. The solid residue was purified by recrystallisation from ethanol, giving a white crystalline solid.

Yield 3.30 g (92%). Transitions (°C) Cryst 119.4 SmC 204.3 N 219.4 Iso (lit. Cryst 120 SmC 209 N 220 Iso).[16] ^{1}H–NMR ($CDCl_3$) δ_H 0.81 (3H, t), 1.22–1.38 (16H, m), 1.47 (2H, m), 1.79 (2H, quint), 4.05 (2H, t), 7.07 (2H, d, $J = 7.8$ Hz), 7.35 (2H, d, $J = 7.8$ Hz), 8.02 (4H, 2 × d, $J = 7.8$ Hz). MS *m/z* 426 (M^+).

4.5 4-(4-Dodecyloxyphenylcarbonyloxy)phenol (15)

To a stirred solution of **13** (4.20 g, 8.61 mmol) in ethyl acetate (500 ml) was added palladium on charcoal (10%, 1.00 g) and the reaction mixture was stirred in an atmosphere of dry hydrogen at room temperature for 8 h. The palladium on charcoal was filtered off and the ethyl acetate removed *in vacuo*. The solid residue was purified by recrystallisation from ethanol) to give a white crystalline solid.

Yield 2.60 g (76%). mp = 109–110°C. ^{1}H–NMR ($CDCl_3$) δ_H 0.71 (3H, t), 1.20–1.24 (16H, m), 1.51 (2H, quint), 1.92 (2H, quint), 3.87 (2H, t), 6.69 (2H, d, $J = 7.8$ Hz), 6.81 (4H, 2 × d, $J = 7.8$ Hz), 7.94 (2H, d, $J = 7.8$ Hz). MS *m/z* 398 (M^+).

4.6 3-Benzyloxybenzoic acid (17)

Compound **17** was prepared using a similar procedure to that used for the preparation of **9**, but with the following reagents and quantities: benzyl bromide (30.00 g, 0.175 mol), **16** (12.00 g, 0.0870 mol), potassium hydroxide (9.80 g, 0.175 mol), water (20 ml), ethanol (250 ml), potassium hydroxide (9.80 g, 0.175 mol) and water (40 ml). The crude product was purified by recrystallisation from ethanol to yield colourless crystals.

Yield 14.08 g (71%). mp = 132–135°C (lit. 134°C).[17] ^{1}H– NMR ($CDCl_3$) δ_H 5.13 (2H, s), 7.23 (1H, ddd, $J = 7.5$ Hz, $J = 1.9$ Hz, $J = 1.4$ Hz), 7.32–7.47 (6H, m), 7.71–7.75 (2H, m). MS *m/z*: 228 (M^+).

4.6 1,3,5-Tri(3-benzyloxyphenylcarbonyloxy) benzene (19)

Compound **19** was prepared using a similar procedure to that for **12**, but using the following reagents and quantities: **18** (2.40 g, 0.0191 mol), **17** (13.72 g, 0.0602 mol), DCC (12.40 g, 0.0602 mol), DCM (250 ml) and DMAP (2.2 g, 0.0181 mol). The crude product was purified by column chromatography (silica gel, hexane with gradual introduction of DCM) to yield colourless crystals.

Yield 12.50 g (87%). mp = 127–131°C. ^{1}H–NMR ($CDCl_3$) δ_H 5.13 (6H, s), 7.15 (3H, s), 7.25 (3H, ddd, $J = 7.5$, J = 1.9 Hz, $J = 1.4$ Hz), 7.34–7.47 (18H, m), 7.79 (3H, dd, $J = 7.5$ Hz, $J = 7.5$ Hz), 7.80 (3H, dd, $J = 1.9$ Hz, $J = 1.5$ Hz). MS *m/z*: 780 ($M^+ + Na$).

4.7 1,3,5-Tri(3-hydroxyphenylcarbonyloxy) benzene (20)

Compound **20** was prepared by using a similar procedure to that for **14**, but using the following reagents and quantities: **19** (9.70 g, 0.0128 mol), palladium on charcoal (10%, 1.50 g) and THF (400 ml) and the reaction mixture was stirred in an atmosphere of dry hydrogen at room temperature for 8 h to yield a colourless solid. Compound **20** was used without further purification.

Yield 6.02 g (97%). mp = 222–223°C. ^{1}H–NMR ($CDCl_3$) δ_H 6.50 (3H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 6.52 (3H, s), 6.74 (4H, dd, $J = 7.5$ Hz, $J = 7.5$ Hz), 6.97–7.02 (6H, m), 9.00 (3H, s). MS *m/z*: 509 ($M^+ + Na$).

4.8 1,3,5-Tri(3-(4-(4-dodecyloxyphenylcarbonyloxy) phenylcarbonyloxy)phenylcarbonyloxy) benzene (1)

Compound **1** was prepared using a similar procedure to that for **12**, but using the following reagents and quantities: **20** (0.57 g, 1.17 mmol), **14** (1.65 g, 3.87 mmol), DCC (0.80 g, 3.88 mmol), DCM (dry; 100 ml) and DMAP (0.14 g, 1.17 mmol). The crude product was purified by column chromatography (silica gel / hexane, with the gradual introduction of ethyl acetate), followed by recrystallisation from ethanol / ethyl acetate (2:1), yielding colourless crystals.

Yield 0.98 g (49 %). Transitions (°C) Cryst 132.2 (Col_h 96.0) Iso. ^{1}H–NMR ($CDCl_3$) δ_H 0.88 (9H, t), 1.23–1.41 (48H, m), 1.48 (6H, quint), 1.83 (6H, quint), 4.05 (6H, t), 6.99 (6H, d), 7.20 (3H, s), 7.39 (6H, d, $J = 7.8$ Hz), 7.54 (3H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 7.60 (3H, dd, $J = 7.5$ Hz, $J = 1.4$ Hz), 8.09 (3H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 8.15 (6H, d, $J = 7.8$ Hz), 8.30 (6H, d, $J = 7.8$ Hz). ^{13}C–NMR ($CDCl_3$) δ_C 14.12, 22.68, 25.96, 29.06, 29.34, 29.54, 29.57, 29.62, 29.64, 31.91, 68.38, 113.30, 114.40, 120.88, 122.19, 123.61, 126.37, 127.48, 127.82, 129.85, 130.60, 131.92, 132.43, 151.01, 151.40, 155.58, 163.46, 163.82, 164.23, 164.29. MS *m/z*: 1735 ($M^+ + Na$). Elemental analysis for $C_{105}H_{114}O_{21}$ requires C 73.66%, H 6.71%; found: C 73.58%, H 6.92%.

4.9 1-Benzyloxy-3-bromobenzene (22)

A stirred mixture of **21** (20.00 g, 0.116 mol), benzyl bromide (18.00 g, 0.105 mol) and potassium carbonate (32.00 g, 0.232 mol) in butanone (200 ml) was heated under reflux for 24 h. The mixture was cooled to room temperature, the potassium carbonate filtered off and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel, 1:1 hexane / DCM) and recrystallised from ethanol to yield colourless crystals.

Yield 29.42 g (96%). mp = 61–62°C (lit. 61–62°C).[18] ^{1}H–NMR ($CDCl_3$) δ_H 5.03 (2H, s), 6.91 (1H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 7.09 (1H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 7.12–7.16 (2H, m), 7.31–7.43 (5H, m), MS *m/z*: 264 (M^+), 262 (M^+).

4.10 3-Benzyloxyphenylboronic acid (23)

A solution of **22** (34.16 g, 0.130 mol) in dry THF (200 ml) was added drop-wise to a stirred mixture of magnesium (4.00 g, 0.169 mol) and dry THF (300 ml) under dry nitrogen. The stirred mixture was heated under reflux for 1 h, cooled to –78 °C, and trimethyl borate (27.00 g, 0.260 mol) added drop-wise. The stirred mixture was allowed to warm to room temperature (overnight), acidified with 10% hydrochloric acid solution and stirred for 1 h. The product was extracted with diethyl ether (3 × 200 ml) and the combined extracts washed with water (2 × 100 ml) and dried ($MgSO_4$). The crude product was purified by stirring in suspension in hexane (1 h) to yield an off-white powder.

Yield 21.61 g (73%). mp = 139–141°C. ^{1}H–NMR (DMSO–D_6) δ_H 5.07 (2H, s), 7.02 (1H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 7.23 (1H, dd, $J = 7.5$ Hz, $J = 7.5$ Hz), 7.30–7.44 (7H, m), 8.03 (2H, s). MS *m/z*: 630 (M^+ of trimeric anhydride).

4.11 1,3,5-Tri(3-benzyloxyphenyl)benzene (25)

Compound **23** (12.00 g, 0.0528 mol) was added to a stirred heated mixture of **24** (5.04 g, 0.0160 mol),

sodium carbonate (11.24 g, 0.106 mol), tetrakis(triphenylphosphine)palladium(0) (0.90 g, 0.80 mmol), water (60 ml) and 1,2-dimethoxyethane (180 ml) under nitrogen. The stirred mixture was heated under reflux for 48 h, cooled to room temperature and filtered to remove traces of palladium catalyst. The mixture was extracted into diethyl ether (3 × 150 ml), and the combined organic extracts were washed with water and brine and finally dried ($MgSO_4$). The crude product was purified by column chromatography (silica gel, 1:1 hexane / DCM) and recrystallised from ethanol / ethyl acetate (2:1) to yield off-white crystals.

Yield 9.00 g (90%). mp = 99–102°C. ^{1}H–NMR (CD_2Cl_2) δ_H 5.07 (6H, s), 6.94 (3H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 7.24–7.41 (24H, m), 7.70 (3H, s). MS *m/z*: 624 (M^+).

4.12 1,3,5-Tri(3-hydroxyphenyl)benzene (26)

Compound **26** was prepared using a similar procedure to that for **14,** but using the following quantities: **25** (8.80 g, 0.0141 mol), palladium on charcoal (10%, 2.00 g) and THF (400 ml).

Yield 4.74 g (95%). mp = 281–284°C. ^{1}H–NMR ($CDCl_3$ & DMSO–d_6) δ_H 6.30 (3H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 6.56–6.59 (6H, m), 6.74 (3H, dd, $J = 7.5$ Hz, $J = 7.5$ Hz), 7.17 (3H, s). MS *m/z*: 377 (M^+ + Na).

4.13 1,3,5-Tri(3-(4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy)phenyl)-benzene (2)

Compound **2** was prepared by a similar procedure to **12** but using the following quantities: **26** (0.45 g, 1.27 mmol), **14** (1.79 g, 4.20 mmol), DCC (0.87 g, 4.22 mmol), DMAP (0.15 g, 1.23 mmol) and dry DCM (170 ml). The crude product was purified by column chromatography (silica gel, hexane) and recrystallised from ethanol / ethyl acetate, (2:1) to yield a colourless solid.

Yield 0.88 g (44%). mp = 185°C. ^{1}H–NMR ($CDCl_3$) δ_H 0.89 (9H, t), 1.26–1.38 (48H, m), 1.48 (6H, quint), 1.82 (6H, quint), 4.05 (6H, t), 6.98 (6H, d, $J = 7.8$ Hz), 7.28 (3H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 7.38 (6H, d, $J = 7.8$ Hz), 7.75 (3H, dd, $J = 7.5$ Hz, $J = 7.5$ Hz), 7.56 (3H, dd, $J = 7.5$ Hz, $J = 1.9$ Hz), 7.63 (3H, ddd, $J = 7.5$, $J = 1.9$ Hz, $J = 1.4$ Hz), 7.82 (3H, s), 8.15 (6H, d, $J = 7.8$ Hz), 8.31 (6H, d, $J = 7.8$ Hz). ^{13}C–NMR ($CDCl_3$) δ_C 14.11, 22.67, 25.95, 29.06, 29.33, 29.54, 29.57, 29.61, 29.64, 31.90, 68.34, 114.36, 120.64, 120.93, 122.08, 124.91, 125.52, 126.79, 129.90, 131.81, 132.39, 141.45, 142.48, 151.35, 155.37, 163.77, 164.26, 164.49. MS *m/z*: 1602 (M^+ + Na). Elemental analysis for $C_{102}H_{114}O_{15}$ requires C 77.54%, H 7.27%; found: C 77.69%, H 7.17%.

4.14 1,3,5-Tri(4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy)benzene (3)

Compound **3** was prepared by a similar procedure to that for **12**, but using the following reagents and quantities: **18** (0.28 g, 2.22 mmol), **14** (3.12 g, 7.30 mmol), DCC (1.50 g, 7.30 mmol), DMAP (0.28 g, 2.30 mmol) and DCM (120 ml). The crude product was purified by column chromatography (silica gel, 1:1 hexane / DCM and silica gel, and hexane with increasing volume fractions of DCM), and recrystallisation from ethanol / ethyl acetate (10:1) to yield colourless crystals.

Yield 1.14 g (38%). Transition (°C) Cryst 79.9 Col_r 87.7 Iso. ^{1}H–NMR ($CDCl_3$) δ_H 0.88 (9H, t), 1.24–1.41 (48H, m), 1.49 (6H, quint), 1.83 (6H, quint), 4.06 (6H, t), 6.99 (6H, d, $J = 7.8$ Hz), 7.19 (3H, s), 7.38 (6H, d, $J = 7.8$ Hz), 8.16 (6H, d, $J = 7.8$ Hz), 8.29 (6H, d, $J = 7.8$ Hz). ^{13}C–NMR ($CDCl_3$) δ_C 8.53, 14.12, 22.68, 25.96, 29.07, 29.35, 29.56, 29.58, 29.62, 29.65, 31.91, 68.38, 114.41, 120.89, 122.19, 126.32, 131.91, 132.43, 134.45, 148.72, 151.51, 155.56, 163.82, 164.28. MS *m/z*: 1374 (M^+ + Na). Elemental analysis for $C_{84}H_{102}O_{15}$ requires C 74.64%, H 7.61%; found: C 74.89%, H 7.89%.

4.15 1,3,5-Tri(4-(4-dodecyloxyphenylcarbonyloxy)phenyloxycarbonyl)benzene (4)

Compound **4** was prepared by a similar procedure to that for **12**, but using the following reagents and quantities: **15** (2.40 g, 6.09 mmol), **27** (0.42 g, 2.00 mmol), DCC (0.50 g, 2.42 mmol), dry DCM (100 ml) and DMAP (0.20 g, 1.64 mmol). The crude product was purified by column chromatography (silica gel, DCM) and recrystallised from acetone to yield a colourless solid.

Yield 0.83 g (30%). Transitions (°C) Cryst 71.4 Col_h 107.8 Iso. ^{1}H–NMR ($CDCl_3$) δ_H 0.89 (9H, t), 1.33 (54H, m), 1.81 (6H, quint), 4.05 (6H, t), 6.98 (6H, d, $J = 7.8$ Hz), 7.33 (12H, m), 8.15 (6H, d, $J = 7.8$ Hz), 9.26 (3H, s). MS (MALDI) *m/z* 1374 (M^+ + Na). Elemental analysis for $C_{84}H_{102}O_{15}$ requires C 74.66% and H 7.58%; found: C 74.61%, H 7.70%.

4.16 3,5-Dibenzyloxybenzoic acid (29)

Benzyl bromide (21.4 g, 0.125 mol) was added dropwise to a stirred mixture of **28** (10.0 g, 0.059 mol) and potassium carbonate (18.0 g, 0.130 mol) in DMF

(50 ml). The stirred mixture was heated at 60°C for 16 h, cooled, and the potassium carbonate filtered off. The DMF and unreacted benzyl bromide were removed by distillation under reduced pressure. The crude product was dissolved in dichloromethane (400 ml) and the dichloromethane extract washed with water (3 × 150 ml) and dried ($MgSO_4$). The crude product was dissolved in ethanol (50 ml) and aqueous potassium hydroxide (40%, 100 ml) was added. The reaction mixture was stirred under reflux for 14 h. The cooled reaction mixture was poured into water (300 ml) and acidified with concentrated hydrochloric acid. The precipitated carboxylic acid was filtered off, washed with water and dried. Recrystallisation from acetone gave a white solid.

Yield 8.30 g (42%). mp = 212–214°C. ^{1}H–NMR (acetone–d_6) δ_H 5.17 (4H, s), 6.91 (1H, dd, J = 7.8 Hz, J = 1.5 Hz), 7.27 (2H, dd, J = 7.8 Hz, J = 1.5 Hz), 7.30–7.51 (10H, m). MS m/z 334 (M^+).

4.17 4-(3,5-Dibenzyloxyphenylcarbonyloxy)phenyl 4-dodecyloxybenzoate (30)

Compound **29** was prepared using a similar procedure to that for **2**, but using the following reagents and quantities: **15** (0.90 g, 2.26 mmol), **28** (0.80 g, 2.40 mmol), DCC (0.50 g, 2.42 mmol), dry DCM (60 ml) and DMAP (0.20 g, 1.64 mmol). The crude product was purified by column chromatography (silica gel, DCM) and recrystallised from hexane to give a white crystalline solid.

Yield 1.19 g (73%). mp = 96°C. ^{1}H–NMR ($CDCl_3$) δ_H 0.87 (3H, t), 1.20–1.24 (18H, m), 1.83 (2H, quint), 4.05 (2H, t), 5.11 (4H, s), 6.88 (1H, dd, J = 7.8 Hz, J = 1.5 Hz), 6.98 (2H, d, J = 7.8 Hz), 7.44 (16H, m), 8.14 (2H, d, J = 7.8 Hz). MS m/z 715 ($M^+ + H$).

4.18 4-(3,5-Dihydroxyphenylcarbonyloxy)phenyl 4-dodecyloxybenzoate (31)

Compound **31** was prepared using a similar procedure to that for **14**, but using the following reagents and quantities: **30** (1.20 g, 1.29 mmol), THF (500 ml) and palladium on charcoal (10%, 1.00 g). Recrystallisation from DCM gave a white crystalline solid.

Yield 0.69 g (78%). mp = 150–152°C. ^{1}H–NMR ($CDCl_3$ with DMSO–d_6) δ_H 0.61 (3H, t), 0.91–1.13 (18H, m), 1.55 (2H, quint), 3.79 (2H, t), 6.37 (1H, dd, J = 7.8 Hz, J = 1.5 Hz), 6.48 (2H, d, J = 1.4 Hz), 6.71 (2H, d, J = 7.8 Hz), 6.87 (2H, d, J = 7.5 Hz), 6.93 (4H, 2 × d, J = 7.8 Hz), 7.85 (2H, d). MS m/z 534 (M^+).

4.19 1-(4-(4-Dodecyloxyphenylcarbonyloxy) phenyloxycarbonyl)-3,5-di-(4-(4-dodecyloxy phenylcarbonyloxy)phenylcarbonyloxy)benzene (5)

Compound **5** was prepared using a similar procedure to that for **12**, but using the following reagents and quantities: **31** (0.69 g, 1.29 mmol), **14** (1.01 g, 2.58 mmol), DCC (0.53 g, 2.58 mmol), dry DCM (40 ml) and DMAP (0.20 g, 1.64 mmol). The crude product was purified by column chromatography (silica gel, DCM) and recrystallised from ethanol to give a white crystalline solid.

Yield 0.19 g (11%). Transitions (°C) Cryst 92.3 Col_h 93.2 Iso. ^{1}H–NMR ($CDCl_3$) δ_H 0.80 (9H, t), 1.25 (54H, m), 1.73 (6H, quint), 3.95 (6H, quint), 6.89 (6H, d, J = 7.8 Hz), 7.19 (4H, d, J = 7.8 Hz), 7.30 (4H, d, J = 7.8 Hz), 7.44 (1H, dd, J = 1.4 Hz, J = 1.4 Hz), 7.93 (2H, d, J = 1.4 Hz), 8.06 (6H, d, J = 7.8 Hz), 8.21 (4H, d, J = 7.8 Hz). MS (MALDI) m/z 1374 (M^++Na).
Elemental analysis for $C_{84}H_{102}O_{15}$ requires C 74.66% and H 7.58%; found: C 75.01%, H 7.69%.

4.20 Dimethyl 5-benzyloxyisophthalate (33)

To a stirred solution of **32** (10.50 g, 49.45 mmol) in butanone (200 ml) were added benzyl bromide (10.30 g, 60.23 mmol), potassium carbonate (34.50 g, 0.25 mol) and potassium iodide (0.50 g). The reaction mixture was stirred in an atmosphere of dry nitrogen at room temperature for 48 h. The potassium salts were filtered off and the butanone removed by distillation under reduced pressure. The solid residue was purified by column chromatography (silica gel, 1:1 dichloromethane / hexane) and recrystallised from hexane to give a white crystalline solid.

Yield 1.19 g (73%). mp = 96–97°C. ^{1}H–NMR ($CDCl_3$) δ_H 3.93 (6H, s), 5.13 (2H, s), 7.44 (5H, m), 7.84 (2H, d, J = 7.8 Hz), 8.29 (1H, dd, J = 1.5 Hz, J = 1.5 Hz). MS m/z 300 (M^+).

4.21 5-Benzyloxyisophthalic acid (34)

To a stirred solution of **33** (11.2 g, 3.73 mmol) in ethanol (300 ml) and water (40 ml) was added sodium hydroxide (6.70 g, 0.170 mol). The reaction mixture was stirred at room temperature for 5 h. The ethanol was removed by distillation under reduced pressure and water (100 ml) added, and the mixture was then acidified with 20% hydrochloric acid. The product was extracted with ether (3 × 150 ml) and the combined extracts washed with water (2 × 150 ml) and dried ($MgSO_4$). The crude product was recrystallised from ethanol and gave a white crystalline solid.

Yield 4.23 g (42%). mp = 268–270°C. ^{1}H–NMR ($CDCl_3$) δ_H 5.15 (2H, s), 7.41 (5H, m), 7.81 (2H, d, J = 7.8 Hz), 8.30 (1H, dd, J = 1.5 Hz, J = 1.5 Hz). MS m/z 272 (M^+).

4.22 1-Benzyloxy-3,5-di(4-(4-dodecyloxyphenylcarbonyloxy)phenyloxycarbonyl)benzene (35)

Compound **35** was prepared using a similar procedure to that for **12**, but using the following reagents and quantities: **34** (0.50 g, 1.84 mmol), **15** (1.46 g, 3.67 mmol), DCC (0.80 g, 3.88 mmol), dry DCM (200 ml) and DMAP (0.20 g, 1.64 mmol). The crude product was purified by column chromatography (silica gel, DCM) and recrystallised from ethanol to give a white crystalline solid.

Yield 1.43 g (76%). mp = 110–112°C. ^{1}H–NMR ($CDCl_3$) δ_H 0.89 (6H, t), 1.27 (36H, m), 1.47 (4H, m), 4.05 (4H, t), 5.23 (2H, s), 6.98 (4H, d, J = 7.8 Hz), 7.30 (8H, m), 7.43 (5H, m), 8.06 (2H, d, J = 7.8 Hz), 8.14 (4H, d, J = 7.8 Hz), 8.62 (1H, dd, J = 1.5 Hz, J = 1.5 Hz). MS (MALDI) m/z 1056 (M^+ + Na).

4.23 3,5-Di(4-(4-dodecyloxyphenylcarbonyloxy)phenyloxycarbonyl)-1-hydroxybenzene (36)

Compound **36** was prepared using a similar procedure to that for **14**, but using the following reagents and quantities: **35** (1.43 g, 1.40 mmol), ethyl acetate (500 ml) and palladium on charcoal (10%, 1.00 g). The crude product was purified by recrystallisation from ethanol to give a white crystalline solid.

Yield 1.07 g (82%). mp = 163–164°C. ^{1}H–NMR ($CDCl_3$ with DMSO–d_6) δ_H, 0.88 (6H, t,), 1.33 (36H, m), 1.82 (4H, quint), 4.06 (4H, t), 6.99 (4H, d, J = 7.8 Hz), 7.27 (8H, m), 7.92 (2H, d, J = 7.8 Hz), 8.12 (4H, d, J = 7.8 Hz), 8.45 (1H, dd, J = 1.5 Hz, J = 1.5 Hz). MS (MALDI) m/z 965 (M^+ + Na).

4.24 1-(4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy)-3,5-di(4-(4-dodecyloxyphenylcarbonyloxy)phenyloxycarbonyl) benzene (6)

Compound **6** was prepared using a similar procedure to that for **12**, but using the following reagents and quantities: **35** (1.07 g, 1.47 mmol), **14** (0.64 g, 1.50 mmol), DCC (0.31 g, 1.50 mmol), dry DCM (100 ml) and DMAP (0.20 g, 1.64 mmol). The crude product was purified by column chromatography (silica gel, DCM) and recrystallised from acetone to give a white solid.

Yield 0.83 g (30%). Transitions (°C) Cryst 79.8 Col_h 99.8 Iso. ^{1}H–NMR ($CDCl_3$) δ_H 0.89 (9H, t), 1.20–1.41 (54H, m), 1.81 (6H, quint), 4.05 (6H, m), 6.98 (6H, m), 7.30 (8H, m), 7.42 (2H, d, J = 7.8 Hz), 8.15 (6H, m), 8.34 (4H, m), 8.95 (1H, dd, J = 1.5 Hz, J = 1.5 Hz). MS (MALDI) m/z 1374 (M^+ + Na).

Elemental analysis for $C_{84}H_{102}O_{15}$ requires C 74.66% and H 7.58%; found: C 74.97%, H 7.81%.

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