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The creation of long-lasting glassy columnar discotic liquid crystals using 'dimeric' discogens

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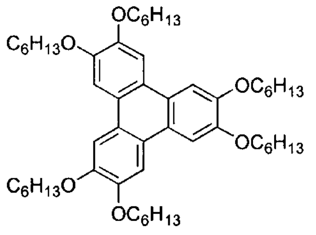
'Dimeric' discogens have been synthesised which have two triphenylene nuclei, each of which bears five β-OC_6H_{13} substituents, which are linked through the remaining β positions by a flexible $O(CH_2)_nO$ polymethylene chain (n = 3–16). Calculations show that the minimum chain length for bridging between columns in the Col_h phase of these compounds is $O(CH_2)_7O$. It was found that only those dimers for which $n > 7$ formed a Col_h phase. This mesophase can be supercooled into a metastable glass which is relatively hard and in which the columnar order and orientation is retained. These glasses revert to the crystalline state within a few hours but we have shown that longer-lasting Col_h glasses can be engineered through introducing an extra degree of disorder into the glass by making the 'dimers' subtly unsymmetrical. These 'dimers' either have differently substituted triphenylene rings at the two ends of the linking chain or an amide group within the chain itself. They give Col_h aligned glasses which last for months at room temperature.

Most suggested applications for the columnar phases of discotic liquid crystals[1] depend on their unique alignment and conduction[2] properties but, in any real application, the ease with which they can be processed and mechanical robustness will also be important issues. This paper is concerned with attempts to synthesise oligomers which combine the desirable alignment properties of monomeric discogens with the desirable robustness of glassy films obtained from polymeric discogens.



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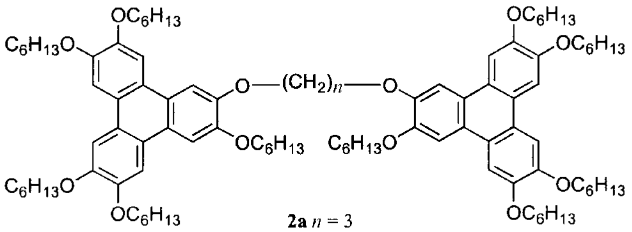
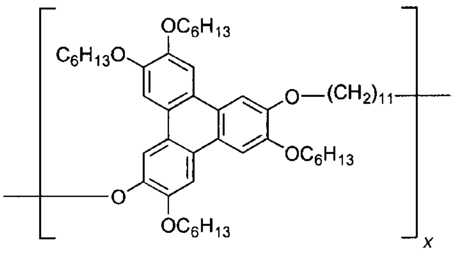


2a $n = 3$
2b $n = 5$
2c $n = 7$
2d $n = 8$
2e $n = 9$
2f $n = 10$
2g $n = 12$
2h $n = 16$



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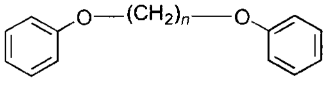
In the columnar phases of discotic liquid crystals, the aromatic cores are stacked on top of each other and the columns thus formed are ordered on a two-dimensional lattice. The space between the columns is filled by mobile, fluid, disordered alkyl chains. Provided the aromatic cores are the same and the 'packing fraction' for the core and the alkyl chains is about the same, more-or-less the same phase behaviour is observed regardless of whether the system is monomeric, oligomeric or polymeric. For example, HAT6 **1** shows Cr 70 Col_h 100 °C I[3] whereas the dimer **2g** shows Cr 68 Col_h 107 °C I and the polymer **3** Cr 98 Col_h 118 °C I.[4] Similarly, the low angle X-ray diffraction patterns obtained for the Col_h phases of these three are virtually indistinguishable. In other ways there are very significant differences. Unlike their low molar mass counterparts the polymeric systems are difficult to order using surface effects, they give very different optical textures (for example, Fig. 1 in ref. 5) and, whereas the Col_h phases of monomers such as **1** show some tendency to supercool, polymeric systems such as **3** display very marked supercooling.[5] In supercooled materials a metastable glassy columnar state is often formed in which the alignment, the architecture of the columns and the disorder of the chains are preserved, but in which the motion of the chains is 'frozen out'. They are mechanically stiff and relatively hard and for some applications (for example, in the preparation of LEDs where it is necessary to vapour deposit metal electrodes on very thin aligned films[6]) this is important. In a previous paper[7] we showed that 'dimeric' and 'trimeric' oligomers combine some of the desirable properties of monomers and polymers. They can be aligned by surface interactions and supercooled to form a glassy Col_h state. Compared to the polymers they are much easier to process as ordered glassy films but, unfortunately, these are also much less long-lived and the glass reverts to the crystalline state over a period of a few hours or days.



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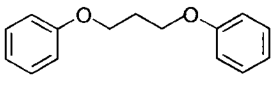
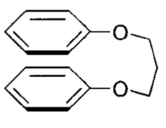
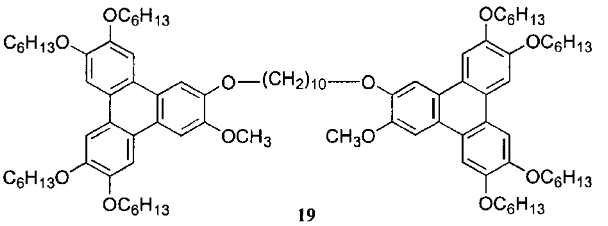


4a



4b



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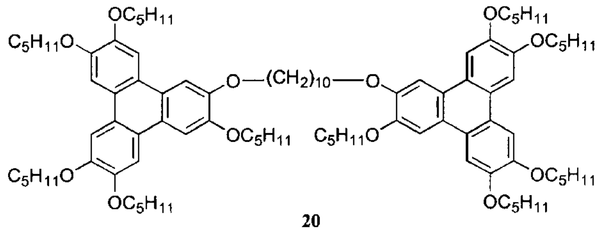

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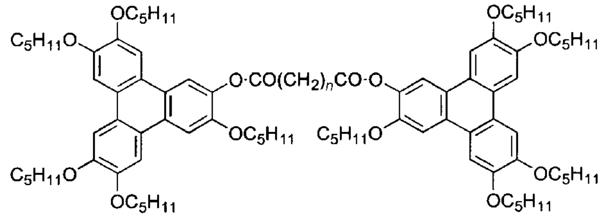
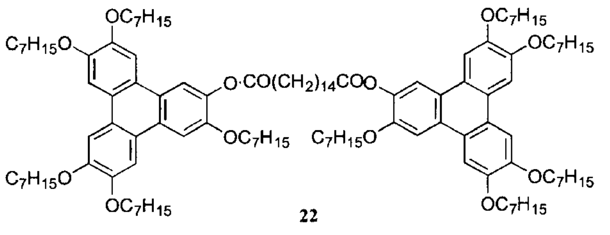


21a $n = 10$
21b $n = 12$
21c $n = 14$



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The first aim of this study was to systematically investigate the phase behaviour and glass-forming properties of discotic oligomers.[7–13] It was hoped that, by optimising the length of the $O(CH_2)_nO$ chain in the 'dimeric' oligomers **2a**–**h**, it would be possible to produce a glassy state that combined the ease of alignment of the monomers with the long life of the polymer Col_h glasses. The other main aim of this investigation was to investigate the effect of the length of the $(CH_2)_n$ chain on the stability of the Col_h phase itself; a problem relevant to the design of polymers and oligomers alike. In this respect we were following calamitic liquid crystal science studies in which 'dimers' or 'twins' have often been used as tractable models for the polymers.[14] We found that the Col_h phase was only formed by those systems **2** with $n > 7$. None of the simple dimers (produced by the route shown in Scheme 1) showed particularly long-lived glassy states. More successful strategies for producing persistent glasses were developed which involved the synthesis of an unsymmetrical hexyloxy/butoxy substituted 'dimer' (Scheme 3), and an unsymmetrical 'amide-linked' dimer (Scheme 4).

Modelling studies

In polymeric and oligomeric discotic liquid crystals a constraint exists at the molecular level which does not apply to monomeric systems. The chains linking the nuclei must be long enough and flexible enough to bridge between the aromatic cores. This bridging can be visualised as occurring in several different ways; in an intracolumnar manner (intra-1,2; intra-1,3; intra-1,4; intra-1,5; intra-1,6 *etc.*; Fig. 1) and/or in an intercolumnar manner (inter-1,2; inter-1,3 *etc.*; Fig. 1). Each of these introduces different amounts of strain into the system and this must have some bearing on the stability of the phase. The enthalpic cost of each type of bridging can be calculated using force field methods. To minimise computing time, α,ω-diphenoxyalkanes **4** were initially chosen as models for the 'dimers'. MM2 calculations[15] on **4** show that (for the isolated molecules with $n > 2$) an equilibrium mixture exists between an extended (all-*trans*) conformation **4a** which minimises the energy of the chain and a 'stacked' conformation **4b** which gives a less favourable chain conformation but benefits from the attractive ring–ring van der Waals interaction. For these isolated molecules it is this attractive ring–ring interaction (which MM2 calculates to about 6 kcal mol^{-1}) that dominates the conformational equilibrium and conformer **4b** is the more stable. In the columnar phase of **2** the attractive ring–ring van der Waals interaction between the rings is not an issue. Each ring is always 'sandwiched' between two others regardless of whether bridging is intracolumnar or intercolumnar. It is the strain within the chain itself which we need to know. This figure can be obtained from the calculations by factoring out the effect of the rings (Experimental section). Table 1 gives the MM2 calculated difference between all-*trans* $H\text{-}(CH_2)_n\text{-}H$ chains and $H\text{-}(CH_2)_n\text{-}H$ chains which have been folded as required for different types of bridging. As can be seen from Table 1 and Fig. 4, low strain bridging in an intracolumnar manner in the Col_h phase 1,2 requires $n > 2$, 1,3 requires $n > 5$, 1,4 requires $n > 7$, 1,5 requires $n > 10$, and 1,6 requires $n > 12$. Low strain bridging in an intercolumnar manner in the Col_h

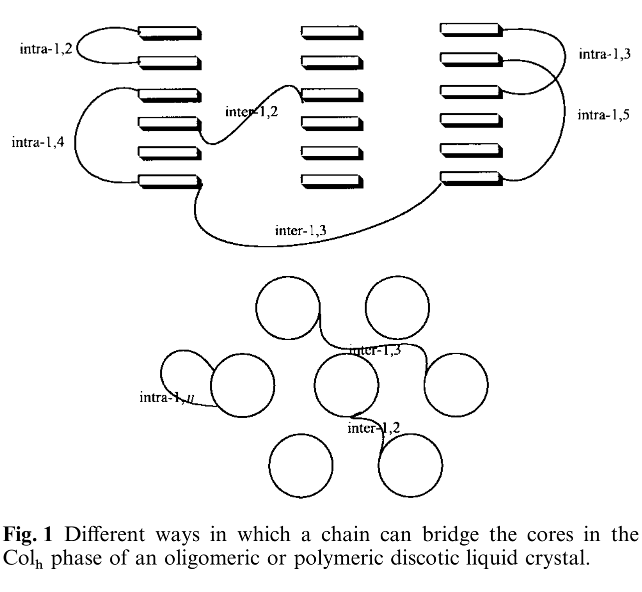


Fig. 1 Different ways in which a chain can bridge the cores in the Col_h phase of an oligomeric or polymeric discotic liquid crystal.

Table 1 Differences in energy calculated by the MM2 force field method between all-*trans* H-$(CH_2)_n$-H chains and H-$(CH_2)_n$-H chains folded in the requisite manner for **4b**, for 1,2-, 1,3-, 1,4-, 1,5- and 1,6-intrastack bridging, and 1,2- and 1,3-interstack bridging (see text)

	Energy difference/kcal mol^{-1}							
n	**4b**	intra-1,2	intra-1,3	intra-1,4	intra-1,5	intra-1,6	inter-1,2	inter-1,3
2	(1.11)	12.47						
3	1.00	1.12						
4	1.57	4.03	113.7					
5	3.91	4.74	18.04				107.8	
6	1.97	2.79	1.9	111.7			15.6	
7	4.27	4.8	1.25	27.68			4.43	
8	4.48	5.49	3	3.4			3.61	
9	4.83	5.55	3.01	2.57	109.1		4.49	
10	3.47	6.16	4.79	2.1	15.36		2.12	
11	4.73	4.99	3.07	1.77	4.04	107.3	3.19	
12	4.05	4.28	6.39	3.58	4.46	59.54	3.92	
13	3.43	3.6	3.95	4.68	4.68	5.26	5.59	
14	3.73	3.73	4.37	4.19	2.58	2.34	6.86	
15	5.41	6.14	5.18	5.06	4.45	3.64	7.12	
16	4.76	6.05	5.14	6.17	4.07	3.72	6.53	
17							4.86	142.0
18							6.45	47.34
19							6.37	11.52
20							6.99	1.41
21							6.8	3.5

phase 1,2 requires $n > 6$ and 1,3 requires $n > 19$. Examples of optimised geometries are shown in Fig. 2 and 3.

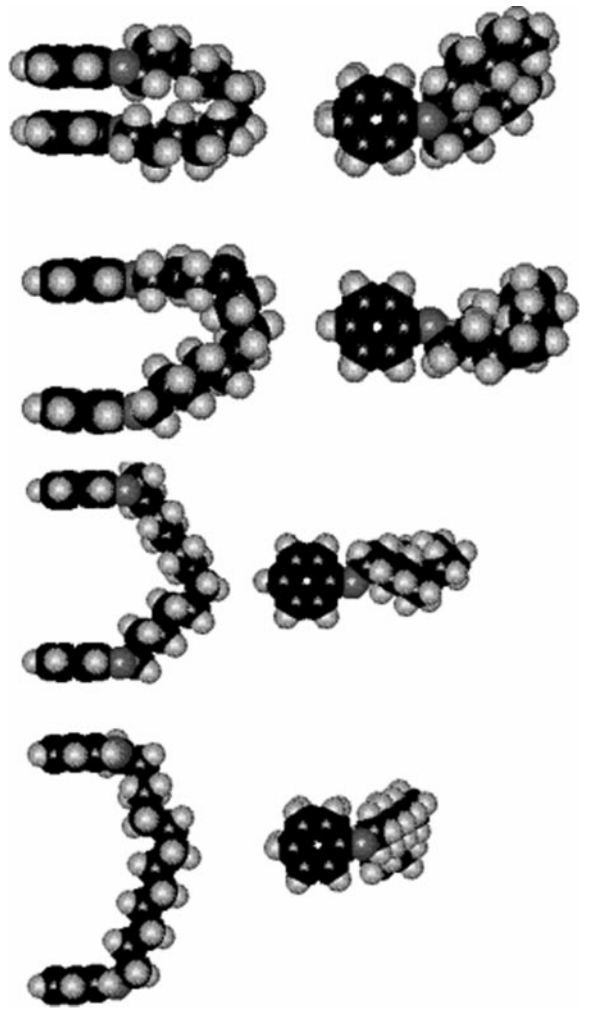


Fig. 2 Examples of geometries as optimised by the force field calculations ($n = 14$). Views from the side (left) and top (right) of the column. 1,2-Intracolumnar bridging (top), 1,3-intracolumnar bridging, 1,4-intracolumnar bridging, and 1,5-intracolumnar bridging (bottom).

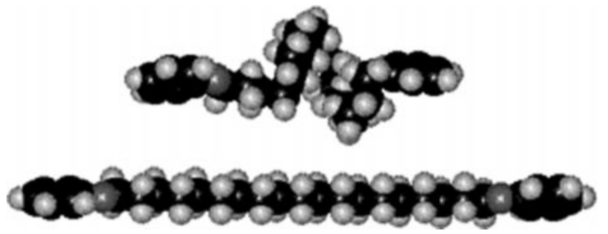
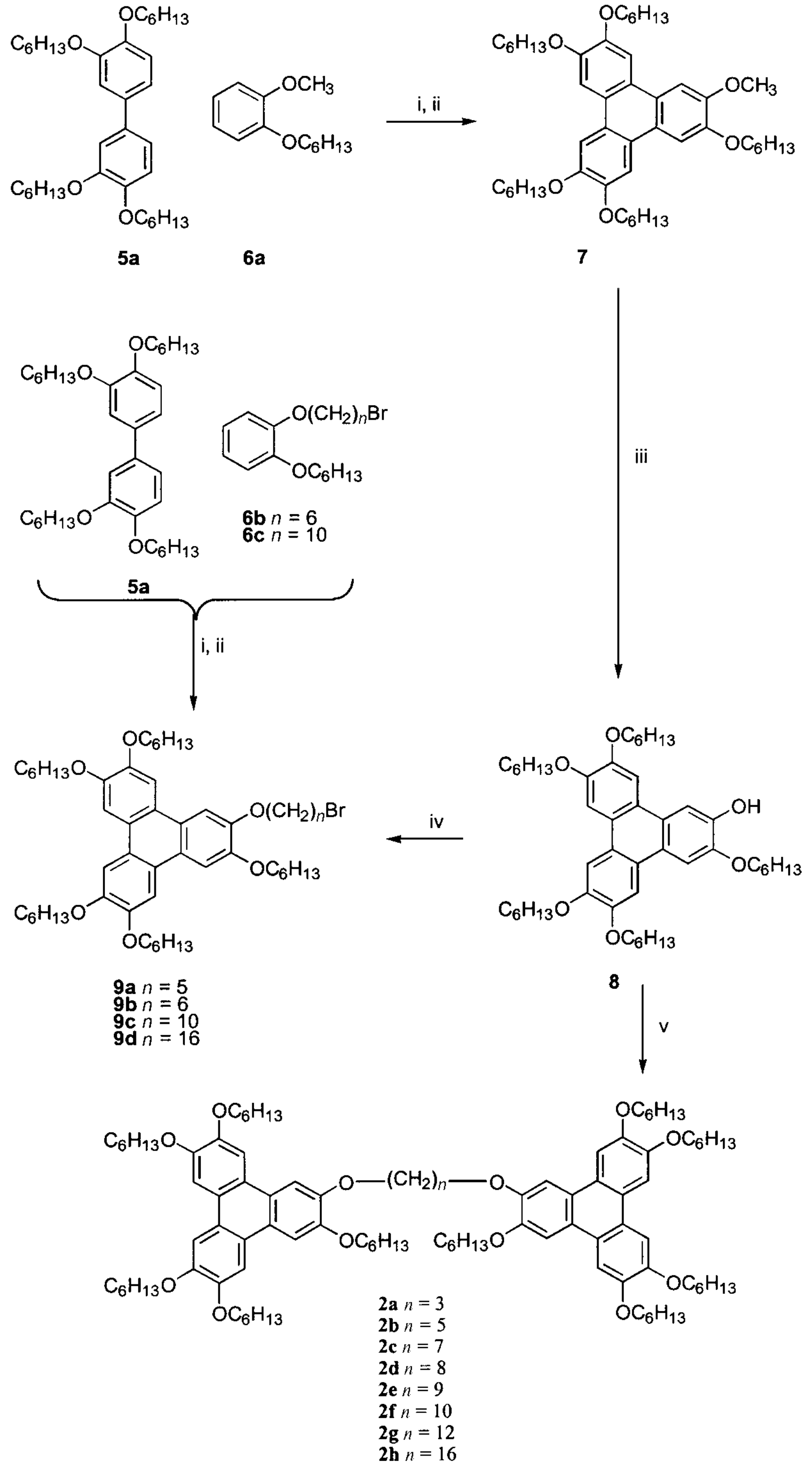


Fig. 3 Examples of geometries as optimised by the force field calculations ($n = 19$). View from the side. 1,2-Intercolumnar bridging (top) and 1,3-intercolumnar bridging (bottom).

Synthesis

The synthesis of the oligomers **2a–h** is shown in outline in Scheme 1. Iron(III) chloride mediated oxidative coupling of 3,3′,4,4′-tetrahexyloxybiphenyl **5a** with 1-hexyloxy-2-methoxybenzene **6a** followed by a reductive methanol workup gave 3,6,7,10,11-pentahexyloxy-2-methoxytriphenylene **7**.[16,17] Demethylation using lithium diphenylphosphide[18] gave 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8,** which was reacted with anhydrous potassium carbonate and 0.5 equiv. of the appropriate α,ω-dibromoalkane in refluxing ethanol to give the 'dimer' **2**. A by-product sometimes observed in these reactions was the ω-brominated product **9**. These ω-bromo products proved useful intermediates in our subsequent work. They could be obtained as the major product (yields 25–40%) by using a 1 : 1 molar ratio of the reactants. Alternatively, they could be made in better yield through the reaction of 3,3′,4,4′-tetrahexyloxybiphenyl **5a** with a 1-(ω-bromoalkoxy)-2-hexyloxybenzene **6b**,c using iron(III) chloride followed by a reductive methanol workup.

The synthesis of the symmetrical butoxy substituted oligomers shown in Scheme 2 was an essentially trivial variant on the route to the hexyloxy substituted oligomers. Iron(III) chloride mediated oxidative coupling of 3,3′,4,4′-tetrabutyloxybiphenyl **5b** with 1-butoxy-2-methoxybenzene **6d** followed by a reductive methanol workup gave 3,6,7,10,11-pentabutoxy-2-methoxytriphenylene **10**. Demethylation using lithium diphenylphosphide gave 3,6,7,10,11-pentabutoxy-2-hydroxytriphenylene **11**, which was reacted with anhydrous potassium carbonate and 0.5 equiv. of the appropriate α,ω-dibromoalkane in refluxing ethanol to give the 'dimer' **12**.



Scheme 1 *Reagents and conditions*: (i) $FeCl_3$, CH_2Cl_2; (ii) MeOH, 61% (two steps); (iii) Ph_2PLi, THF, 69%; (iv) $Br(CH_2)_nBr$, K_2CO_3, EtOH, 25% ($n=5$), 34% ($n=10$), 40% ($n=16$); (v) $Br(CH_2)_nBr$, K_2CO_3, EtOH, 20–68% ($n=3$–16).

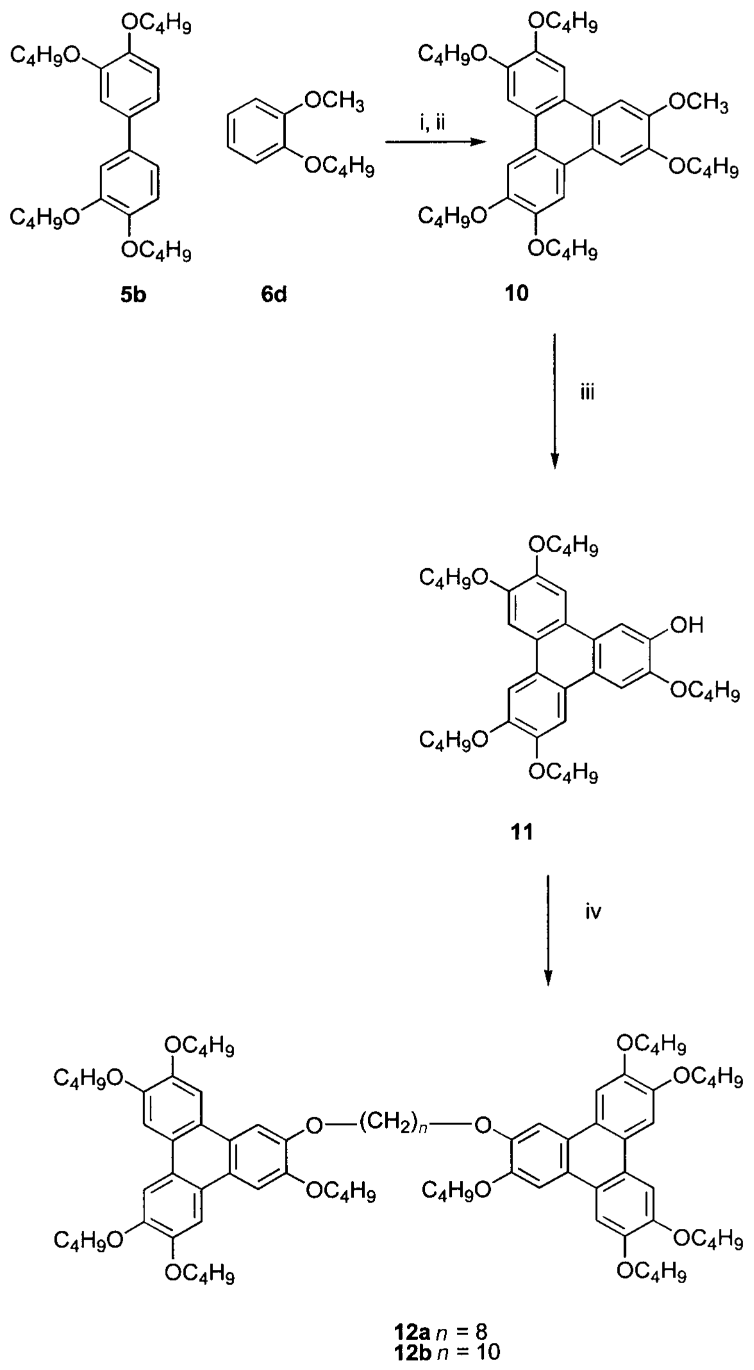
An unsymmetrical hexyloxy/butoxy substituted 'dimer' **13** was synthesised as shown in Scheme 3. The reaction of 3,6,7,10,11-pentabutoxy-2-hydroxytriphenylene **11** with the α-triphenylenyloxy-ω-bromo derivative **9c** gave the 'mixed dimer' **13**.

The synthesis of a dimer **18**, in which there is an amide group in the linking chain, is shown in Scheme 4. Ethyl 6-(3,6,7,10,11-pentahexyloxytriphenylen-2-yloxy)hexanoate **14** was made by reacting 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** with ethyl 6-bromohexanoate. Hydrolysis and reaction with oxalyl chloride gave the acid chloride **16** which was reacted with the amine **17** to give the amide **18**. The amine **17** was made from the bromide **9b** by reaction with sodium azide followed by a lithium aluminium hydride reduction.

Characterisation

The phase behaviour of the new compounds was investigated by low angle X-ray diffraction, optical polarising microscopy and differential scanning calorimetry (DSC). The results of these investigations and data for related systems are summarised in Table 2.

Compounds **2a–c** did not show liquid crystal behaviour but **2d–h** gave enantiotropic liquid crystal Col_h phases. Low angle X-ray investigations of the unoriented mesophases showed a

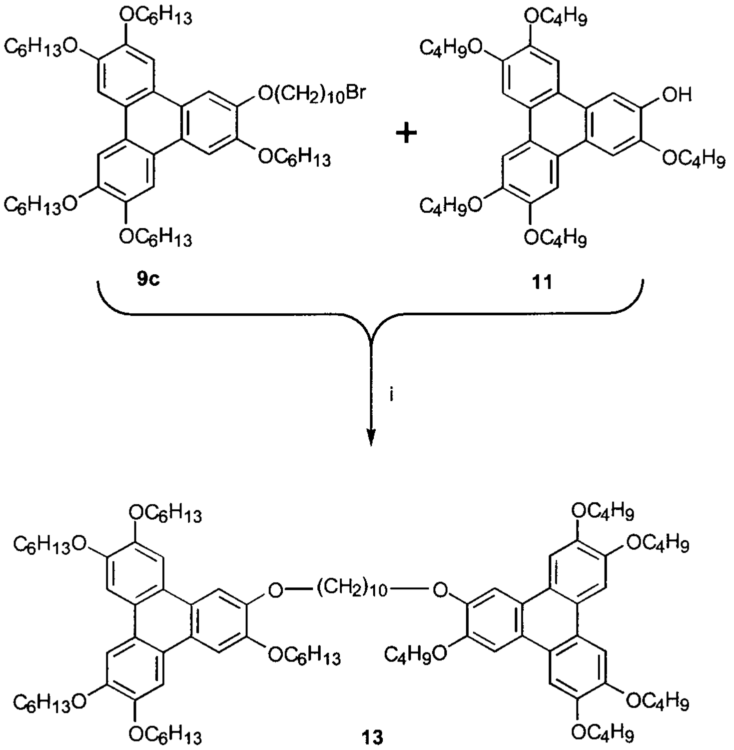


Scheme 2 *Reagents and conditions*: (i) $FeCl_3$, CH_2Cl_2; (ii) MeOH, 68% (two steps); (iii) Ph_2PLi, THF, 68%; (iv) $Br(CH_2)_nBr$, K_2CO_3, EtOH, 46% ($n = 8$), 34% ($n = 10$).

single diffraction ring corresponding to the column–column separation. Optical textures for compounds **2d–h** obtained were similar to those obtained for $\mathrm{Col_h}$ phases of HATN monomers and samples annealed just below the $\mathrm{Col_h}$–I transition temperature between glass slides quite rapidly became homeotropic.[5] On heating, the DSC results for compounds **2d–h** showed endotherms for both Cr–$\mathrm{Col_h}$ and $\mathrm{Col_h}$–I transitions (Table 2). On cooling, only the I-$\mathrm{Col_h}$ transition and a glass transition at *ca.* 35 °C were observed. At room temperature the glassy $\mathrm{Col_h}$ samples formed crystallised over a period of 3–18 h and the slow growth of the endotherm corresponding to the Cr–$\mathrm{Col_h}$ transition (apparent in the DSC scan on reheating) could be used to follow the crystallisation process. In general the longer the linking chain the shorter was the lifetime of the glass and the more rapidly did crystallisation occur.

The DSC scans for the butoxy-substituted 'dimers' **12a** and **12b** showed single reversible phase transitions at 154 and 147 °C, respectively. Compound **12b** has previously been reported by Bacher *et al.*[8] who report a single transition at 149 °C which they identified as that of the plastic columnar ($\mathrm{Col_p}$) to isotropic (I) type.

Both of the unsymmetrical 'dimers' **13** and **18** gave an enantiotropic $\mathrm{Col_h}$ phase. In the case of compound **13** low angle X-ray diffraction showed a column–column separation of 17.7 Å which compares to a value calculated using eqn. (1) (Experimental section) of 17.9 Å. Compounds **13** and **18** formed glasses when the $\mathrm{Col_h}$ phase was cooled to *ca.* 30 °C but, unlike the glasses formed from compounds **2d–h,** these glasses persist for several months at room temperature. In the case of compound **18**, a sample stored at room temperature for three months showed 15% recrystallisation as estimated by DSC.



Scheme 3 *Reagents and conditions*: (i) K_2CO_3, EtOH, 26%.

Discussion

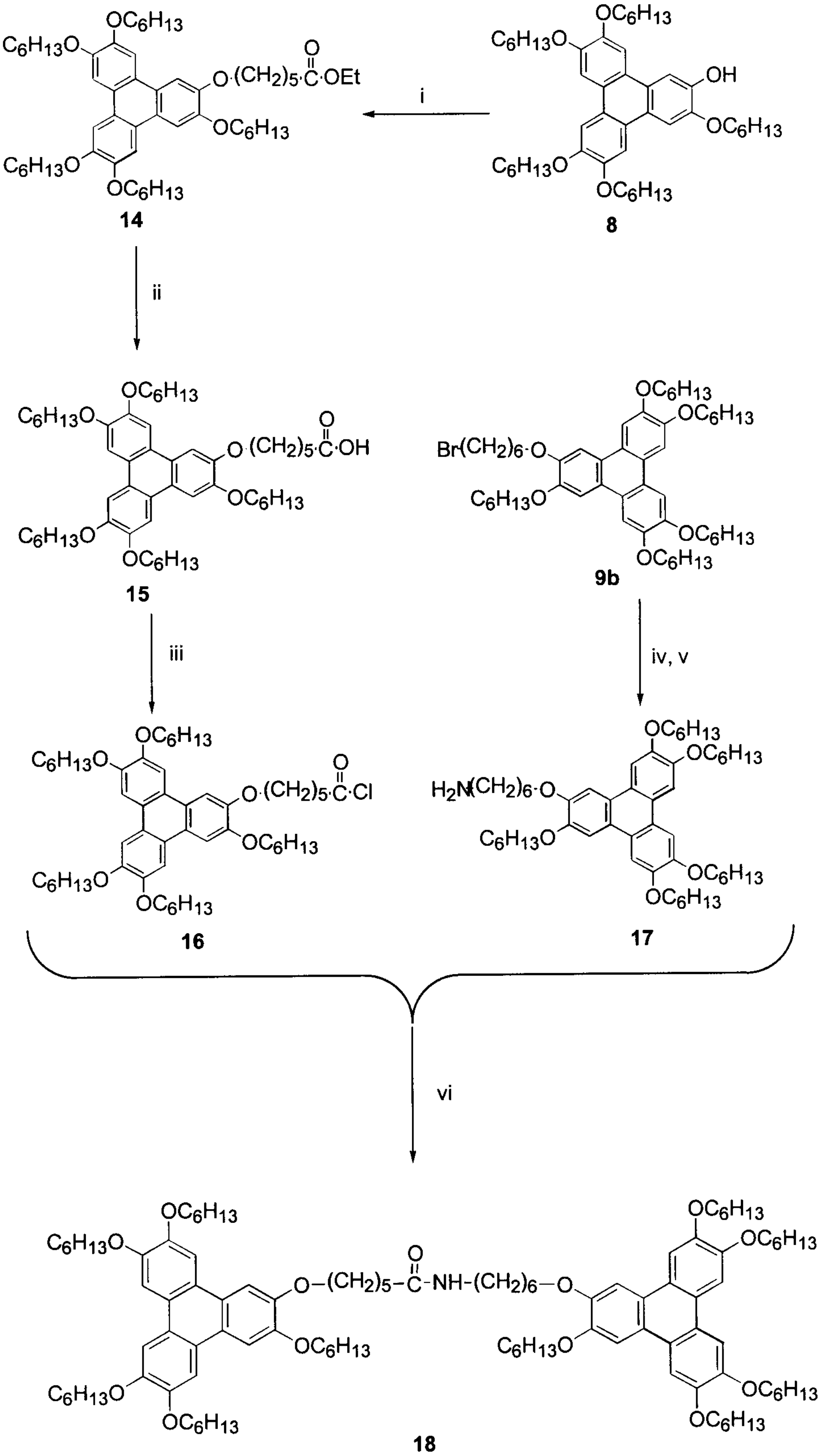
The failure of the 'dimers' **2a–c** to form a Col_h phase is not surprising since the short nature of the connecting chain precludes most forms of stacking in a hexagonal array (Table 1 and Fig. 1). Furthermore modelling studies suggest that, for compound **2a**, steric crowding makes conformations in which both rings are coplanar unlikely. Compound **2d** ($n = 8$) possesses the shortest chain for which the Col_h phase was observed. Such a compound has a sufficiently long chain for low strain bridging in an intracolumnar manner (1,2-, 1,3- or 1,4-) and has one more methylene than the minimum required to bridge in a 1,2-intercolumnar manner (Table 1 and Fig. 1). This is in accordance with previous studies of 'dimers'. Indeed, previous studies of 'dimers' have been interpreted in terms of bridging being 'normally intercolumnar'.[9,10] Whereas we cannot disprove this claim it is difficult to understand on the basis of the data presented in Table 1 and Fig. 4, which suggests little energy difference between intercolumnar and intracolumnar bridging.

None of the 'dimers' **2d–h** shows phase behaviour significantly different to that of HAT6 **1** (Cr 70 Col_h 100 °C I). Comparison with our previous studies of oligomers shows that the dimer **2f** gives a more stable mesophase (enantiotropic, Cr 50 Col_h 104 °C I) than the less symmetrical dimethoxy derivative **19** (monotropic, Cr 112 I 98 Col_h 33 °C glassy Col_h).[7] Other interesting comparisons can be made between the dimers **2a–h** and related dimers **20**,[10] **21a–c**[11] and **22**[11] (Table 2).

The glassy Col_h states formed by dimers **2d–h** are all short-lasting and in general their lifetimes seem to decrease as the length of the linking chain (n) increases (Table 2). This led to a search for variations in the molecular design that would give longer-lasting glasses. It is well known that the crystallisation of glassy Col_h phases of monomeric discogens is slowed down by the introduction of small changes in the symmetry of the disc.[19] Presumably their slow crystallisation relates to the need to order this 'defect' as shown schematically in Fig. 5(a). In the case of 'dimers' there is a need not only to rotate the discs but formation of a crystal lattice also requires exchange of discs between columns [Fig. 5(b)] and this makes it more likely that disorder will be locked into the structure when it is cooled. This 'problem' is even more acute for main-chain discotic polymers [Fig. 5(c)] and this presumably accounts, at least in part, for the long lives of the polymer Col_h glasses and the slowness with which they crystallise. We reasoned that the lifetime of Col_h glasses of 'dimers' would also be enhanced by making the dimer unsymmetric, as shown in Fig. 5(d), since this introduces an additional constraint. The unsymmetrical 'dimers' should align as easily as symmetric dimers but give longer lived glasses. This proved to be the case. Hence polarising microscopy showed that the dimers **13** and **18** can be aligned in a homeotropic manner by annealing the sample for a few hours between glass slides just below the Col_h–I transition temperature. When these aligned liquid crystals are cooled they give aligned long-lasting Col_h glasses. We interpret the increased lifetimes of the glasses as being a result of their lower symmetry. In the case of dimer **18** an alternative explanation is possible; namely that hydrogen bonding between the amide groups is significant and makes this oligomer behave more like a polymer.

Experimental

NMR spectra were recorded on a General Electric QE300, a Bruker AC200 or a Bruker AM400 instrument. Chemical shifts are relative to tetramethylsilane, coupling constants (J) are given in Hz. Mass spectra were obtained on a VG Autospec instrument. All peaks >20% of M^+ (and less intense peaks of particular significance) are reported. Solvents were routinely purified according to the procedures recommended by Perrin.[20] Column chromatography on silica refers to the use of Merck silica gel 9385 Type 60 and thin layer chromatography to Whatman AL SIL G/UV plates. Phase behaviour was investigated using an Olympus BH-2 optical polarising microscope with a Mettler FP82 HT hot stage and Perkin-Elmer 7 thermal analysis system (cooling and heating rate, 10 °C min^{-1}). The glass transitions were very weak but could (usually) just be detected by DSC. The point at which samples sandwiched



Scheme 4 *Reagents and conditions*: (i) $Br(CH_2)_5CO_2Et$, K_2CO_3, EtOH, 37%; (ii) NaOH, H_2O, MeOH, 61%; (iii) ClCOCOCl, CH_2Cl_2, 75% (crude); (iv) NaN_3, EtOH; (v) $LiAlH_4$, THF, 77% (two steps); (vi) THF, 16%.

between glass slides became difficult to shear was used to provide independent confirmation. Small angle X-ray diffraction experiments were conducted with a pinhole camera consisting of a Phillips generator and tubes, nickel-filtered Cu-Kα radiation of wavelength $\lambda = 0.154$ nm, and a Lindemann sample tube (0.7 mm i.d.) to plate distance of 112.8 mm. Ether refers to diethyl ether.

1,16-Dibromohexadecane[21]

Phosphorous tribromide (0.69 g, 0.0025 mol) was added dropwise to a vigorously stirred solution of hexadecane-1,16-diol (1 g, 3.8 mmol) in dry ether (20 cm^3), and the mixture refluxed for 5 h before being poured into water (50 cm^3) and extracted with dichloromethane (2×50 cm^3). The solvent was evapor-

Table 2 DSC data (onset temperatures) for the compounds described in the text

Compound	T_{Col}/°C	T_I/°C	T_g/°C[a]
2a $n=3$	—	81[b]	—
2b $n=5$	—	98[b]	—
2c $n=7$	—	69[b]	—
2d $n=8$	58	91[c]	35 (*ca.* 18 h)
2e $n=9$	72	92[c]	35 (*ca.* 15 h)
2f $n=10$	50	104[c]	35 (*ca.* 11 h)
2g $n=12$	68	107[c]	35 (*ca.* 12 h)
2h $n=16$	41	84[c]	35 (*ca.* 3 h)
9a $n=5$	62	68[c]	—
9b $n=6$	—	50[b]	—
9c $n=10$	—	40[b]	—
9d $n=16$	—	31[b]	—
12a $n=8$	—	154[d]	—
12b $n=10$	—	147[d,e]	—
13	—	98[c]	30 (>1 month)
18	89	99[c]	30 (>6 months)
19[f]	112	98[f]	33 (several hours)
20[g]	64	135[c]	−59 (several days)[h]
21a[i] $n=10$	—	180[c]	—
21b[i] $n=12$	—	168[c]	—
21c[i] $n=14$	—	147[c]	—
22[i]	—	147[c]	47

[a] Figure in parentheses is the approximate time taken for the glass to crystallise at room temperature. [b] Cr–I. [c] Col_h–I. [d] Col_p–I. [e] Bacher *et al.* (ref. 8) give 149 °C. [f] I–Col monotropic (ref. 7). [g] Ref. 10. [h] 'Lifetime' of the supercooled Col_h phase at room temperature. [i] Ref. 11.

ated, and the crude product recrystallised from ethanol (20 cm^3) to give crude 1,16-dibromohexadecane (0.6 g, 43%) as a white solid which was used directly in the next step; δ_H 3.43 (4H, t, *J* 7, C*H*$_2$Br), 1.85 (4H, t, *J* 7, C*H*$_2$CH$_2$Br), 1.25–1.60 (24H, m, C*H*$_2$). All of the other α,ω-dibromides used were commercially available.

1,3-Bis(33′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)propane 2a and related compounds 2b–2h

A stirred mixture of 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene[4] **8** (500 mg, 0.67 mmol), 1,3-dibromopropane (70 mg, 0.34 mmol) and anhydrous potassium carbonate (3 g) was refluxed in ethanol (10 cm^3) for 7 days. The solution was decanted into water (50 cm^3), and extracted with dichloromethane (2 × 50 cm^3), the solvent evaporated, and the product purified by column chromatography on silica eluting with benzene–light petroleum (7: 3). Reprecipitation from dichloromethane (5 cm^3) with methanol (20 cm^3) gave *the product* **2a** (0.1 g, 20%) as a white powder, mp 81 °C (Found: C, 77.45; H, 9.70. $C_{99}H_{148}O_{12}$ requires: C, 77.70; H, 9.74%); δ_H 8.0 (2H, s, Ar*H*), 7.85 (10H, s, Ar*H*), 4.60 (4H, t, *J* 7, OC*H*$_2$CH$_2$C*H*$_2$O), 4.25 (20H, t, *J* 7, OC*H*$_2$), 2.58 (2H, t, *J* 7, OCH$_2$C*H*$_2$CH$_2$O), 1.78–1.98 (20H, m, OCH$_2$C*H*$_2$), 1.3–15 (60H, m, C*H*$_2$), 0.95 (30H, t, *J* 7, C*H*$_3$).

In a similar manner, 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (500 mg, 0.67 mmol) and 1,5-dibromopentane (75.8 mg, 0.33 mmol) for 55 h gave *1,5-bis(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)pentane* **2b** (0.15 g, 30%) as a white powder (Found: C, 77.75; H, 10.05. $C_{101}H_{152}O_{12}$ requires: C, 77.85; H, 9.82%); δ_H 7.85 (12H, s, Ar*H*), 4.22 (24H, t, *J* 7, OC*H*$_2$), 1.95 (24H, m, OCH$_2$C*H*$_2$), 1.35–1.55 (62H, m, C*H*$_2$), 0.95 (30H, t, *J* 7, CH$_2$C*H*$_3$).

In a similar manner 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (500 mg, 0.67 mmol) and 1,7-dibromoheptane (89 mg, 0.34 mmol) for 60 h gave *1,7-bis(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)heptane* **2c** (0.22 g, 42%) as a white powder (Found: C, 77.55; H, 9.65. $C_{103}H_{156}O_{12}$ requires: C, 77.99; H, 10.05%).

In a similar manner 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (500 mg, 0.67 mmol) and 1,8-dibromooctane (91 mg, 0.34 mmol) for 60 h gave *1,8-bis(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)octane* **2d** (0.22 g, 21%) as a white powder (Found: C, 77.75; H, 9.9. $C_{104}H_{158}O_{12}$ requires: C, 78.05; H, 9.95%).

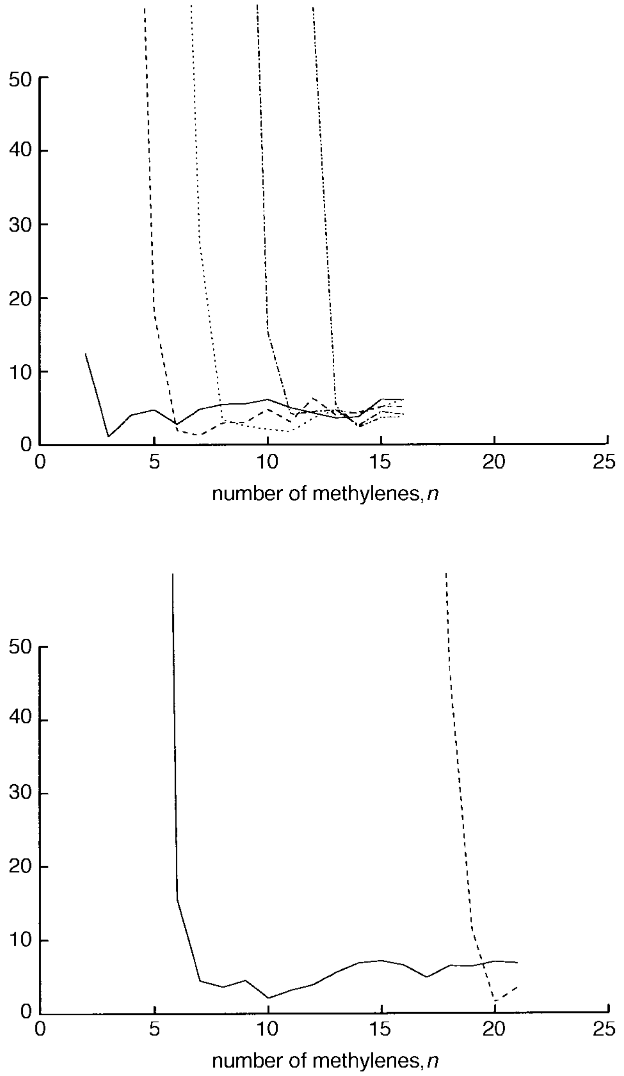


Fig. 4 Differences in energy (kcal mol^{-1}) calculated by the MM2 force field method between all-*trans* H-(CH$_2$)$_n$-H chains and H-(CH$_2$)$_n$-H chains folded in the requisite manner for 1,2-intrastack bridging (upper —), for 1,3-intrastack bridging (upper ---), for 1,4-intrastack bridging (upper ···), for 1,5-intrastack bridging (upper –·–), for 1,6-intrastack bridging (upper –··–), for 1,2-interstack bridging (lower —) and for 1,3-interstack bridging (lower ---) (see text and Table 1).

In a similar manner 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (500 mg, 0.67 mmol) and 1,9-dibromononane (96 mg, 0.34 mmol) for 60 h gave *1,9-bis(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)nonane* **2e** (0.27 g, 25%) as a white powder (Found: C, 77.9; H, 10.25. $C_{105}H_{160}O_{12}$ requires: C, 78.11; H, 9.98%).

In a similar manner 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (500 mg, 0.67 mmol) and 1,10-dibromodecane (98 mg, 0.33 mmol) for 40 h gave *1,10-bis(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)decane* **2f** (0.26 g, 24%) as a white powder (Found: C, 77.90; H, 10.25. $C_{106}H_{162}O_{12}$ requires: C, 78.18; H, 10.02%).

In a similar manner 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (500 mg, 0.67 mmol) and 1,10-dibromododecane (109 mg, 0.33 mmol) for 48 h gave *1,12-bis(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)dodecane* **2g** (0.30 g, 27%) as a white solid (Found: C, 78.3; H, 10.4. $C_{108}H_{166}O_{12}$ requires: C, 78.15; H, 10.1%); *m*/*z* (FAB) 1655 ([M+1]$^+$, 5%).

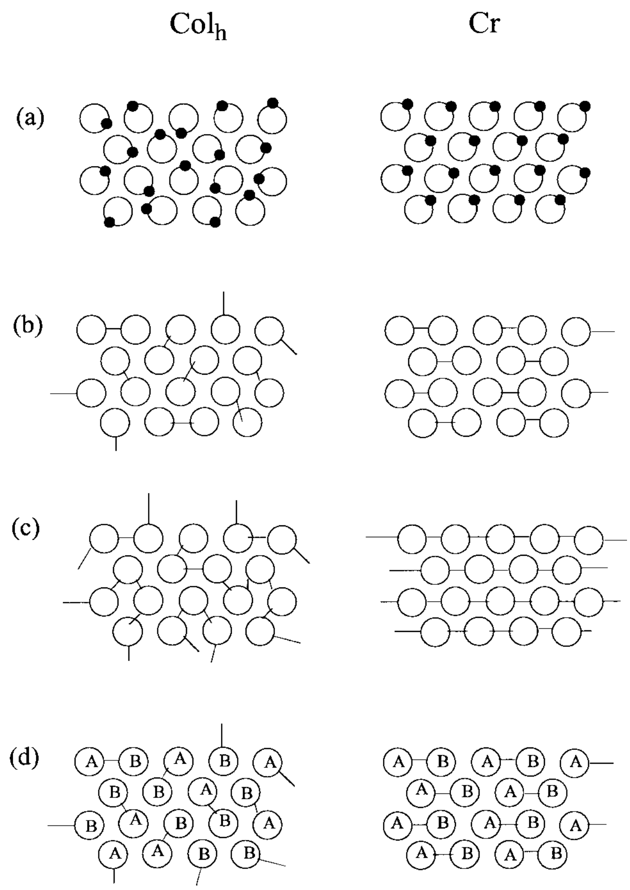


Fig. 5 Schematic representation of 'frozen-in disorder' within the glassy form of the Col$_h$ phase which needs to be overcome as the sample crystallises: (a) monomeric discogen with lowered symmetry to the disc, (b) 'dimeric' discogen, (c) discogenic main-chain polymer, and (d) unsymmetrical 'dimeric' discogen.

In a similar manner 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (500 mg, 0.67 mmol) and 1,16-dibromohexadecane (130 mg, 0.34 mmol) for 60 h gave *1,16-bis(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)hexadecane* **2h** (0.40 g, 68%) as a white solid (Found: C, 78.35; H, 10.0. $C_{112}H_{174}O_{12}$ requires: C, 78.55; H, 10.23%).

Transition data for compounds **2a–h** are given in Table 2. The ^{1}H-NMR spectra of compounds **2c–h** were virtually identical to that for **2b** except for the integration of the multiplet at δ_H 1.35–1.55 due to the methylenes. All compounds **2a–h** showed the expected parent ions in the mass spectrum.

1-(6′-Bromohexyloxy)-2-hexyloxybenzene 6b

A mixture of 1,6-dibromohexane (14.6 g, 60 mmol, 2 equiv.), 2-hexyloxyphenol[22] (5.8 g, 30 mmol), and anhydrous potassium carbonate (27.8 g, 0.2 mol) in ethanol (20 cm^3) was refluxed for 72 h. The mixture was poured onto water (50 cm^3), extracted with dichloromethane (2 × 50 cm^3) and the organic solvent was removed *in vacuo*. The crude product was purified by chromatography on silica eluting with light petroleum–dichloromethane (2:1) to give 1-(6′-bromohexyloxy)-2-hexyloxybenzene **6b** as a clear colourless oil (8.56 g, 80%); δ_H 6.87 (4H, s, Ar*H*), 3.97 (4H, t, *J* 7, OCH_2), 3.45 (2H, t, *J* 7, CH_2Br), 1.85 (4H, m, OCH_2CH_2), 1.3–1.7 (12H, m, CH_2), 0.97 (15H, t, *J* 7, CH_2CH_3).

1-(10′-Bromodecyloxy)-2-hexyloxybenzene 6c

A mixture of 2-hexyloxyphenol (3.88 g, 20 mmol),[22] 1,10-dibromodecane (10 g, 33 mmol, 1.6 equiv.) and anhydrous potassium carbonate (11.1 g, 80 mmol, 4 equiv.) in ethanol (25 cm^3) was heated under reflux for 24 h. The mixture was cooled, filtered, the filtrate washed with water (50 cm^3), extracted with dichloromethane (2 × 50 cm^3), the extracts concentrated *in vacuo* and the product purified by column chromatography on silica eluting with dichloromethane–light petroleum (1:1) to give 1-(10′-bromodecyloxy)-2-hexyloxybenzene **6c** as a colourless liquid (6.56 g, 80%); δ_H 6.88 (4H, s, ArH), 4.00 (4H, t, *J* 6.6, OCH_2), 3.40 (2H, t, *J* 6.7, $BrCH_2$), 1.75–1.95 (6H, m, OCH_2CH_2 and $BrCH_2CH_2$), 1.10–1.60 [18H, m, $OCH_2CH_2(CH_2)_3$ and $BrCH_2CH_2(CH_2)_3$], 0.90 [3H, t, *J* 6.8, $O(CH_2)_5CH_3$].

2-(5′-Bromopentyloxy)-3,6,7,10,11-pentahexyloxytriphenylene 9a and related compounds 9c and 9d

A stirred mixture of 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (500 mg, 0.67 mmol),[4] 1,5-dibromopentane (460 mg, 2 mmol) and anhydrous potassium carbonate (7 g) in ethanol (30 cm^3) was refluxed for 17 h before being poured into water (50 cm^3) and extracted with dichloromethane (2 × 50 cm^3). The solvent was evaporated and the crude product purified by column chromatography on silica eluting with benzene–light petroleum (7:3) and recrystallisation from dichloromethane–methanol gave *2-(5′-bromopentyloxy)-3,6,7,10,11-pentahexyloxytriphenylene* **9a** (0.15 g, 25%) as a white solid, mp 68 °C (Found: C, 71.60; H, 9.35; Br, 8.70. $C_{53}H_{81}O_6Br$ requires: C, 71.21; H, 9.12; Br, 8.94%); δ_H 7.85 (6H, s, Ar*H*), 4.20 (12H, t, *J* 9, OCH_2), 3.55 (2H, t, *J* 7, CH_2Br), 1.95 (12H, m, OCH_2CH_2), 1.35–1.5 (34H, m, CH_2), 0.95 (15H, t, *J* 7, CH_2CH_3).

In a similar manner 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (220 mg, 0.29 mmol) and 1,10-dibromodecane (43 mg, 0.15 mmol) for 40 h gave *2-(10′-bromodecyloxy)-3,6,7,10,11-pentahexyloxytriphenylene* **9c** (0.1 g, 34%) as a white solid, mp 50 °C (Found: C, 71.85; H, 9.45; Br, 7.95. $C_{58}H_{91}O_6Br$ requires: C, 72.2; H, 9.50; Br, 8.28%); δ_H 7.85 (6H, s, Ar*H*), 4.22 (12H, t, *J* 7, OCH_2), 3.45 (2H, t, *J* 7, CH_2Br), 1.95 (12H, m, OCH_2CH_2), 1.35–1.5 (44H, m, CH_2), 0.95 (15H, t, *J* 7, CH_2CH_3).

In a similar manner 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (220 mg, 0.29 mmol) and 1,16-dibromohexadecane (280 mg, 0.72 mmol) for 30 h gave *2-(16′-bromohexadecyloxy)-3,6,7,10,11-pentahexyloxytriphenylene* **9d** (0.12 g, 40%) as a white solid (Found: C, 73.50; H, 10.1; Br, 7.35. $C_{64}H_{103}O_6Br$ requires: C, 73.32; H, 9.89; Br, 7.62%); δ_H 7.85 (6H, s, Ar*H*), 4.22 (12H, t, *J* 7, OCH_2), 3.45 (2H, t, *J* 7, CH_2Br), 1.95 (12H, m, OCH_2CH_2), 1.35–1.5 (56H, m, CH_2), 0.95 (15H, t, *J* 7, CH_2CH_3).

2-(6′-Bromohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene 9b

Ferric chloride (5.0 g) was carefully added to a vigorously stirred solution of 3,3′,4,4′-tetrahexyloxybiphenyl[5] (1.5 g, 2.7 mmol) and 1-(6-bromohexyloxy)-2-hexyloxybenzene **6b** (2.0 g, 5.6 mmol) in dichloromethane (40 cm^3). The mixture was stirred for 2 h, carefully poured into methanol (100 cm^3) and the crude product was filtered off and purified by column chromatography on silica eluting with dichloromethane–light petroleum (2:3) to give *2-(6′-bromohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene* **9b** as a white solid (1.37 g, 56%); δ_H 7.84 (6H, s, Ar*H*), 3.97 (12H, t, *J* 7, OCH_2), 3.45 (2H, t, *J* 7, CH_2Br), 1.85 (12H, m, OCH_2CH_2), 1.35–1.7 (36H, m, CH_2), 0.97 (15H, t, *J* 7, CH_2CH_3).

2-(10′-Bromodecyloxy)-3,6,7,10,11-pentahexyloxytriphenylene 9c

Ferric chloride (3.6 g, 22 mmol) was added to a stirred solution of 3,3′,4,4′-tetrahexyloxybiphenyl[5] (6.0 g, 11 mmol) in dichloromethane (50 cm^3) at 0 °C. After 30 min, 1-(10-bromodecyloxy)-2-hexyloxybenzene **6c** (6.56 g, 16 mmol) and further ferric chloride (3.6 g) were added. The mixture was stirred at room temperature for 2 h, carefully poured into methanol (300 cm^3), cooled to 0 °C, and the crude product was filtered off and purified by column chromatography on silica eluting with dichloromethane–light petroleum (1 : 1) and recrystallised from ethanol to give *2-(10′-bromodecyloxy)-3,6,7,10,11-pentahexyloxytriphenylene* **9c** as a white solid (6.56 g, 73%), mp 50 °C (Found: C, 72.5; H, 9.75; Br, 8.3. $C_{58}H_{91}BrO_6$ requires C, 72.25; H, 9.51; Br, 8.29%); δ_H 7.84 (6H, s, Ar*H*), 4.23 (12H, t, *J* 6.5, OCH_2), 3.40 (2H, t, *J* 6.8, CH_2Br), 1.85 (14H, m, OCH_2CH_2 and Br CH_2CH_2), 1.1–1.7 (42H, m, CH_2), 0.93 (15H, t, *J* 6.8, CH_2CH_3); *m*/*z* (FAB) 964 (M$^+$, 100%).

1,2-Dibutoxybenzene[23]

A mixture of catechol (22 g, 0.2 mol), 1-bromobutane (68.5 g, 0.5 mol) and anhydrous potassium carbonate (70 g, 0.5 mol) in ethanol (100 cm^3) was heated under reflux for 24 h. The reaction mixture was filtered, poured onto water (50 cm^3), extracted with dichloromethane (2 × 50 cm^3) and concentrated *in vacuo* to give 1,2-dibutoxybenzene as a colourless liquid (41 g, 92%) (Found: C, 75.35; H, 10.0. $C_{14}H_{22}O_2$ requires C, 75.64; H, 9.97%); δ_H 6.88 (4H, s, ArH), 4.00 (4H, t, *J* 6.6, OCH_2), 1.80 (4H, m, OCH_2CH_2), 1.52 (4H, m, $OCH_2CH_2CH_2$), 0.98 (6H, t, *J* 6.3, $OCH_2CH_2CH_2CH_3$); *m*/*z* (EI) 222 (M$^+$, 14%).

1,2-Dibutoxy-4-iodobenzene

Iodine monochloride (50 g, an excess) in chloroform (150 cm^3) was added dropwise to 1,2-dibutoxybenzene (41 g, 0.19 mol) in chloroform (100 cm^3) with stirring. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. Once the reaction was complete, the liquid was decanted off, washed with sodium metabisulfite solution (1 M, 100 cm^3) and water (100 cm^3), concentrated *in vacuo* and the residue purified by column chromatography on silica eluting with dichloromethane–light petroleum (2 : 3) to give *1,2-dibutoxy-4-iodobenzene* as an orange oil (47 g, 71%) (Found: C, 47.65; H, 6.0. $C_{14}H_{21}IO_2$ requires C, 48.28; H, 6.08%); δ_H 7.18 (1H, d, *J* 8.4, Ar*H*), 7.16 (1H, s, Ar*H*), 6.60 (1H, d, *J* 8.4, Ar*H*), 3.95 (4H, t, *J* 6.6, $ArOCH_2$), 1.78 (4H, m, OCH_2CH_2), 1.50 (4H, m, $OCH_2CH_2CH_2$), 0.97 (6H, t, *J* 6, $OCH_2CH_2CH_2CH_3$); *m*/*z* (EI) 348 (M$^+$, 25%).

3,3′,4,4′-Tetrabutoxybiphenyl 5b[24]

1,2-Dibutoxy-4-iodobenzene (20 g) was added to copper powder (20 g) and mixed intimately. The mixture was heated carefully to about 270 °C. An exothermic reaction occurred and the temperature rose to about 300 °C. The mixture was cooled, extracted with dichloromethane (2 × 100 cm^3), concentrated *in vacuo*, and ethanol was added to initiate crystallisation to give *3,3′,4,4′-tetrabutoxybiphenyl* **5b** as a white solid (4.4 g, 35%), mp 93–94 °C (Found: C, 75.85; H, 9.8. $C_{28}H_{42}O_4$ requires C, 75.98; H, 9.56%); δ_H 7.07 (4H, m, Ar*H*), 6.94 (2H, d, *J* 8.7, Ar*H*), 4.03 (8H, t, *J* 6.6, OCH_2), 1.82 (8H, m, OCH_2CH_2), 1.53 (8H, m, $OCH_2CH_2CH_2$), 0.98 (12H, t, *J* 7.4, $OCH_2CH_2CH_2CH_3$); *m*/*z* (EI) 442 ([M]$^+$, 100%).

1-Butoxy-2-methoxybenzene 6d[25]

A mixture of 2-methoxyphenol (12.4 g, 0.1 mol), 1-bromobutane (16.4 g, 0.12 mol) and anhydrous potassium carbonate (27.8 g, 0.2 mol) in ethanol (50 cm^3) was heated under reflux for 24 h. After the reaction had finished, the reaction mixture was filtered, washed with water (50 cm^3), extracted with dichloromethane (2 × 50 cm^3) and concentrated *in vacuo* to give *1-butoxy-2-methoxybenzene* **6d** as a colourless liquid (15 g, 83%) (Found: C, 73.0; H, 9.0. $C_{11}H_{16}O_2$ requires C, 73.30; H, 8.94%); δ_H 6.89 (4H, s, Ar*H*), 4.02 (2H, t, *J* 6.8, OCH_2), 3.85 (3H, s, OCH_3), 1.83 (2H, m, OCH_2CH_2), 1.51 (2H, m, $OCH_2CH_2CH_2$), 0.97 (3H, t, *J* 7.0, $OCH_2CH_2CH_2CH_3$); *m*/*z* (EI) 180 (M$^+$, 30%).

3,6,7,10,11-Pentabutoxy-2-methoxytriphenylene 10

3,3′,4,4′-Tetrabutoxybiphenyl **5b** (6.6 g, 15 mmol), ferric chloride (8.4 g, 50 mmol) and 1-butoxy-2-methoxybenzene **6c** (5.4 g, 30 mmol, 2 equiv.) were added to dichloromethane (20 cm^3), stirred at room temperature and the progress of the reaction monitored by TLC. After the reaction was complete, the mixture was carefully poured into methanol (300 cm^3), and the resultant mixture cooled to 0 °C. The crude product was filtered off, purified by column chromatography on silica eluting with dichloromethane–light petroleum (2 : 1), and recrystallised from ethanol to give *3,6,7,10,11-pentabutoxy-2-methoxytriphenylene* **10** as a white solid (6.3 g, 68%); Cr 92.1 (36) Col$_1$ 101 (4) Col$_2$ 119.3 (6) I 116.6 (6) Col$_2$ 98.3 °C (4 J g^{-1}) Col$_1$ glass (Found: C, 75.5; H, 8.85. $C_{39}H_{54}O_6$ requires C, 75.69; H, 8.79%); δ_H 7.81 and 7.82 (6H, m, Ar*H*), 4.24 (10H, t, *J* 6.6, OCH_2), 4.10 (3H, s, OCH_3), 1.94 (10H, m, OCH_2CH_2), 1.62 (10H, m, $OCH_2CH_2CH_2$), 1.05 (15H, t, *J* 7.4, $OCH_2CH_2CH_2CH_3$); *m*/*z* (EI) 618 (M$^+$, 100%).

3,6,7,10,11-Pentabutoxy-2-hydroxytriphenylene 11

Diphenylphosphine[15] (3.35 g, 18 mmol) was added to stirred dried tetrahydrofuran (30 cm^3) under argon at 0 °C followed by butyllithium solution in hexane (11.2 cm^3, 1.6 M, 18 mmol) over 30 min. After a further 30 min, 3,6,7,10,11-pentabutoxy-2-methoxytriphenylene **10** (5.56 g, 9.0 mmol) was added, the mixture heated under reflux and the progress of the reaction monitored by TLC. Once the reaction was complete the mixture was poured onto ice, extracted with dichloromethane (2 × 100 cm^3), the organic phase washed with aqueous hydrochloric acid (2 M, 100 cm^3) and water (100 cm^3) and concentrated *in vacuo*. The crude product was subjected to column chromatography on silica eluting with dichloromethane–light petroleum (1 : 1), and the product recrystallised from ethanol to give *3,6,7,10,11-pentabutoxy-2-hydroxytriphenylene* **11** as a white crystalline solid (3.70 g, 68%), mp 101.5–102.5 °C (Found: C, 74.75; H, 8.65. $C_{38}H_{52}O_6$ requires C, 75.46; H, 8.66%); δ_H 7.90 (1H, s, Ar*H*), 7.83 (4H, m, Ar*H*), 7.78 (1H, s, Ar*H*), 5.91 (1H, s O*H*), 4.24 (10H, m, OCH_2), 1.93 (10H, m, OCH_2CH_2), 1.57 (10H, m, $OCH_2CH_2CH_2$), 1.04 (15H, t, *J* 7.0, $OCH_2CH_2CH_2CH_3$); *m*/*z* (EI), 604 (M$^+$, 100%).

1,8-Bis(3′,6′,7′,10′,11′-pentabutyloxytriphenylen-2′-yloxy)octane 12a

A mixture of 2-hydroxy-3,6,7,10,11-pentabutyloxytriphenylene **11** (1.21 g, 2.0 mmol), 1,8-dibromooctane (0.28 g, 1.0 mmol) and anhydrous potassium carbonate (1.0 g) in ethanol (5 cm^3) was heated under reflux for 72 h. The mixture was cooled to 0 °C, filtered, washed with water (25 cm^3), and extracted with dichloromethane (2 × 25 cm^3), the solvent removed *in vacuo*, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallised from ethanol to give 1,8-bis(3′,6′,7′,10′,11′-pentabutoxytriphenylen-2′-yloxy)octane **12a** as a white solid (0.60 g, 46%) (Found: C, 76.25; H, 9.10. $C_{84}H_{118}O_{12}$ requires C, 76.21; H, 8.98%); δ_H 7.83 (12H, s, Ar*H*), 4.24 (24H, t, *J* 6.5, OCH_2), 1.93 (24H, m, OCH_2CH_2), 1.62 (24H, m, $OCH_2CH_2CH_2$), 1.04 [30H, t, *J* 7.1, $O(CH_2)_3CH_3$].

1,10-Bis(3′,6′,7′,10′,11′-pentabutyloxytriphenylen-2′-yloxy)decane 12b

A mixture of 2-hydroxy-3,6,7,10,11-pentabutoxytriphenylene **11** (1.05 g, 1.7 mmol), 1,10-dibromodecane (0.26 g, 0.9 mmol) and anhydrous potassium carbonate (1.0 g) in ethanol (5 cm^3) was heated under reflux for 72 h. The mixture was cooled, filtered, washed with water (20 cm^3), and extracted with dichloromethane (2×20 cm^3), the solvent removed *in vacuo*, and the residue purified by column chromatography on silica eluting with dichloromethane–light petroleum (2:1) and finally recrystallised from ethanol to give *1,10-bis(3′,6′,7′,10′,11′-pentabutoxytriphenylen-2′-yloxy)decane* **12b** as a white solid (0.40 g, 34%) (Found: C, 76.35; H, 9.20. $C_{86}H_{122}O_{12}$ requires C, 76.64; H, 9.12%); δ_H 7.84 (12H, s, Ar*H*), 4.24 (24H, t, *J* 6.5, OCH_2), 1.93 (24H, m, OCH_2CH_2), 1.35–1.70 (32H, m, CH_2), 1.05 [30H, t, *J* 7.3, $O(CH_2)_3CH_3$]; *m*/*z* (FAB) 1346 (M^+, 100%).

1-(3′,6′,7′,10′,11′-Pentabutoxytriphenylen-2′-yloxy)-10-(3″,6″,7″,10″,11″-pentahexyloxytriphenylen-2″-yloxy)decane 13

A mixture of 2-(10-bromodecyloxy)-3,6,7,10,11-pentahexyloxytriphenylene **9c** (0.30 g, 0.3 mmol), 3,6,7,10,11-pentabutoxy-2-hydroxytriphenylene **11** (0.15 g, 0.25 mmol) and anhydrous potassium carbonate (1.0 g) in ethanol (5 cm^3) was heated under reflux for 72 h. The mixture was cooled, filtered, washed with water (50 cm^3), and extracted with dichloromethane (2×50 cm^3), the solvent removed *in vacuo,* and the residue purified by column chromatography on silica eluting with dichloromethane–light petroleum (2:1) and finally recrystallised from ethanol to give *1-(3′,6′,7′,10′,11′-pentabutoxytriphenylen-2′-yloxy)-10-(3″,6″,7″,10″,11″-pentahexyloxytriphenylen-2″-yloxy)decane* **13** as a white solid (0.10 g, 26%) (Found: C, 77.6; H, 9.9. $C_{96}H_{142}O_{12}$ requires C, 77.48; H, 9.62%); δ_H 7.83 (12H, s, ArH), 4.23 and 4.24 (24H, $2 \times$t, *J* 0.5, OCH_2), 1.85–2.05 (24H, m, OCH_2CH_2), 1.25–1.70 (52H, m, CH_2), 1.04 [15H, t, *J* 7.4, $O(CH_2)_3CH_3$], 0.93 [15H, t, *J* 6.7, $O(CH_2)_5CH_3$]; *m*/*z* (FAB) 1487, ($[M+1]^+$, 60%).

Ethyl 6-(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)hexanoate 14

A stirred mixture of 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **8** (2.78 g, 3.7 mmol),[4] ethyl 6-bromohexanoate (1.06 g, 4.6 mmol) and anhydrous potassium carbonate (1.17 g) in ethanol (50 cm^3) was refluxed for 36 h. The cooled solution was decanted into water (100 cm^3), the mixture extracted with dichloromethane (2×100 cm^3), the solvent was removed *in vacuo*, and the product purified by column chromatography on silica eluting with light petroleum–dichloromethane (3:2). Recrystallisation from ethanol (20 cm^3) gave *ethyl 6-(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)hexanoate* **14** (1.21 g, 37%) as a white solid; Cr 36 Col_h 53 °C I (Found: C, 75.7; H, 9.80. $C_{56}H_{86}O_8$ requires: C, 75.85; H, 9.70%); δ_H 7.85 (6H, s, Ar*H*), 4.20 (12H, t, *J* 7, OCH_2), 4.15 (2H, q, *J* 7, OCH_2CH_3), 2.35 (2H, t, *J* 7, CH_2CH_2CO), 1.95 (12H, t, *J* 7, O CH_2CH_2), 1.75 (2H, m, CH_2CH_2CO), 1.5–1.35 (47H, m, CH_2), 1.20 (3H, t, *J* 7, OCH_2CH_3), 0.85 (15H, t, *J* 7, CH_2CH_3).

6-(3′,6′,7′,10′,11′-Pentahexyloxytriphenylen-2′-yloxy)hexanoic acid 15

A vigorously stirred mixture of ethyl 6-(3,6,7,10,11-pentahexyloxytriphenylen-2-yloxy)hexanoate **14** (1.27 g, 1.43 mmol) and sodium hydroxide (1 pellet) in water (10 cm^3) and methanol (20 cm^3) was refluxed for 24 h. The cooled mixture was carefully poured into dilute aqueous hydrochloric acid (50 cm^3; 2 M), extracted with dichloromethane (2×50 cm^3), and the solvent evaporated. The crude product was purified by column chromatography on silica eluting with dichloromethane–ethyl acetate (1:1) and was recrystallised from ether (10 cm^3) at 0 °C to give *6-(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)hexanoic acid* **15** (750 mg, 61%) as a white solid; Cr 60 Col_h 72 °C I (Found: C, 75.35; H, 9.6. $C_{54}H_{84}O_8$ requires: C, 75.5; H, 9.56%); δ_H 7.85 (6H, s, Ar*H*), 4.20 (12H, t, *J* 7, OCH_2), 2.75 (1H, s, CO_2H), 2.35 (2H, t, *J* 7, CH_2CH_2COOH), 1.95 (12H, t, *J* 7, O CH_2CH_2), 1.5–1.35 (47H, m, CH_2), 0.85 (15H, t, *J* 7, CH_2CH_3).

6-(3′,6′,7′,10′,11′-Pentahexyloxytriphenylen-2′-yloxy)hexanoyl chloride 16

A solution of oxalyl chloride (0.5 g) in dry dichloromethane (5 cm^3) was slowly added to a stirred solution of 6-(3′,6′,7′,10′,11′-pentahexyloxytriphenylen-2′-yloxy)hexanoic acid **15** (700 mg, 0.78 mmol) in dry dichloromethane (20 cm^3) under nitrogen and the mixture left at room temperature for 24 h. The solvent was then evaporated *in vacuo*. The product **16** was used in its crude state for the next step.

2-(6′-Aminohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene 17

A stirred mixture of 2-(6′-bromohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene **9b** (1.35 g, 1.5 mmol) and sodium azide (500 mg) in ethanol (50 cm^3) was refluxed for 24 h. The mixture was poured into water (50 cm^3), extracted with dichloromethane (2×50 cm^3) and the solvent evaporated *in vacuo*. The crude azide was dissolved in dry tetrahydrofuran (50 cm^3), lithium aluminium hydride (5 equiv.) carefully added, and the mixture stirred for 1 h. Dilute aqueous hydrochloric acid (20 cm^3, 2 M) was carefully added and the mixture extracted with dichloromethane (2×50 cm^3). The organic solvent was evaporated *in vacuo* and the crude residue purified by column chromatography on silica eluting with methanol–dichloromethane (1:9) to give *2-(6′-aminohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene* **17** (950 mg, 77%) as a white solid which quite rapidly turned brown on exposure to the air and hence was used directly for the next step; Cr 52 Col 185 °C I; δ_H 7.78 (6H, s, ArH), 5.4–6.0 (2H, br s, NH_2), 4.20 (12H, t, *J* 7, $ArOCH_2R$), 3.03 (2H, m, CH_2NH_2), 1.20–1.95 (48H, m, CH_2), 0.97 (15H, t, *J* 7, CH_3).

6,6′-Bis(3″,6″,7″,10″,11″-pentahexyloxytriphenylen-2″-yloxy)-*N*-hexylhexanamide 18

6-(3′,6′,7′,10′,11′-Pentahexyloxytriphenylen-2′-yloxy)hexanoyl chloride **16** (525 mg, 0.6 mmol) in dry tetrahydrofuran (10 cm^3) was added to a stirred solution of 2-(6′-aminohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene **17** (930 mg, 1.2 mmol) in dry tetrahydrofuran (10 cm^3). After 1 h at room temperature the mixture was poured into water (50 cm^3), extracted with dichloromethane (2×50 cm^3) and the organic solvent removed *in vacuo*. The crude product was purified by column chromatography on silica eluting with dichloromethane to give *the amide* **18** (160 mg, 16%) as a white solid; Cr 88.5 Col 99.1 I 94.5 Col ~30 °C glass (Found: C, 77.3; H, 9.6; N, 0.71. $C_{108}H_{165}O_{13}N$ requires: C, 77.0; H, 9.8; N, 0.83%); δ_H 7.78 (12H, s, Ar*H*), 4.25 (24H, t, *J* 7, $ArOCH_2R$), 3.30 (2H, m, CH_2NHCO), 2.25 (2H, t, *J* 7, CH_2CONH), 1.20–1.95 (48H, m, CH_2), 0.97 (15H, t, *J* 7, CH_3); *m*/*z* (FAB) 1684 (M^+, 40%).

Force field calculations

The MM2 force field method was used throughout.[15] To calculate strain energies for intracolumnar bridging (Table 1) we needed to know the separation between aromatic cores within the columns. In 1,2-intrastack bridging it was assumed that the aryl ring–oxygen bonds were parallel and 3.56 Å apart, in the case of 1,3-intrastack bridging 7.12 Å apart, in the case of 1,4-intrastack bridging 10.68 Å apart, in the case of 1,5-intrastack bridging 14.24 Å apart, and in the case of 1,6-intrastack bridging 17.80 Å apart. For calculations on intercolumn bridging we also need to know the separation between the columns (y). This was estimated using eqn. (1) which was obtained by fitting X-ray diffraction data for the

HATN series[26] to a second order polynomial,

$$y = 7.50 + 0.388c - 0.00139c \qquad (1)$$

where y is in angstroms and c is the total number of carbons in the side chains per aromatic core ($6N$ in HATN, $[5N+n/2]$ for **2**). Hence, for the oligomer **2c**, $n=7$, $c=33.5$ and in the $\mathrm{Col_h}$ phase y would be 18.94 Å. For calculations of the amounts of strain involved in 1,2-interstack bridging the constraint applied was that the aryl ring–oxygen bonds were co-linear and parallel with the oxygens $(y-9.85)$ Å apart and in the case of 1,3-intrastack bridging the oxygens $(1.732y-9.85)$ Å apart. Obtaining the energy minimum for extended all-*trans* conformations (analogous to **4a**) is a trivial exercise but, for the folded chains (analogous to **4b**) it is difficult to be sure that the absolute minimum energy structure has been located. This is a common problem in all cases of 'folding' of polymethylene chains since the energy surfaces are characterised by a multitude of local energy minima. For each data point in Table 1, at least three independent minimisations starting from different initial conformations were performed and the best minimum generated was taken as (at least close to) the absolute minimum. To abstract the chain component of the strain energy for each optimised geometry the PhO groups were each replaced by H and (without changing any other atomic positions) the energy of the chain recalculated. Hence Table 1 gives the MM2 calculated difference between all-*trans* $\mathrm{H\text{-}(CH_2)_{\mathit{n}}\text{-}H}$ chains and $\mathrm{H\text{-}(CH_2)_{\mathit{n}}\text{-}H}$ chains which have been folded as required for the different types of bridging.

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References

1 N. Boden, R. Bissell, J. Clements and B. Movaghar, *Curr. Sci.*, 1996, **6**, 599; N. Boden and B. Movaghar, *Handbook of Liquid Crystals*, vol. 2B, ed. D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess and V. Vill, VCH, Weinheim, 1998, p. 781.

2 N. Boden, R. J. Bushby, J. Clements, M. V. Jesudason, P. F. Knowles and G. Williams, *Chem. Phys. Lett.*, 1988, **152**, 94; N. Boden, R. J. Bushby and J. Clements, *J. Chem. Phys.*, 1993, **98**, 5920; D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher and K. Siemensmeyer, *Phys. Rev. Lett.*, 1993, **70**, 457; N. Boden, R. C. Borner, R. J. Bushby and J. C. Clements, *J. Am. Chem. Soc.*, 1994, **116,** 10807; N. Boden, R. J. Bushby, J. Clements, B. Movaghar, K. J. Donovan and T. Kreouzis, *Phys. Rev. B*, 1995, **52**, 13274; M. Funahashi and J. Hanna, *Jpn. J. Appl. Phys.*, 1996, **35**, L703; *Appl. Phys. Lett.*, 1997, **71**, 602; *Phys. Rev. Lett.*, 1997, **78**, 2184; T. Christ, B. Glusen, A. Greiner, A. Kettner, R. Sander, V. Stumpflen, V. Tsukruk and J. H. Wendorff, *Adv. Mater.*, 1997, **9**, 48; N. Boden, R. J. Bushby, J. Clements and B. Movaghar, *J. Appl. Phys.*, 1998, **83**, 3207; N. Boden, R. J. Bushby, J. Clements, K. Donovan, B. Movaghar and T. Kreouzis, *Phys. Rev. B*, 1998, **58**, 3063.

3 C. Destrade, M. C. Mondon and J. Malthete, *J. Phys. Colloq. C3*, 1979, **40**, 17.

4 N. Boden, R. J. Bushby and A. N. Cammidge, *J. Chem. Soc., Chem. Commun.*, 1994, 465; *J. Am. Chem. Soc.*, 1995, **117**, 924.

5 N. Boden, R. J. Bushby and Z. Lu, *Liq. Cryst.*, 1998, **25**, 47.

6 T. Christ, B. Glusen, A. Greiner, A. Kettner, R. Sander, V. Stumpflen, V. Tsukruk and J. H. Wendorff, *Adv. Mater.*, 1997, **9**, 48.

7 N. Boden, R. J. Bushby, A. N. Cammidge and P. S. Martin, *J. Mater. Chem.*, 1995, **5**, 1857.

8 A. Bacher, I. Bleyl, C. H. Erdelen, D. Haarer, W. Paulis and H.-W. Schmidt, *Adv. Mater.*, 1997, **9**, 1031.

9 C. P. Lillya and Y. L. N. Murthy, *Mol. Cryst. Liq. Cryst.*, 1985, **2**, 121.

10 S. Zamir, R. Poupko, Z. Luz, B. Huser, C. Boeffel and H. Zimmerman, *J. Am. Chem. Soc.*, 1994, **116**, 1973; D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, W. Paulis, K. Siemensmeyer, K.-H. Etzbach, H. Ringsdorf and D. Haarer, *Adv. Mater.*, 1995, **7**, 276.

11 W. Kranig, B. Huser, H. W. Spiess, W. Krender, H. Ringsdorf and H. Zimmermann, *Adv. Mater.*, 1990, **2**, 36.

12 B. Kohne, P. Marquardt, K. Praefke, P. Psaras, W. Stephan and K. Turgay, *Chimia*, 1986, **40**, 360; V. Percec, C. G. Cho, C. Pugh and D. Tomazos, *Macromolecules*, 1992, **25**, 1164; G. C. Bryant, M. J. Cook, S. D. Haslam, R. M. Richardson, T. G. Ryan and A. J. Thorne, *J. Mater. Chem.*, 1994, **4**, 209; A. Takaragi, M. Sugiura, M. Minoda, T. Miyamoto and J. Watanabe, *Macromol. Chem. Phys.*, 1997, **8**, 2583.

13 S. Zamir, E. J. Wachtel, H. Zimmerman, S. Dai, N. Speilberg, R. Poupko and Z. Luz, *Liq. Cryst.*, 1997, **23**, 689.

14 J. W. Emsley, G. R. Luckhurst and G. N. Shilstone, *Mol. Cryst. Liq. Cryst. Lett.*, 1984, **102**, 223.

15 N. L. Allinger, *J. Am. Chem. Soc.*, 1997, **99**, 8127; U. Burket and N. L. Allinger, *Molecular Mechanics*, A.C.S. Monograph, 1982.

16 N. Boden, R. J. Bushby, A. N. Cammidge and G. Headdock, *UK Pat.* 94118288, 11th June 1993; *Synthesis*, 1995, 31; *J. Mater. Chem.*, 1995, **5**, 2275.

17 R. E. Ireland and D. M. Warlba, *Org. Synth.*, 1998, **Col. Vol. 6**, 567.

18 M. Werth, S. H. Vallerien and H. W. Spiess, *Liq. Cryst.*, 1991, **10**, 759.

19 *Purification of Laboratory Chemicals*, ed. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 2nd edn., Pergamon Press, Oxford, 1980.

20 P. Chuit and J. Hauser, *Helv. Chim. Acta*, 1929, **12**, 850.

21 E. Klarman, L. W. Gates and V. A. Shternov, *J. Am. Chem. Soc.*, 1932, **54**, 1204.

22 K. H. Slotta and W. Franke, *Chem. Ber.*, 1930, **63**, 678.

23 S. Kumar and M. Manicham, *Chem. Commun.*, 1998, 1427.

24 J. Allan and R. Robinson, *J. Chem. Soc.*, 1926, 376.

25 C. R. Safinya, N. A. Clark, K. S. Liang, W. A. Varady and L. A. Chiang, *Mol. Cryst. Liq. Cryst.*, 1985, **123**, 205.

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