Modular assembly of elliptical mesogens

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Modular assembly of elliptical mesogens

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Discotic mesogens featuring a pyridine ring were synthesized, and were found either to form ordered hexagonal columnar liquid crystalline phases or melt directly from a crystal to an isotropic liquid, depending on the position of the pyridyl nitrogen atom. Binary mixtures of the mesogenic pyridine derivatives with a similar discotic mesogen having a carboxylic acid group resulted in the formation of modular elliptical complexes through hydrogen bonding. The binary mixtures were found to exhibit ordered hexagonal columnar or ordered rectangular columnar and nematic mesophases, depending on the length of the alkyl chains, and displayed dramatically different properties from their constituent components. Binary mixtures of the non-mesogenic pyridine derivatives with carboxylic acid-functionalized discotic mesogens did not result in the formation of hydrogen-bonded complexes.

1. Introduction

Shape plays a prominent role in determining whether a molecule will form a liquid crystalline phase and, if so, what kind of mesophases it will exhibit. Thus, rod-shaped mesogens tend to give rise to both nematic and smectic phases, whereas discotic mesogens generally form only columnar structures [1]. Comparatively little is known regarding the mesophase behaviour of molecules of intermediate shape, although unconventionally-shaped mesogens have received increased attention over the past several years [2, 3]. Elliptical structures created by rigidly linking together two disc-shaped building blocks comprise a conceptually simple yet surprisingly neglected class of mesogens that resides in the middle ground between rods and discs [4].

We have recently reported a series of tetraalkoxydibenzo[a,c]phenazine carboxylic acid derivatives (**A6**, **A8**, **A10**) that assemble into elliptical hydrogen-bonded dimers [5]. While employing acid dimers is useful for creating such structures, it unfortunately imposes the restriction that only symmetrical systems can be studied. Since both symmetry and shape are expected to have a profound impact on phase behaviour [6], we were interested in exploring a more versatile approach that would permit the construction of ellipses from two different disc-shaped components. The strong tendency of carboxylic acids to hydrogen bond with pyridine derivatives has been used to assemble rod-like mesogens [7, 8], and therefore suggested itself as a convenient method for the creation of elliptical structures. We report herein the synthesis and properties of four disc-shaped molecules bearing a pyridine fragment (**P6**, **P10**, **SP6**, **SP10**), and their use in the modular assembly of elliptical mesogens by means of hydrogen bonding with complementary tetraalkoxydibenzo[a,c]phenazine derivatives bearing a carboxylic acid group (**A6**, **A10**).

It was also anticipated that the differences in phase behaviour between the four pyridine derivatives could provide key insights into the effect of the presence and position of a single heteroatom on column formation and on the π–π interactions which drive this self-assembly process. Although there is some evidence to suggest that the presence of heteroatoms can alter the strength and geometry of π-stacked dimers in solution [9], it is unclear how the introduction of nitrogen atoms will perturb the thermodynamic stability of extended columnar structures. Such insight would be relevant both to understanding the self-assembly of π-stacked structures such as DNA and RNA, where the factors that govern base-stacking remain a matter of some debate [10], and to the development of n-dopable organic semiconductors. Indeed, several groups have recently prepared nitrogen-containing discotic mesogens in order to create liquid crystals that can act as electron-carrier materials [11, 12].

2. Experimental
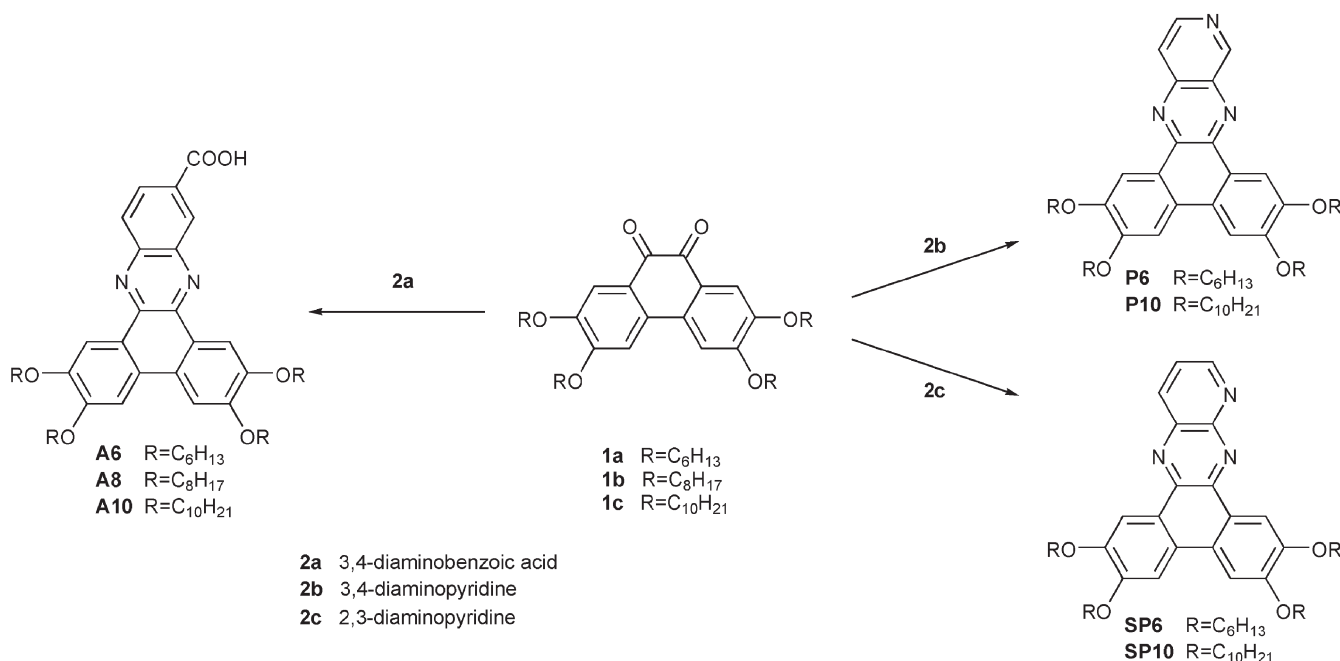
2.1. *Materials and methods*

Acetic acid, dichloromethane and acetone were purchased from Anachemia; chloroform was purchased

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from Fisher; methanol was purchased from Caledon and ethanol was purchased from Commercial Alcohols. All solvents were used without further purification. 3,4-Diaminopyridine and 2,3-diaminopyridine were purchased from Aldrich and used without further purification. 2,3,6,7-Tetrahexyloxyphenanthrene-9,10-dione and 2,3,6,7-tetradecyloxyphenanthrene-9,10-dione [13, 14], and compounds **A6** and **A10** [5] were synthesized as previously reported. ^{1}H NMR spectra were acquired using a Bruker AMX-400 400 MHz NMR spectrometer, and ^{13}C NMR spectra (125 MHz) were obtained using a Varian AS500 Unity Inova 500 MHz spectrometer. Microanalyses (C, H, N) were performed at Simon Fraser University. Matrix-assisted laser desorption ionization time of flight mass spectra (MALDI-TOF MS) were acquired on a Perseptive Biosystems Voyager-DE STR spectrometer with a nitrogen laser (337 nm) and using 2,5-dihydroxybenzoic acid as a matrix. Polarized optical microscopy was carried out using an Olympus BX50 microscope with crossed polarizers and equipped with a Linkam LT5350 heating stage. Differential scanning calorimetry was performed on a Perkin-Elmer DSC7 instrument at a heating and cooling rate of 5°C min^{-1}. X-ray diffraction studies were carried out on a Rigaku R-Axis Rapid diffractometer equipped with a temperature controller.

2.2. Synthesis

The synthesis route is shown in scheme 1.

2.2.1. 2,3,6,7-Tetrahexyloxy-9,12,14-triazabenzo[b] triphenylene (P6).

This compound was prepared by refluxing for 12 h a solution of 2,3,6,7-tetrahexyloxy-phenanthrene-9,10-dione **1a** (0.3 mmol) and 3,4-diaminopyridine **2b** (0.9 mmol) in 15 ml acetic acid. Upon cooling, 150 ml of water was added and the mixture was extracted three times with 25 ml of dichloromethane. The dichloromethane extracts were combined, washed with water, dried (MgSO$_4$), filtered and evaporated under reduced pressure. The resulting product was purified using a short plug of silica with dichloromethane followed by chloroform as eluant, and was recrystallized from a mixture of boiling ethanol, acetone and dichloromethane yielding a yellow solid (60%). ^{1}H NMR (CDCl$_3$) (ppm) 0.95 (t, 12H, $J=6.5$ Hz), 1.35–1.48 (m, 16H), 1.56–1.66 (m, 8H), 1.93–2.04 (m, 8H), 4.25–4.37 (m, 8H), 7.68 (s, 2H), 8.12 (d, 1H, $J=5.9$ Hz), 8.73 (s, 1H), 8.74 (s, 1H), 8.81 (d, 1H, $J=5.9$ Hz), 9.73 (s, 1H). ^{13}C NMR (CDCl$_3$) (ppm) 14.0, 22.6, 25.7, 29.2, 31.6, 69.1, 69.4, 69.5, 105.8, 106.1, 108.6, 109.1, 122.7, 123.0, 126.6, 127.8, 143.5, 149.3, 149.5, 152.3, 152.9. MALDI-TOF MS m/z 683 (M+2). Elemental analysis: calculated for C$_{43}$H$_{59}$N$_3$O$_4$, C 75.73, H 8.72, N 6.16; found, C 75.35, H 8.89, N 5.86%.

2.2.2. 2,3,6,7-Tetradecyloxy-9,12,14-triazabenzo[b] triphenylene (P10).

This compound was synthesized by the condensation of 2,3,6,7-tetradecyloxyphenanthrene-9,10-dione **1b** and 3,4-diaminopyridine **2b** according to

Scheme 1.   Synthesis of acid derivatives **A6**, **A8** and **A10** and pyridine derivatives **P6**, **P10**, **SP6** and **SP10**.

the method described above, and recrystallized from a mixture of boiling dichloromethane and methanol, yielding a yellow solid (54%). ^{1}H NMR: (CDCl$_3$) (ppm) 0.84–0.94 (m, 12H), 1.53–1.67 (m, 56H), 1.94–2.04 (m, 8H), 4.26–4.39 (m, 8H), 7.68 (s, 2H), 8.18 (d, 1H, J=5.6 Hz), 8.72 (s, 1H), 8.74 (s, 1H), 8.80 (d, 1H, J=5.6 Hz), 9.75 (s, 1H). ^{13}C NMR: (CDCl$_3$) (ppm) 14.4, 22.9, 26.4, 29.6, 29.7, 29.8, 29.9, 32.2, 69.4, 69.7, 69.8, 106.2, 106.4, 109.0, 109.5, 122.9, 123.3, 127.1, 128.3, 144.0, 146.1, 149.7, 149.9, 152.7, 153.3. MALDI-TOF MS: m/z 907 (M+1). Elemental analysis: calculated for C$_{59}$H$_{91}$N$_3$O$_4$, C 78.18, H 10.12, N 4.64; found, C 77.86, H 10.08, N 4.46%.

2.2.3. 2,3,6,7-Tetrahexyloxy-9,13,14-triazabenzo[*b*]triphenylene (SP6).

This compound was synthesized by the condensation of 2,3,6,7-tetrahexyloxyphenanthrene-9,10-dione **1a** and 2,3-diaminopyridine **2c** according to the method described above, and recrystallized from a mixture of boiling ethanol and acetone, yielding a yellow solid (80%). ^{1}H NMR (CDCl3) (ppm) 0.92–0.97 (m, 12H), 1.37–1.45 (m, 16H), 1.58–1.64 (m, 8H), 1.93–2.01 (m, 8H), 4.27–4.36 (m, 8H), 7.73 (s, 1H), 7.74 (s, 1H), 7.76 (dd, 1H, J=4.1 Hz, J=8.4 Hz), 8.69 (dd, 1H, J=1.9 Hz, J=8.4 Hz), 8.75 (s, 1H), 8.91 (s, 1H), 9.25 (dd, 1H, J=1.9 Hz, J=4.1 Hz). ^{13}C NMR (CDCl3) (ppm) 13.9, 22.6, 25.7, 29.2, 31.6, 69.2, 69.6, 105.4, 106.2, 108.9, 113.5, 119.8, 127.3, 128.3, 130.1, 139.0, 148.5, 150.9, 151.8, 152.5. MALDI-TOF MS: m/z 682 (M+1). Elemental analysis: calculated for C$_{43}$H$_{59}$N$_3$O$_4$, C 75.73, H 8.72, N 6.16; found, C 75.95, H 8.98, N 6.04%.

2.2.4. 2,3,6,7-Tetradecyloxy-9,13,14-triazabenzo[*b*]triphenylene (SP10).

This compound was synthesized by the condensation of 2,3,6,7-tetradecyloxyphenanthrene-9,10-dione **1b** and 2,3-diaminopyridine **2c** according to the method described above, and recrystallized from a mixture of boiling ethanol, acetone and dichloromethane, yielding a yellow solid (69%). ^{1}H NMR (CDCl$_3$) (ppm) 0.85–0.91 (m, 12H), 1.22–1.65 (m, 56H), 1.91–2.02 (m, 8H), 4.25–4.36 (m, 8H), 7.72 (s, 2H), 7.75 (dd, 1H, J=4.1 Hz, J=8.4 Hz), 8.66 (dd, 1H, J=1.9 Hz, J=8.4 Hz), 8.73 (s, 1H), 8.90 (s, 1H), 9.24 (dd, 1H, J=1.9 Hz, J=4.1 Hz). ^{13}C NMR (CDCl$_3$) (ppm) 14.1, 22.7, 26.2, 29.4, 29.5, 29.6, 29.7, 31.9, 69.2, 69.3, 69.6, 69.7, 106.4, 109.0, 109.4, 123.1, 124.1, 127.0, 127.2, 136.6, 138.1, 144.5, 149.5, 149.7, 152.3, 152.4, 153.6. MALDI-TOF MS: m/z 907 (M+1). Elemental analysis: calculated for C$_{59}$H$_{91}$N$_3$O$_4$, C 78.18, H 10.12, N 4.64; found, C 78.42, H 10.20, N 4.75%.

2.3. *Characterization and complex preparation*

Binary mixtures were obtained by heating equimolar mixtures of the appropriate carboxylic acid and pyridine compounds to above their clearing temperatures in order to ensure homogeneous mixing. The thermal behaviour of the six compounds and their resulting binary mixtures (**A6-P6**, **A6-P10**, **A10-P6**, **A10-P10**, **A6-SP6**, **A6-SP10**, **A10-SP6**, **A10-SP10**) were studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Variable temperature X-ray diffraction (XRD) was also used to characterize liquid crystalline phases of pure compounds and complexes. The phase behaviour and lattice parameters of **A6** and **A10** were reported previously [5] and are summarized in tables 1 and 2 along with those of **P6**, **P10**, **SP6**, **SP10** and four hydrogen-bonded complexes. Typical textures observed by POM are shown in figure 1.

3. Results and discussion

The versatile approach previously developed for the synthesis of discotic liquid crystals by the coupling of a 2,3,6,7-tetraalkoxyphenanthrene-9,10-dione with 1,2-diamines such as **2a**, **2b** or **2c** [5, 6, 14] provides a simple route to discotic mesogens containing a pyridine ring (**P6**, **P10**, **SP6**, **SP10**), as illustrated in scheme 1.

Compounds **P6** and **P10** both exhibit an ordered hexagonal columnar phase (Col$_{ho}$) and crystallize upon cooling, which is typical for molecules of this type that form no hydrogen bond on their own [5, 6]. Both the melting and clearing temperatures of **P6** were found to be higher than those of **P10**, and **P6** is liquid crystalline over a broader temperature range. A similar trend has been observed for series of both triphenylenes [15] and other dibenzophenazines [5], wherein increased chain lengths lead to depression of the phase transition temperatures and narrowing of the liquid crystalline phase range. The presence of the pyridyl nitrogen atom in these compounds appears to promote the formation of a liquid crystalline phase, since the previously reported phenyl analogues, **Phen6** [16] and **Phen10** [14] (figure 2), melt directly from a crystal to an isotropic liquid without forming a liquid crystalline phase.

The position of the pyridyl nitrogen atom also has a large effect on phase behaviour since **SP6** and **SP10**, which are isomers of **P6** and **P10**, melt directly from crystalline solids to isotropic liquids without forming liquid crystalline phases. Thus, while the introduction of a nitrogen atom *may* encourage columnar phases, as shown by the comparison of **Phen6** versus **P6** or **Phen10** versus **P10**, the position of this heteroatom is also an important consideration, as demonstrated by the failure

Table 1. Phase behaviour of acid dimers **A6**, **A10**, pyridines **P6**, **P10**, **SP6**, **SP10** and four binary mixtures as observed by DSC on first heating at $5°C\,min^{-1}$ (Cr=crystalline; Col_{ho}=ordered hexagonal columnar; Col_{ro}=ordered rectangular columnar; N=nematic; I=isotropic).

Compound	Phase →			$T_t/°C$ $(\Delta H/J\,g^{-1})$			Phase	
A6[a]	Cr →	173 (66)	Col_{ho} ↔	263 (18) 257 (−17)	I			
A10[a]	Cr →	122 (32)	Col_{ro} ↔	196 (11) 192 (−10)	N ↔	210 (1) 208 (−1)	I	
P6	Cr ↔	155 (84) 95 (−76)	Col_{ho} ↔	179 (5) 175 (−3)	I			
P10	Cr ↔	123 (77) 71 (−71)	Col_{ho} ↔	135 (3) 118 (−2)	I			
SP6	Cr ↔	145 (84) 100 (−79)	I					
SP10	Cr ↔	113 (78) 85 (−75)	I					
A6-P6	Cr →	108 (1)[b]	Col_{ho} ↔	223 (10) 219 (−7)	I			
A6-P10	Cr →	107 (5)	Col_{ro} ↔	148 (1) 140 (−1)	N ↔	170 (1) 174 (−1)	I	
A10-P6	Cr ↔	137 (1) 123 (−1)	Col_{ro} ↔	160 (2) 155 (−1)	N ↔	174 (1) 172 (−1)	I	
A10-P10	Cr →	101 (34)	Col_{ro} ↔	144 (3) 138 (−2)	N ↔	154 (1) 153 (−1)	I	

[a]From Foster *et al.* [5]. [b]Very weak transition (see text).

of the **P6** and **P10** isomers, **SP6** and **SP10**, to exhibit any liquid crystallinity.

The dramatic differences between **P6**, **SP6** and **Phen6**, or **P10**, **SP10** and **Phen10**, are probably due to changes in electrostatic interactions between neighbouring aromatic cores, which are known to influence the strength of π–π interactions and thus the stability of columnar phases [9]. The introduction of a nitrogen atom will tend to polarize the electronic distribution of the molecules, which could in turn, depending on the position of the nitrogen atom, lead to a favourable alignment of complementary charges on neighbouring molecules, hence promoting π–π interactions and column formation. We are aware of only a few other examples of molecules in which both a discotic *N*-heterocycle and the corresponding hydrocarbon have been investigated. In all those cases, a large effect was observed but arose from replacing several CH groups with nitrogen atoms [12, 17, 18], whereas in the present example, a dramatic effect was observed due to the presence and position of a single heteroatom in the core. These observations could prove important to the understanding of the effect of heteroatoms on a variety of π-stacked systems, ranging form n-dopable materials to RNA and DNA.

As previously reported, the acid derivatives form either a Col_{ho} phase in the case of **A6**, or both an ordered rectangular columnar phase (Col_{ro}) and a nematic phase in the case of **A10**. This more varied

mesomorphic behaviour was attributed to the ability of the acids to form elliptical dimers [5], as shown in figure 3. As one would expect for stoichiometric complexes, each of the binary mixtures of these acids with **P6** or **P10** behaved as a single component upon heating, displayed thermal properties distinct from those of their two individual constituents, and showed no phase separation by optical microscopy. The proposed shape of these complexes is shown in figure 3. Hydrogen bonding between the pyridyl and the acid group is expected to be strongly favoured, as it is both in the solid state [19] and in other liquid crystalline phases [7]. The pyrazine nitrogen atoms should not compete effectively as hydrogen bond acceptors, since pyrazine is a much weaker base than pyridine [20] and the ability of a group to act as an acceptor is strongly correlated to its basicity [21].

The binary mixture **A6-P6** formed a liquid crystal phase over an extremely broad temperature range (108–223°C). A single intense peak was observed in the low-angle region of the XRD pattern and was assigned as the (100) reflection of a Col_h phase, although this assignment could not be made unambiguously since higher order reflections such as a (110) peak were not observed. The assignment was supported by dendritic textures with approximately 60° angles observed by POM (figure 1 c), which are indicative of a Col_h phase. This compound shares several features with the parent acid **A6**, which also has a Col_h phase with a similar

Table 2. X-ray diffraction data of compounds **A6**, **A10**, **P6**, **P10** and four binary mixtures.

Compound	Temp./°C	d spacing/Å	Miller index (hkl)	Phase (Lattice constants)
A6[a]	175	16.6	(100)	Col_{ho} ($a=19.1$ Å)
		4.2	alkyl halo	
		3.6	$\pi-\pi$	
A10[a]	140	22.7	(200)	Col_{ro} ($a=45.4$ Å) ($b=19.5$ Å)
		17.7	(110)	
		11.6	(400)	
		4.4	alkyl halo	
		3.6	$\pi-\pi$	
P6	160	16.2	(100)	Col_{ho} ($a=18.7$ Å)
		4.1	alkyl halo	
		3.5	$\pi-\pi$	
P10	125	19.3	(100)	Col_{ho} ($a=22.3$ Å)
		4.4	alkyl halo	
		3.5	$\pi-\pi$	
A6-P6	160	16.3	(100)	Col_{ho} ($a=18.8$ Å)
		4.2	alkyl halo	
		3.5	$\pi-\pi$	
A6-P10	135	20.6	(200)	Col_{ro} ($a=41.1$ Å) ($b=17.5$ Å)
		16.1	(110)	
		11.0	(310)	
		4.3	alkyl halo	
		3.5	$\pi-\pi$	
A10-P6	150	21.3	(200)	Col_{rd} ($a=42.5$ Å) ($b=17.7$ Å)
		16.3	(110)	
		11.1	(310)	
		4.3	alkyl halo	
		3.5	$\pi-\pi$	
A10-P10	125	22.9	(200)	Col_{ro} ($a=45.8$ Å) ($b=18.6$ Å)
		17.3	(110)	
		11.7	(400)	
		9.1	(020)	
		4.3	alkyl halo	
		3.5	$\pi-\pi$	

[a]From Foster *et al.* [5]

lattice parameter ($a=19.1$ Å versus $a=18.8$ Å for **A6-P6**) and a high clearing temperature. As was previously suggested for **A6**, it is possible that the elliptical **A6-P6** complexes stack in a tilted manner within the columns, which would explain the hexagonal packing and the comparatively small lattice parameter observed for this complex. Both the mixture and the pure acid also formed a highly ordered supercooled mesophase upon cooling to room temperature. This supercooling, which is observed for most of the complexes and dimers, made it difficult to observe the crystal-to-liquid crystal transitions, particularly in the case of **A6-P6**.

Similar parallels hold between the acid **A10** and the **A10-P10** mixture. Notably, both displayed nematic phases, and Col_{ro} phases with comparable lattice parameters ($a=45.4$ Å and $b=19.5$ Å for **A10**, $a=45.8$ Å and $b=18.6$ Å for **A10-P10**). Although the phase behaviour of the mixture is qualitatively similar to that of its parent acid, it differs significantly from that of the pyridine compound **P10**, which exhibits only

a Col_{ho} phase with a considerably smaller lattice parameter and a relatively low clearing temperature.

These results suggest that shape is an important factor governing the mode of self-assembly for these elliptical mesogens. Indeed, the complexes having the same alkyl chains on both components (**A6-P6** and **A10-P10**) and the corresponding carboxylic acid dimers (**A6** and **A10**), which should have comparable shapes (figure 3), were found to have a very similar behaviour. One major difference that was observed, however, was the lower melting and clearing temperatures of the mixtures compared with the pure acids. This depression of the phase transition temperatures may reflect the lower symmetry of the mixed complexes relative to the acid dimers, since less symmetrical structures generally undergo order–disorder transitions at lower temperatures [6].

In the examples described above, the qualitative features of the phase behaviours of the complexes were similar to those of the parent acid compounds. In
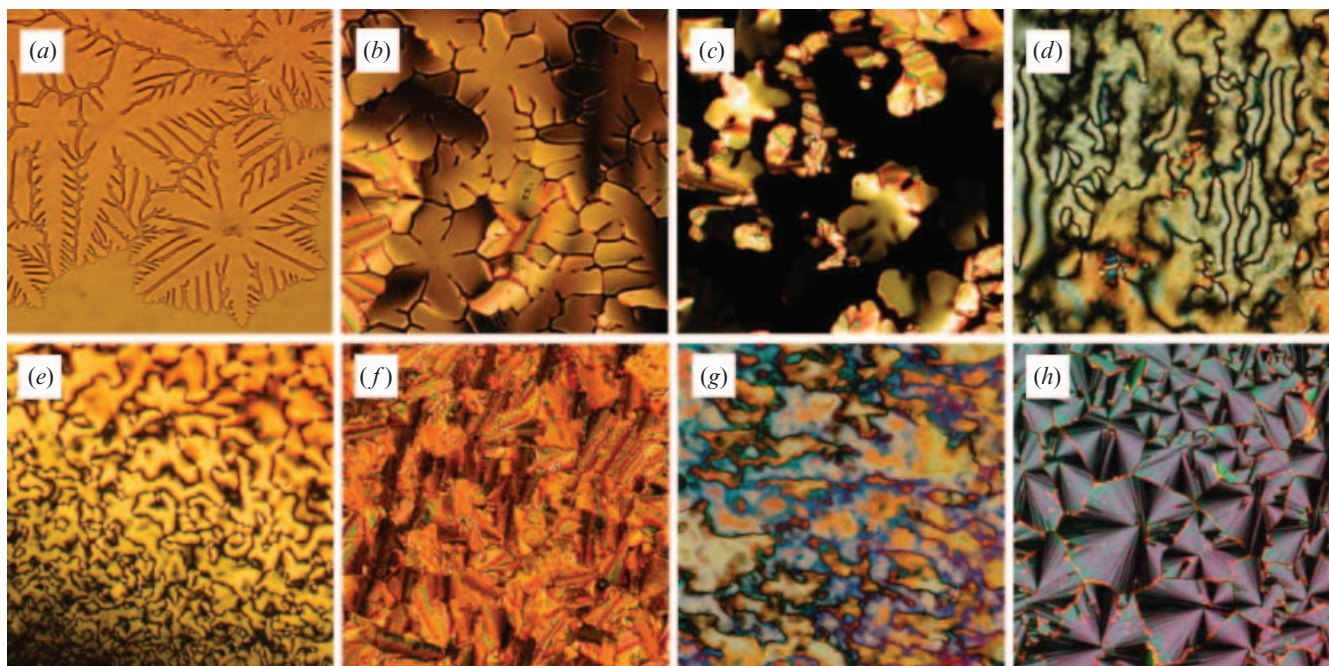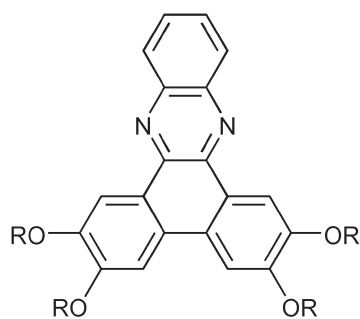
Figure 1. Photomicrographs: (a) **P6** at 177°C (Col$_{ho}$); (b) **P10** at 115°C (Col$_{ho}$); (c) **A6-P6** at 120°C (Col$_{ho}$); (d) **A6-P10** at 155°C (N); **A10-P6** at (e) 170°C (N) and (f) 155°C (Col$_{ro}$); **A10-P10** at (g) 150°C (N) and (h) 75°C (supercooled Col$_{ro}$).

Phen6 R=C$_6$H$_{13}$
Phen10 R=C$_{10}$H$_{21}$

Figure 2. Structure of phenyl analogues **Phen6** [12] and **Phen10** [10].

contrast, the phase behaviour of the mixture **A6-P10** differs markedly from that of either of its building blocks. While both **A6** and **P10** form exclusively Col$_{ho}$ mesophases, their mixture exhibits both Col$_{ro}$ and nematic phases. Again, this is consistent with the phase behaviour being determined in large part by the structure of the complex rather than by the properties of the component acid and pyridine derivatives.

This can also be seen by comparing the properties of **A6-P10** with those of the isomeric complex **A10-P6**. Both mixtures form nematic and Col$_{ro}$ phases, and both supercool to room temperature without crystallizing.

A6   R=C$_6$H$_{13}$
A10 R=C$_{10}$H$_{21}$

(a)

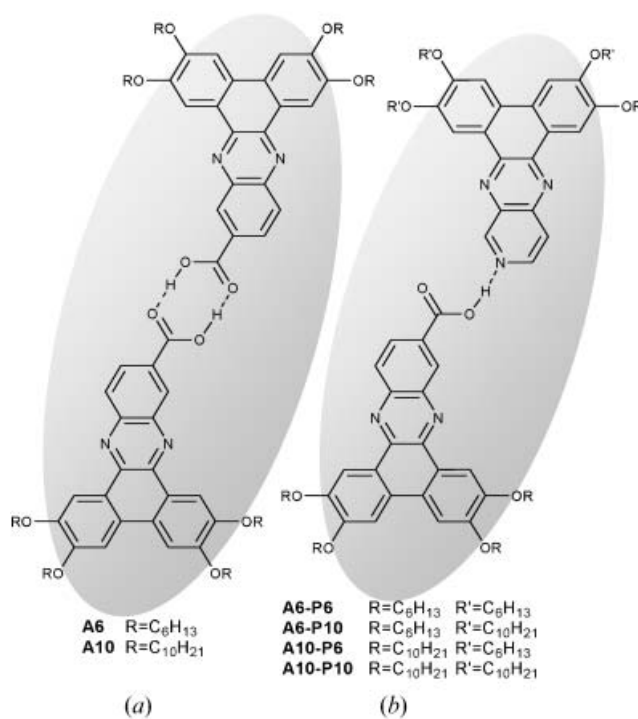|	
A6-P6	R=C$_6$H$_{13}$ R'=C$_6$H$_{13}$
A6-P10	R=C$_6$H$_{13}$ R'=C$_{10}$H$_{21}$
A10-P6	R=C$_{10}$H$_{21}$ R'=C$_6$H$_{13}$
A10-P10	R=C$_{10}$H$_{21}$ R'=C$_{10}$H$_{21}$

(b)

Figure 3. Elliptical structures formed from carboxylic acid derivatives (a) and mixtures of pyridine and acid derivatives (b).

The lattice parameters of their Col$_{ro}$ phases were also similar, with a=41.1 Å, b=17.5 Å for **A6-P10**, and a=42.5 Å, b=17.7 Å for **A10-P6**. Moreover, the clearing

temperatures of these compounds were almost identical: 170°C for **A6-P10** and 174°C for **A10-P6**. These results again indicate the importance of shape to the self-assembly process since the complexes **A6-P10** and **A10-P6** should be very similar in this regard, as they differ only in which of the acid or the pyridine component bears the hexyloxy or decyloxy chains. The formation of rectangular and nematic phases, which appears to be promoted by the presence of longer chains, occurs regardless of whether these chains are present on the pyridine or the acid derivative.

Although the small differences between these two complexes, which can be described as a reversal of the linking group, have only a minor effect on the clearing temperatures, there is a much more pronounced effect on the transitions between the more ordered phases (crystalline-to-columnar and columnar-to-nematic). The lowering of these two transition temperatures in **A6-P10** compared with **A10-P6** caused the former to have a broader liquid crystalline range than **A10-P6** and a broader nematic phase than either **A10-P6** or **A10**.

It is also useful to compare the phase behaviour of these complexes with that of the previously reported octyloxy-acid derivative **A8** [5], which has the same average alkyl chain length, and therefore overall size, as **A6-P10** and **A10-P6**. This acid forms a rectangular columnar phase between 162 and 227°C, and a nematic phase that clears to an isotropic liquid at 232°C. As such, it displays the same type of mesophases as **A6-P10** and **A10-P6**, but has a significantly higher clearing temperature and a somewhat larger mesophase range than either mixture. Again, the lower transition temperatures for the acid–pyridine mixtures may in part reflect the lower symmetry of these complexes. Interestingly, the temperature range of the nematic phase of **A8** is considerably narrower than that of either **A6-P10** or **A10-P6**. This may also be a symmetry effect, since it is anticipated that lowering the symmetry of a mesogen should have a greater impact on the more ordered columnar phase than on the nematic phase. As a result, the columnar-to-nematic transition is depressed to a greater extent than the clearing temperature, resulting in a broader nematic phase range. This observation could be useful in the rational design of nematic discotic phases, which have been commercialized as optical compensation layers for LCDs [22], yet remain relatively uncommon.

In contrast to the binary mixtures formed by **P6** and **P10**, those formed by **SP6** and **SP10** (**A6-SP6**, **A6-SP10**, **A10-SP6**, **A10-SP10**) did not behave as single components. In the case of **A10-SP6** and **A10-SP10**, separate domains showing different textures were clearly apparent by POM, and in the case of **A6-SP10** a liquid crystalline phase and an isotropic liquid phase coexisted over more than 50°C. Dendritic textures typical of columnar phases were observed growing out of the isotropic phase for **A6-SP6**, but these domains emerged over more than a 30°C range. Furthermore, only very broad and weak transitions were observed by DSC for this mixture ($1.3\,\mathrm{J\,g^{-1}}$ over more than 20°C). These binary mixtures therefore apparently do not result in the formation of stoichiometric hydrogen bonded complexes. If **SP6** or **SP10**, in which the pyridyl nitrogen atom is located on the side of the core rather than at the top, formed hydrogen-bonded complexes, they would be expected to have a very different shape compared with the complexes formed by **P6** or **P10**. It is possible that the shape of these complexes would be incompatible with the formation of liquid crystalline phases, thus hindering the formation of complexes and explaining the observed phase separation. Moreover, added steric hindrance around the pyridyl nitrogen atom in **SP6** and **SP10** compared with **P6** and **P10** could prevent the formation of hydrogen-bonded complexes.

In conclusion, we have prepared a number of supramolecular elliptical mesogens through the use of complementary hydrogen bonding between disc-shaped carboxylic acid and pyridine derivatives. This approach has facilitated the rapid assembly of modular 'ellipsotic' mesogens having a different chain length on each half of the complex. The observed properties of these complexes have corroborated the idea that the shape and size of the ellipsotic mesogens are the primary factors determining their mesomorphic behaviour. It was observed that past a certain chain length, the complexes pack in rectangular columnar or nematic phases, which may be a general feature of elliptical mesogens. Furthermore, it appears that lowering the symmetry of the ellipsotic mesogens promotes the formation of a nematic phase that is stable over a wider temperature range. The pyridine-containing disc-shaped molecules prepared for this study have also provided insight into the effect of heteroatoms on π-stacked structures. It was shown that the presence and position of a single nitrogen atom in the core of a disc-shaped molecule can determine whether liquid crystalline phases are formed.

Acknowledgements

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