Synthesis and characterisation of novel hexaalkoxytriphenylenes bearing an additional alkyl chain in the α-position

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ABSTRACT

Exhaustive alkylation of hexahydroxytriphenylene results in production of significant quantities of a side product bearing one additional alkyl chain originating from C-alkylation. A series of these novel materials have been isolated and characterised to gain further insight on factors controlling mesophase formation in triphenylene discotics.

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Certain disc-like molecules ('discotics') can form liquid crystal phases. Most usually, the molecules assemble as columns to give so-called columnar mesophases (which can be likened to the smectic mesophases formed by rod-like/calamitic molecules) (Fig. 1). Substituted triphenylene derivatives which present a flat, aromatic core surrounded by flexible chains, are the most widely studied class of discotic liquid crystals.[1] In some cases a less ordered nematic phase is exhibited in which the molecules retain only orientational order. Triphenylene discotics have received particular interest because of their ability to act as one-dimensional charge transport materials, acting as photoconductors or semiconductors on doping[2] and, alongside other discotic frameworks, lend themselves to diverse electronic and optical applications.[3]

Synthetic and applications science has advanced in parallel and a significant challenge has revolved around unravelling and understanding the structural factors that control the formation of stable mesophases. Triphenylene has proved to be a versatile scaffold for such fundamental interrogation of structural factors controlling mesophase behaviour (stability, type, etc.). New and improved synthetic protocols have now led to characterisation of a wide range of symmetrical (most common) and unsymmetrically substituted derivatives.[4]

We have established a set of qualitative parameters governing mesophase formation and stability in triphenylene discotics and have argued that the central core of such discotic molecules extends beyond the central aromatic triphenylene unit to include the attached conjugated substituents.[5,6] Perturbation of this ex-tended core has a dramatic effect on the mesophase behaviour. For example, hexaalkoxytriphenylenes (HATs) such as HAT6 are the most studied triphenylene-based discotic liquid crystals and are typically characterised as giving columnar hexagonal mesophases (Fig. 1).[7] Replacement of one conjugating substituent with another tends to maintain the mesophase behaviour.[4d,7–9] However, exchange with, or addition of, a non-conjugating group tends to destroy the mesophase (Fig. 1).[4g,8,10–12]

We recently reported the unexpected first examples of mesophase-forming triphenylenes bearing a substituent linked to the core by a saturated methylene group.[13] These derivatives were formed as side products when attempts were made to introduce terminal alkene functionality on typical hexaalkoxytriphenylenes. Observation of mesophase behaviour was surprising but it was unclear if this series represented something of a special case or whether this general structural motif supports mesophase stability. Consequently we decided to investigate the same structural motif within the series of parent alkoxy/alkyl triphenylenes.

Unsymmetrically substituted triphenylenes such as **10**–**13** could conceivably be prepared selectively from appropriate benzene and biphenyl derivatives using precedented methodolgy.[12] However, our previous work has demonstrated that alkylation of hexahydroxytriphenylene produced the C-alkylated side product in some cases and we reasoned that using this route would be both convenient and allow us to investigate the reaction itself to gauge its significance in such triphenylene syntheses (Scheme 1).

In a typical procedure therefore, hexahydroxytriphenylene **9** was reacted with an alkyl bromide (K_2CO_3/EtOH/reflux) for 24 h.

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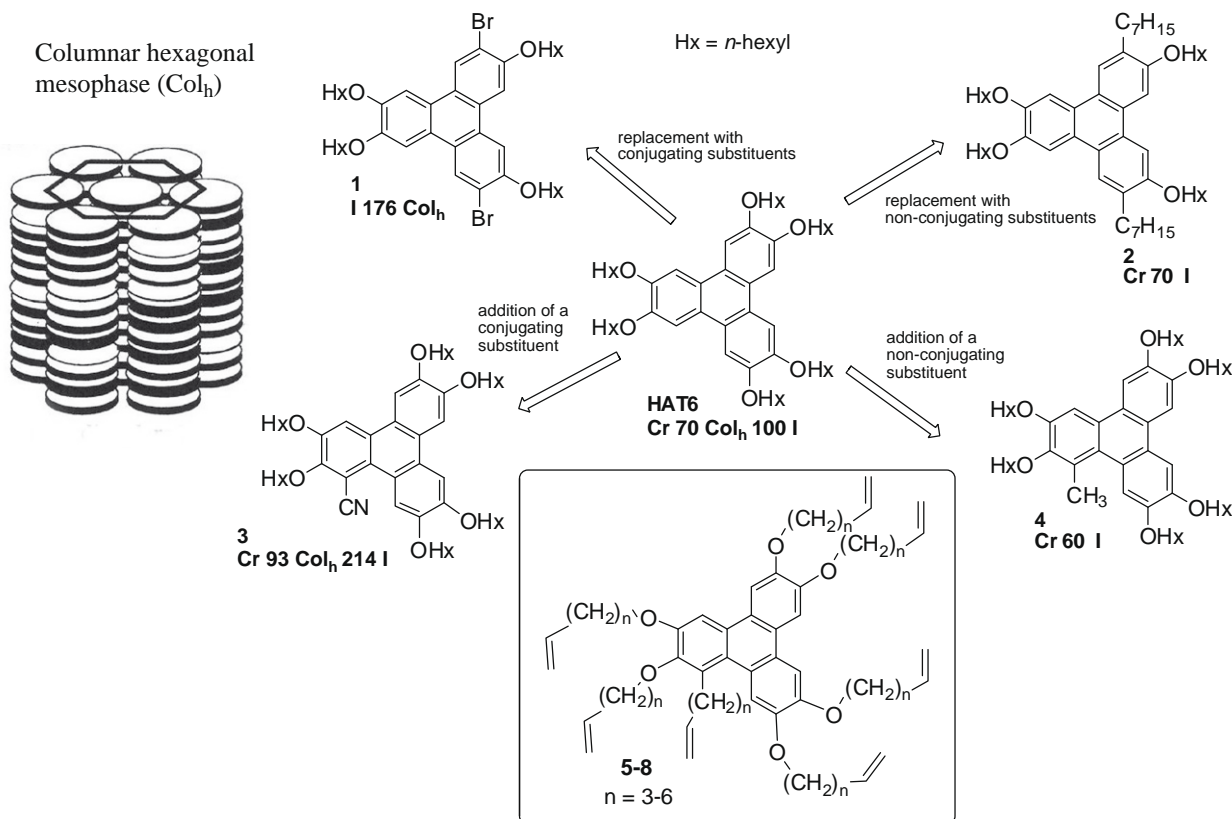
Figure 1. Examples illustrating the importance of a central π-extended core in triphenylene-based liquid crystals. Simple conjugating substituents, such as cyanide or bromide, can lead to formation of columnar mesophases but non-conjugating ones (e.g., alkyl) suppress mesophase formation. The series **5–8** exhibit mesophase behaviour and are the only known exceptions to this trend.
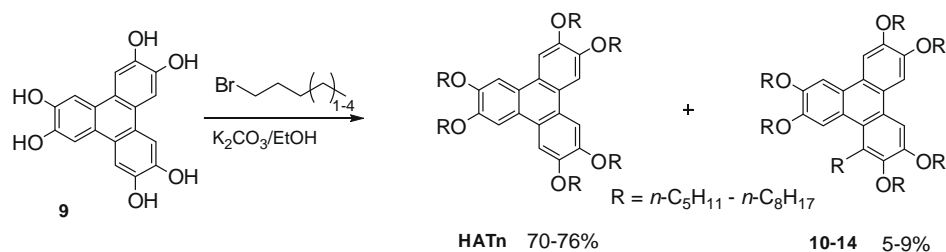
Scheme 1. Alkylation of hexahydroxytriphenylene to give the C-alkylated product.

Symmetrical hexaalkoxytriphenylene (70–76%) was smoothly formed. Once again, however, its formation was always accompanied by the C-alkylated triphenylenes in a low but significant and reproducible yield of 5–9%. Separation of the two compounds was conveniently achieved by careful column chromatography and the C-alkylated derivatives were easily identified by ^{1}H NMR spectroscopy which revealed the unsymmetrical nature of the compounds and showed triplets for the C-alkyl methylene group around 3.2 ppm.[14] Careful inspection of the mass spectra obtained for the crude product mixtures revealed peaks corresponding to formation of trace quantities of doubly C-alkylated materials but no attempts were made to isolate these.

The thermal behaviour of the new materials is shown in Table 1 alongside data for the corresponding parent hexaalkoxytriphenylenes and the previously reported alkene series. All members of the new series of C-alkylated materials melt directly from crystalline solid to isotropic liquid, and therefore follow the previously established trend whereby introduction of a non-conjugating substituent directly onto the core destroys mesophase behaviour. This observation has more important implications for the alkenyl series which further stands out as unique in triphenylene discotic systems. Terminal alkenes are known to have significant effects on calamitic systems,[15] typically lowering transition temperatures compared to their saturated counterparts. However, within the triphenylene discotics we can now conclude that the subtle introduction of terminal unsaturation can actually induce formation of a stable mesophase. This observation further underlines the fine structural balance that contributes to mesophase formation (and destruction) in triphenylene discotics.

Table 1
Comparison of the transition temperatures of alkyl- and alkenyloxytriphenylenes

Chain length	Symmetrical 6-chain alkoxy (HATn) R = CH₂CH₃	7-Chain alkoxy/alkyl (Series **A**) R = CH₂CH₃	7-Chain alkenyloxy/ alkenyl (Series **B**) R = CH=CH₂
C_5 ($n = 3$)	**HAT5** Cr 69 Col$_h$ 122 I	**10** Cr 78 I	**5** Cr 41 Col$_h$ 69 I
C_6 ($n = 4$)	**HAT6** Cr 70 Col$_h$ 100 I	**11** Cr 77 I	**6** Cr 62 Col$_h$ 83 I
C_7 ($n = 5$)	**HAT7** Cr 69 Col$_h$ 93 I	**12** Cr 61 I	**7** Cr 33 Col$_h$ 62 I
C_8 ($n = 6$)	**HAT8** Cr 67 Col$_h$ 86 I	**13** Cr 58 I	**8** Cr 47 I

Acknowledgement

References and notes

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14. *Triphenylene* **10**: A mixture of hexahydroxytriphenylene **9** (0.50 g, 1.54 mmol), 1-bromopentane (2.32 g, 15.4 mmol) and potassium carbonate (4 g) was stirred in refluxing ethanol (30 mL) under nitrogen for 24 h. Aqueous work-up followed by column chromatography (silica gel, CH₂Cl₂/petroleum ether) and recrystallisation (ethanol) gave **10** as a colourless solid. Yield 65 mg, 5%; Mp 78 °C; ¹H NMR (400 MHz, CDCl₃): 0.73–0.99 (m, 21H), 1.33–1.73 (m, 28H), 1.83–2.08 (m, 14H), 3.18 (t, J = 7.8, 2H), 4.03 (t, J = 6.5, 2H), 4.14 (t, J = 6.6, 2H), 4.19–4.24 (m, 8H), 7.73 (s, 1H), 7.77 (s, 1H), 7.79 (s, 1H), 7.80 (s, 1H), 7.88 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): 13.9, 14.0, 19.5, 22.4, 22.5, 22.7, 28.2, 28.3, 28.4, 28.9, 29.0, 29.1, 29.2, 29.6, 29.9, 30.1, 31.1, 31.8, 32.6, 32.9, 68.4, 69.1, 69.4, 69.6, 69.8, 72.8, 104.0, 106.8, 107.5, 108.2, 112.1, 123.9, 124.3, 124.5, 124.6, 126.9, 132.8, 147.4, 147.5, 147.9, 148.8, 149.3, 150.6. HR-MS (EI): calcd for C₅₃H₈₂O₆ [M⁺] 814.6106; found 814.6101.
Triphenylene **11**: Prepared as above using hexahydroxytriphenylene **9** (0.50 g, 1.54 mmol) and 1-bromohexane (2.54 g, 15.4 mmol) to give **11** as a colourless solid. Yield 127 mg, 9%; Mp 77 °C; ¹H NMR (400 MHz, CDCl₃): 0.83–0.95 (m, 21H), 1.25–1.57 (m, 42H), 1.82–2.08 (m, 14H), 3.17 (t, J = 7.7, 2H), 4.03 (t, J = 6.5, 2H), 4.14 (t, J = 6.6, 2H), 4.18–4.24 (m, 8H), 7.73 (s, 1H), 7.77 (s, 1H), 7.79 (s, 1H), 7.80 (s, 1H), 7.88 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): 13.0, 13.1, 13.2, 21.6, 21.7, 21.8, 21.9, 24.8, 24.9, 25.0, 25.1, 28.4, 28.5, 28.7, 29.5, 29.6, 30.2, 30.7, 30.9, 31.1, 67.6, 68.3, 68.6, 68.8, 69.0, 103.2, 106.0, 106.7, 107.4, 111.2, 123.1, 123.5, 123.7, 123.8, 126.0, 131.9, 146.6, 146.7, 147.1, 148.0, 148.5, 149.8; HR-MS (EI): calcd for C₆₀H₉₆O₆ [M⁺] 912.7201; found 912.7206.
Triphenylene **12**: Prepared as above using hexahydroxytriphenylene **9** (0.50 g, 1.54 mmol) and 1-bromoheptane (2.76 g, 15.4 mmol) to give **12** as a colourless solid. Yield 127 mg, 9%; Mp 61 °C; ¹H NMR (400 MHz, CDCl₃): 0.81–0.92 (m, 21H), 1.25–1.62 (m, 56H), 1.82–2.08 (m, 14H), 3.17 (t, J = 7.6, 2H), 4.03 (t, J = 6.5, 2H), 4.13 (t, J = 6.7, 2H), 4.18–4.24 (m, 8H), 7.73 (s, 1H), 7.77 (s, 1H), 7.79 (s, 1H), 7.80 (s, 1H), 7.88 (s, 1H); ¹³C NMR (75 MHz, CDCl₃):14.1, 22.7, 22.8, 22.9, 26.1, 26.2, 26.3, 26.4, 29.2, 29.4, 29.5, 29.6, 29.7, 29.8, 30.6, 30.7, 31.0, 31.3, 31.9, 32.0, 32.1, 68.6, 69.3, 69.6, 69.8, 70.0, 104.3, 107.1, 107.8, 108.5, 112.3, 124.1, 124.5, 124.7, 124.8, 127.1, 133.0, 147.7, 147.8, 148.2, 149.1, 149.6, 150.8; HR-MS (EI): calcd for C₆₇H₁₁₀O₆ [M⁺] 1010.8297; found 1010.8285.
Triphenylene **13**: Prepared as above using hexahydroxytriphenylene **9** (0.50 g, 1.54 mmol) and 1-bromooctane (2.97 g, 15.4 mmol) to give **13** as a colourless solid. Yield 120 mg, 9%; Mp 58 °C; ¹H NMR (400 MHz, CDCl₃): 0.83–0.90 (m, 21H), 1.25–1.62 (m, 70H), 1.82–2.07 (m, 14H), 3.17 (t, J = 7.6, 2H), 4.03 (t, J = 6.6, 2H), 4.13 (t, J = 6.5, 2H), 4.18–4.24 (m, 8H), 7.73 (s, 1H), 7.77 (s, 1H), 7.79 (s, 1H), 7.79 (s, 1H), 7.87 (s, 1H); ¹³C NMR (75 MHz, CDCl₃):14.1, 22.7, 22.8, 26.2, 26.3, 26.4, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 30.6, 30.7, 31.1, 31.3, 31.9, 32.1, 68.6, 69.3, 69.6, 69.8, 70.0, 73.1, 104.2, 107.0, 107.8, 108.5, 112.2, 124.2, 124.5, 124.7, 124.8, 127.1, 133.0, 147.7, 147.8, 148.1, 149.0, 149.5, 150.8; HR-MS (EI): calcd for C₇₄H₁₂₄O₆ [M⁺] 1108.9392; found 1108.9382.
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