

Novel heptasubstituted triphenylene discotic liquid crystals

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The synthesis and characterisation of several hepta-substituted triphenylene derivatives are reported. These unsymmetrically substituted triphenylene derivatives are of three varieties, i) with seven identical peripheral alkoxy chains, ii) two or three out of the seven alkoxy chains have different chain lengths and, iii) the mode of the attachment of two of the peripheral chains is different, *i.e.* via ester linkages. The heptaalkoxytriphenylenes were prepared by two different routes, either starting from monohydroxypentakis(alkoxy)triphenylenes or *via* a biphenyl route using either MoCl₅ or FeCl₃ as oxidants. Unsymmetrical substitution has a large effect on the thermal behaviour but the type of mesophase formed does not change. Photomicroscopic pictures of all the 21 liquid crystalline compounds reported here show classical textures of an ordered hexagonal columnar (Col_h) phase. X-Ray diffraction studies of five representative compounds confirmed the above conclusions. Mixed ether-ester derivatives have smaller core-core separations and higher correlation length, therefore, are better candidates for charge transport studies.

Introduction

Triphenylene with symmetrically substituted six peripheral chains can make excellent discotic liquid crystals (LCs) which show great promise in electronic devices.¹ The potential applications of triphenylene discotic LCs has led to intense activity in their synthesis and various new methods have been developed.² Recently, several efforts have also been made to prepare unsymmetrical and functionalized triphenylene derivatives to modify the physical and electronic properties.²⁻¹² Whereas the synthesis of symmetrically substituted hexakis(alkoxy)triphenylenes by oxidative trimerisation of 1,2-dialkoxybenzenes is quite easy, the synthesis of well defined unsymmetrically substituted derivatives is not straight forward. Breaking of symmetry in a hexakis(alkoxy)triphenylene can be achieved in different ways, *e.g.*, by changing the chain length of some of the side chains, by changing the nature of one or more side chains or by low and high degree of substitution.

While triphenylene derivatives with six alkoxy chains are mesomorphic, triphenylenes having less than six alkoxy chains are nonmesomorphic but can be made mesomorphic by putting other substituents in the periphery.^{5a-d} Triphenylene derivatives with more than six peripheral alkoxy chains have not been well explored. Recently, in a preliminary communication,^{5g} we have reported a novel approach to the synthesis of heptakis(alkoxy)triphenylene discotic liquid crystals. Here we wish to report the preparation, characterization and X-ray studies of different heptakis-substituted triphenylene derivatives in detail.

Experimental

General information

Chemicals and solvents (AR quality) were used without any purification. Column chromatographic separations were performed on silica gel (230–400 mesh) and neutral aluminium oxide. Thin-layer chromatography (TLC) was performed on

aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). Mass spectra were recorded on a JEOL J600H spectrometer in FAB⁺ mode using an *m*-nitrobenzyl alcohol (NBA) matrix. Elemental analysis was provided by Onida Research Services, Inc., USA, Atlantic Microlab, Inc., USA and RRI, India. NMR spectra were recorded on a 200 MHz machine (Bruker) in CDCl₃. All chemical shifts are reported in δ units downfield from Me₄Si, and *J* values are given in Hz. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarizing microscope as well as by differential scanning calorimetry (DSC7 Perkin-Elmer). X-Ray studies were performed using an image plate detector (MAC Science DIP1030).¹³ Unoriented samples contained in sealed Lindemann glass capillaries were irradiated with Cu-K α rays obtained from a sealed-tube generator (Enraf-Nonius FR 590) in conjunction with double mirror focusing optics. The synthesis of different triphenylene derivatives is outlined in Schemes 1, 2 and 3. 2-Hydroxy-3,6,7,10,11-pentakis(alkoxy)triphenylenes **1a–f** were prepared as reported.^{5g}

Synthesis of 3,6,7,10,11-pentakis(alkoxy)triphenylene-1,2-diones (**2a–f**)

To a solution of appropriate 2-hydroxy-3,6,7,10,11-pentakis(alkoxy)triphenylene (**1a–f**) (1.0 mmol) in acetonitrile (10 ml), a solution of ammonium cerium nitrate (2.0 mmol in 10 ml acetonitrile) was added and the mixture was stirred at room temperature for 5 min. The reaction mixture was worked-up by addition of H₂O and extraction with CH₂Cl₂. The crude product was purified by column chromatography over silica gel and the product was isolated by eluting with hexane-dichloromethane mixture to yield black 3,6,7,10,11-pentakis(alkoxy)triphenylene-1,2-diones (**2a–f**) in 85–90% yield.

2a: MS: *m/z* 550.0; ¹H NMR: δ 8.91 (s, 1H), 7.65 (s, 1H), 7.63 (s, 1H), 7.38 (s, 1H), 6.99 (s, 1H), 4.14 (m, 10H), 1.89 (m, 10H) and 1.05 (m, 15H).

2b: MS: *m/z* 620.2; ¹H NMR: δ 8.91 (s, 1H), 7.64 (s, 1H), 7.61 (s, 1H), 7.35 (s, 1H), 6.98 (s, 1H), 4.20 (m, 10H), 1.89 (m, 10H), 1.55 (m, 10H) and 1.05 (m, 15H).

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2c: MS: *m/z* 690.2; ¹H NMR: δ 8.98 (s, 1H), 7.72 (s, 1H), 7.68 (s, 1H), 7.45 (s, 1H), 7.08 (s, 1H), 4.20 (m, 10H), 1.95 (m, 10H), 1.48 (m, 20H) and 0.98 (m, 15H).

2d: MS: *m/z* 758.0; ¹H NMR: δ 8.97 (s, 1H), 7.72 (s, 1H), 7.69 (s, 1H), 7.45 (s, 1H), 7.08 (s, 1H), 4.19 (m, 10H), 1.94 (m, 10H), 1.4 (m, 30H) and 0.93 (m, 15H).

2e: MS: *m/z* 830.1; ¹H NMR: δ 8.93 (s, 1H), 7.67 (s, 1H), 7.64 (s, 1H), 7.40 (s, 1H), 7.02 (s, 1H), 4.18 (m, 10H), 1.94 (m, 10H), 1.47 (m, 40H) and 0.91 (m, 15H).

2f: MS: *m/z* 900.1; ¹H NMR: δ 8.88 (s, 1H), 7.60 (s, 2H), 7.35 (s, 1H), 6.96 (s, 1H), 4.15 (m, 10H), 1.94 (m, 10H), 1.4 (m, 50H) and 0.90 (m, 15H).

Synthesis of 1,2-diacetoxy-3,6,7,10,11-pentakis(alkoxy)triphenylene (3a–f)

To a solution of appropriate *o*-quinone (**2a–f**) (1 mmol) in acetic anhydride (4 ml) and triethylamine (2 ml), was added Zn powder (650 mg, 10 mmol) and the reaction mixture was refluxed under nitrogen for 3 h. The reaction mixture was then cooled, filtered from the inorganics and the filtrate was poured into cold water (20 ml) and extracted with diethyl ether (3 × 20 ml). Combined extracts were dried over anhydrous sodium sulfate, the solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel. The column was eluted with hexane–dichloromethane to yield a homogeneous solid which was crystallised from ethanol in 90–95% yield.

3a: MS: *m/z* 634.0; ¹H NMR: δ 8.49 (s, 1H), 7.84 (3 unresolved s, 3H), 7.79 (s, 1H), 4.16 (m, 10H), 2.45 (s, 3H), 2.39 (s, 3H), 1.95 (m, 10H), and 1.1 (m, 15H); ¹³C NMR: δ 169.4, 167.8, 150.2, 149.4, 149.0, 148.8, 148.4, 140.9, 132.2, 128.9, 125.0, 124.8, 122.8, 122.3, 117.1, 111.1, 108.5, 107.5, 107.1, 103.7, 71.5, 71.1, 71.0, 70.5, 22.8, 22.6, 21.0, 20.3, 10.6; Elemental anal: calcd for C₃₇H₄₆O₉, C 70.01, H 7.30; found, C 70.00, H 7.35%.

3b: MS: *m/z* 704.9; ¹H NMR: δ 8.48 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.81 (s, 1H), 7.78 (s, 1H), 4.19 (m, 10H), 2.44 (s, 3H), 2.38 (s, 3H), 1.92 (m, 10H), 1.60 (m, 10H) and 1.03 (m, 15H); ¹³C NMR: δ 168.0, 167.8, 150.1, 149.3, 148.9, 148.7, 148.4, 140.9, 132.2, 128.9, 124.9, 124.7, 122.7, 122.2, 117.1, 110.8, 108.3, 107.2, 106.7, 103.8, 69.6, 69.2, 69.1, 68.7, 31.5, 31.4, 31.3, 31.2, 21.0, 20.3, 19.3, 19.2, 13.9; Elemental anal: calcd for C₄₂H₅₆O₉, C 71.56, H 8.00; found, C 71.30, H 7.86%.

3c: MS: *m/z* 774.6; ¹H NMR: δ 8.48 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.81 (s, 1H), 7.78 (s, 1H), 4.18 (m, 10H), 2.44 (s, 3H), 2.38 (s, 3H), 1.88 (m, 10H), 1.47 (m, 20H) and 0.97 (m, 15H); Elemental anal: calcd for C₄₇H₆₆O₉, C 72.84, H 8.58; found, C 72.88, H 8.70%.

3d: MS: *m/z* 844.1; ¹H NMR δ 8.47 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.81 (s, 1H), 7.78 (s, 1H), 4.18 (m, 10H), 2.44 (s, 3H), 2.38 (s, 3H), 1.92 (m, 10H), 1.56–1.37 (m, 30H) and 0.95 (m, 15H); Elemental anal: calcd for C₅₂H₇₆O₉, C 73.90, H 9.06; found, C 74.11, H 9.55%.

3e: MS: *m/z* 914.3; ¹H NMR δ 8.47 (s, 1H), 7.82 (3 unresolved s, 1H), 7.78 (s, 1H), 4.18 (m, 10H), 2.44 (s, 3H), 2.38 (s, 3H), 1.91 (m, 10H), 1.6–1.3 (m, 40H) and 0.91 (m, 15H); Elemental anal: calcd for C₅₇H₈₆O₉, C 74.80, H 9.47; found, C 74.84, H 9.37%.

3f: MS: *m/z* 984.6; ¹H NMR δ 8.47 (s, 1H), 7.82 (3 unresolved s, 1H), 7.78 (s, 1H), 4.16 (m, 10H), 2.44 (s, 3H), 2.38 (s, 3H), 1.91 (m, 10H), 1.6–1.3 (m, 50H) and 0.88 (m, 15H); Elemental anal: calcd for C₆₂H₉₆O₉, C 75.57, H 9.82; found, C 75.21, H 9.80%.

Synthesis of 1,2,3,6,7,10,11-heptakis(alkoxy)triphenylenes; (4a–n)

In a typical procedure, powdered KOH (8 mmol) was mixed with DMSO (5 ml) and stirred at room temperature for 10 min. One mmol of diacetate **3a–f** was added followed by alkyl

bromide (4 mmol). The reaction mixture was stirred for 12 h at 50–55 °C and then worked up by addition of water and extraction with diethyl ether. The crude product was purified by column chromatography over silica gel eluting with hexane–ethyl acetate to yield (**4a–n**) in 80–90% yield.

1,2,3,6,7,10,11-Heptakis(propyloxy)triphenylene; 4a. MS: *m/z* 634.4; ¹H NMR (CDCl₃) δ 9.22 (s, 1H), 7.83 (two unresolved s, 3H), 7.67 (s, 1H), 4.16 (m, 12H), 3.99 (t, 2H), 1.94 (m, 14H) and 1.08 (m, 21H); Elemental anal: calcd for C₃₉H₅₄O₇, C 73.78, H 8.57; found, C 73.50, H 8.71%.

1,2,3,6,7,10,11-Heptakis(butyloxy)triphenylene; 4b. MS: *m/z* 732.1; ¹H NMR: δ 9.22 (s, 1H), 7.83 (s, 2H), 7.81 (s, 1H), 7.66 (s, 1H), 4.20 (m, 12H), 4.01 (t, *J* = 7.1, 2H), 1.88 (m, 14H), 1.56 (m, 14H) and 0.99 (m, 21H); Elemental anal: calcd for C₄₆H₆₈O₇, C 75.37, H 9.35; found, C 75.11, H 9.93%.

1,2,3,6,7,10,11-Heptakis(pentyloxy)triphenylene; 4c. MS: *m/z* 830.3; ¹H NMR: δ 9.21 (s, 1H), 7.83 (s, 2H), 7.81 (s, 1H), 7.66 (s, 1H), 4.20 (m, 12H), 4.01 (t, *J* = 7.1, 2H), 1.83 (m, 14H), 1.49 (m, 28H) and 1.02 (m, 21H); ¹³C NMR: δ 151.7 × 2, 149.6, 148.8, 148.5, 148.1, 142.0, 126.5, 124.6, 124.0, 123.8, 123.4, 118.2, 111.9, 108.4, 107.1 × 2, 101.8, 74.0, 70.0, 69.6, 69.3, 68.8, 31.9, 30.3, 30.2, 29.2, 28.4, 22.5, 14.1; Elemental anal: calcd for C₅₃H₈₂O₇, C 76.58, H 9.93; found, C 76.30, H 9.86%.

1,2,3,6,7,10,11-Heptakis(hexyloxy)triphenylene; 4d. MS: *m/z* 928.4; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.82 (two unresolved s, 3H), 7.66 (s, 1H), 4.13 (m, 12H), 3.97 (t, 2H), 1.94 (m, 14H), 1.6–1.2 (m, 42H) and 1.08 (m, 21H); Elemental anal: calcd for C₆₀H₉₆O₇, C 77.54, H 10.41; found, C 77.34, H 10.58%.

1,2,3,6,7,10,11-Heptakis(heptyloxy)triphenylene; 4e. MS: *m/z* 1026.1; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.82 (two unresolved s, 3H), 7.66 (s, 1H), 4.21 (m, 12H), 3.97 (t, 2H), 1.94 (m, 14H), 1.6–1.2 (m, 56H) and 0.90 (m, 21H); ¹³C NMR: δ 151.8 × 2, 149.7, 148.9, 148.6, 148.2, 142.1, 126.6, 124.7, 124.1, 123.9, 123.5, 118.3, 112.0, 108.6, 107.3 × 2, 102.0, 74.1, 70.1, 69.8, 69.7, 69.4, 69.0, 31.9, 30.7, 30.6, 29.6, 29.4, 29.2, 26.2, 22.7, 14.1; Elemental anal: calcd for C₆₇H₁₁₀O₇, C 78.31, H 10.79; found, C 78.13, H 10.91%.

1,2,3,6,7,10,11-Heptakis(octyloxy)triphenylene; 4f. MS: *m/z* 1125.2; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.82 (two unresolved s, 3H), 7.66 (s, 1H), 4.12 (m, 12H), 3.97 (t, 2H), 1.93 (m, 14H), 1.7–1.2 (m, 70H) and 0.89 (m, 21H); ¹³C NMR: δ 151.8 × 2, 149.7, 148.9, 148.6, 148.2, 142.1, 126.6, 124.7, 124.1, 123.9, 123.5, 118.3, 112.0, 108.6, 107.3 × 2, 102.0, 74.1, 74.0, 70.1, 69.8, 69.7, 69.4, 69.0, 31.9, 30.7, 30.6, 29.7, 29.5, 29.4, 26.3, 22.7, 14.1; Elemental anal: calcd for C₇₄H₁₂₄O₇, C 78.96, H 11.00; found, C 78.94, H 10.84%.

1,2-Bis(dodecyloxy)-3,6,7,10,11-pentakis(propyloxy)triphenylene; 4g. MS: *m/z* 886.1; ¹H NMR (CDCl₃) δ 9.22 (s, 1H), 7.83 (two unresolved s, 3H), 7.67 (s, 1H), 4.12 (m, 12H), 3.97 (t, 2H), 1.98 (m, 14H), 1.26 (m, 36H), 1.15 (m, 15H) and 0.88 (t, 6H); Elemental anal: calcd for C₅₇H₉₀O₇, C 77.16, H 10.21; found, C 76.96, H 10.00%.

1,2-Bis(propyloxy)-3,6,7,10,11-pentakis(butyloxy)triphenylene; 4h. MS: *m/z*; 704.3; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.83 (3 unresolved s, 3H), 7.67 (s, 1H), 4.19 (m, 12H), 3.99 (t, 2H), 1.94 (m, 14H), 1.88–1.55 (m, 10H) and 1.05 (m, 21H); Elemental anal: calcd for C₄₄H₆₄O₇, C 74.96, H 9.15; found, C 74.84, H 9.37%.

1,2-Bis(pentyloxy)-3,6,7,10,11-pentakis(butyloxy)triphenylene; 4i. MS: *m/z* 760.5; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.83

(2 unresolved s, 3H), 7.67 (s, 1H), 4.19 (m, 12H), 3.97 (t, 2H), 1.95 (m, 14H), 1.8–1.25 (m, 18H) and 0.98 (m, 21H); Elemental anal: calcd for C₄₈H₇₂O₇, C 75.75, H 9.54; found, C 75.40, H 9.86%.

1,2-Bis(hexyloxy)-3,6,7,10,11-pentakis(butyloxy)triphenylene; 4j. MS: *m/z* 788.5; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.83 (2 unresolved s, 3H), 7.66 (s, 1H), 4.19 (m, 12H), 4.0 (t, 2H), 1.9 (m, 14H), 1.7–1.2 (m, 22H), 1.0 (m, 15H) and 0.88 (m, 6H); ¹³C NMR: δ 151.7 × 2, 149.6, 148.8, 148.5, 148.2, 142.0, 126.5, 124.6, 124.0, 123.8, 123.5, 118.2, 112.0, 108.4, 107.2 × 2, 101.8, 74.1, 69.7, 69.4, 69.1, 68.5, 31.8, 31.5, 30.6, 25.9, 25.8, 22.7, 19.4, 13.9; Elemental anal: calcd for C₅₀H₇₆O₇, C 76.10, H 9.71; found, C 76.01, H 9.79%.

1,2-Bis(heptyloxy)-3,6,7,10,11-pentakis(butyloxy)triphenylene; 4k. MS: *m/z* 816.4; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.83 (2 unresolved s, 3H), 7.66 (s, 1H), 4.19 (m, 12H), 4.0 (t, 2H), 1.9 (m, 14H), 1.7–1.2 (m, 26H), 1.0 (t, 15H) and 0.88 (m, 6H); Elemental anal: calcd for C₅₂H₈₀O₇, C 76.43, H 9.87; found, C 76.21, H 9.98%.

1,2-Bis(butyloxy)-3,6,7,10,11-pentakis(pentyloxy)triphenylene; 4l. MS: *m/z* 802.6; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.82 (2 unresolved s, 3H), 7.66 (s, 1H), 4.19 (m, 12H), 4.0 (t, 2H), 1.9 (m, 14H), 1.7–1.3 (m, 18H) and 1.0 (m, 21H); Elemental anal: calcd for C₅₁H₇₈O₇, C 76.27, H 9.79; found, C 76.00, H 9.92%.

1,2-Bis(hexyloxy)-3,6,7,10,11-pentakis(pentyloxy)triphenylene; 4m. MS: *m/z* 858.7; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.82 (2 unresolved s, 3H), 7.66 (s, 1H), 4.19 (m, 12H), 4.0 (t, 2H), 1.9 (m, 14H), 1.7–1.2 (m, 32H) and 0.97 (m, 21H); ¹³C NMR: δ 151.7 × 2, 149.6, 148.8, 148.5, 148.1, 142.0, 126.5, 124.6, 124.0, 123.8, 123.5, 118.2, 111.8, 108.4, 107.1 × 2, 101.8, 74.1, 70.0, 69.7, 69.3, 68.9, 31.9, 30.6, 29.2, 28.4, 25.9, 25.8, 22.6, 14.1; Elemental anal: calcd for C₅₅H₈₆O₇, C 76.88, H 10.08; found, C 76.44, H 9.96%.

1,2-Bis(decyloxy)-3,6,7,10,11-pentakis(octyloxy)triphenylene; 4n. MS: *m/z* 1181.8; ¹H NMR (CDCl₃) δ 9.21 (s, 1H), 7.82 (2 unresolved s, 3H), 7.66 (s, 1H), 4.19 (m, 12H), 4.0 (t, 2H), 1.9 (m, 14H), 1.7–1.2 (m, 78H) and 0.89 (m, 21H); ¹³C NMR: δ 151.8 × 2, 149.7, 148.9, 148.6, 148.2, 142.1, 126.6, 124.7, 124.1, 123.9, 123.6, 118.3, 112.0, 108.6, 107.3 × 2, 102.0, 74.1, 70.1, 69.8, 69.7, 69.4, 69.0, 31.9, 30.7, 30.6, 29.8, 29.6, 29.4, 26.3, 22.7, 14.1; Elemental anal: calcd for C₇₈H₁₃₂O₇, C 79.27, H 11.26; found, C 79.33, H 11.27%.

Synthesis of 1,2-bis(alkanoyloxy)-3,6,7,10,11-pentakis(alkoxy)triphenylenes; (5a–c)

3,6,7,10,11-Pentakis(alkoxy)triphenylene-1,2-diones (**2a–f**) (0.3 mmol) were taken in 2 ml of dry deoxygenated pyridine. Zn powder (3 mmol) and the corresponding acid chloride (3 mmol) were added and the reaction mixture was refluxed for 5 h under argon. It was then poured over ice–water and extracted with ether (3 × 30 ml). The combined ether extracts were dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the resultant crude product was purified by column chromatography over silica gel eluting with hexane–dichloromethane mixture. The TLC pure white materials (**5a–c**) were crystallised with absolute alcohol in 50–60% yield.

1,2-Bis(butanoyloxy)-3,6,7,10,11-pentakis(butoxy)triphenylene; 5a. MS: *m/z* 760.5; ¹H NMR δ 8.48 (s, 1H), 7.8 (3 unresolved s, 4H), 7.78 (s, 1H), 4.19 (m, 10H), 2.70 (t, 2H), 2.61 (t, 2H), 1.92 (m, 14H), 1.55 (m, 10H) and 1.05 (m, 21H); Elemental anal: calcd for C₄₆H₆₄O₉, C 72.60, H 8.48; found, C 72.32, H 8.65%.

1,2-Bis(pentanoyloxy)-3,6,7,10,11-pentakis(pentyloxy)triphenylenes; 5b. MS: *m/z* 858.7; ¹H NMR δ 8.48 (s, 1H), 7.8 (3 unresolved s, 4H), 7.78 (s, 1H), 4.19 (m, 10H), 2.72 (t, 2H), 2.63 (t, 2H), 1.92 (m, 14H), 1.5 (m, 24H) and 0.98 (m, 21H); Elemental anal: calcd for C₅₃H₇₈O₉, C 74.09, H 9.15; found, C 74.20, H 9.41%.

1,2-Bis(octanoyloxy)-3,6,7,10,11-pentakis(octyloxy)triphenylenes; 5c. MS: *m/z* 1152.8; ¹H NMR δ 8.47 (s, 1H), 7.8 (3 unresolved s, 4H), 7.78 (s, 1H), 4.16 (m, 10H), 2.71 (t, 2H), 2.62 (t, 2H), 1.92 (m, 14H), 1.7–1.2 (m, 66H) and 0.90 (m, 21H); ¹³C NMR: δ 170.8, 170.6, 150.2, 149.5, 149.0, 148.9, 148.5, 141.0, 132.4, 128.9, 125.0, 124.8, 123.0, 122.5, 117.3, 111.4, 108.6, 107.5, 107.1, 103.7, 70.1, 69.7, 69.6, 69.0, 34.6, 34.1, 31.9, 31.8, 29.5, 29.4, 29.1, 26.3, 26.2, 25.2, 25.0, 22.7, 14.1; Elemental anal: calcd for C₇₄H₁₂₀O₉, C 77.04, H 10.47; found, C 76.87, H 10.36%.

Synthesis of heptakis(alkoxy)triphenylenes by the oxidative coupling method

A. Using MoCl₅. The reaction was carried out following the previously reported method.^{5e} MoCl₅ (400 mg, 1.47 mmol) was added to a solution of 3,4,3',4'-tetrakis(butyloxy)biphenyl **6** (200 mg, 0.45 mmol) and 1,2,3-tris(butyloxy)benzene **7** (400 mg, 1.36 mmol) in 5 ml dry CH₂Cl₂ with or without concentrated H₂SO₄ (0.4%). The reaction mixture was stirred at room temperature for one hour under nitrogen. The reaction was worked-up by the addition of 2 ml of cold MeOH followed by water (20 ml) and extraction with CH₂Cl₂. The product was purified by column chromatography over silica gel and characterised by spectral analysis as well as by direct comparison with the authentic sample. In both cases (with or without concentrated H₂SO₄ acid), the yield was almost the same (45%).

B. Using FeCl₃. The reaction was carried out as above but with anhydrous FeCl₃ instead of MoCl₅ and the same product was isolated in 40% yield.

Synthesis of mixed unsymmetrical heptakis(alkoxy)triphenylenes using the biphenyl route; synthesis of 8b

Anhydrous FeCl₃ (240 mg, 1.47 mmol) was added to a solution of 3,4,3',4'-tetrakis(butyloxy)biphenyl **6** (200 mg, 0.45 mmol) and 1,2,3-tris(pentyloxy)benzene **7b** (400 mg, 1.2 mmol) in 5 ml dry CH₂Cl₂ containing 0.4% concentrated H₂SO₄. The reaction mixture was stirred at room temperature for one hour under nitrogen and worked-up as above. Purification of the crude product by column chromatography yielded the 1,2,3-tris(pentyloxy)-6,7,10,11-tetrakis(butyloxy)triphenylene, **8b** in 38% yield. MS: *m/z* 774.4; ¹H NMR (CDCl₃) (9.21 (s, 1H), 7.83 (2 unresolved s, 3H), 7.66 (s, 1H), 4.19 (m, 12H), 4.0 (t, 2H), 1.9 (m, 14H), 1.8–1.25 (m, 20H) and 1.0 (m, 21H); Elemental anal: calcd for C₄₉H₇₄O₇, C 75.93, H 9.62; found, C 75.59, H 9.79%.

Results and discussion

In order to reduce the melting point, the concept of reducing symmetry is adopted by several workers with the basic idea that if the molecular symmetry is reduced, then the molecules would pack less favourably in the crystal state and, therefore, the melting point will decrease. The symmetry of a discoid molecule can be reduced by different ways, such as core asymmetric substitution, for example, putting 5 or 7 peripheral chains in a triphenylene molecule, or side chains asymmetry by attaching alkyl chains of different length in the periphery or by changing the mode of the attachment of the peripheral chains, e.g., mixed ether–ester derivatives. Tinh *et al.* prepared several

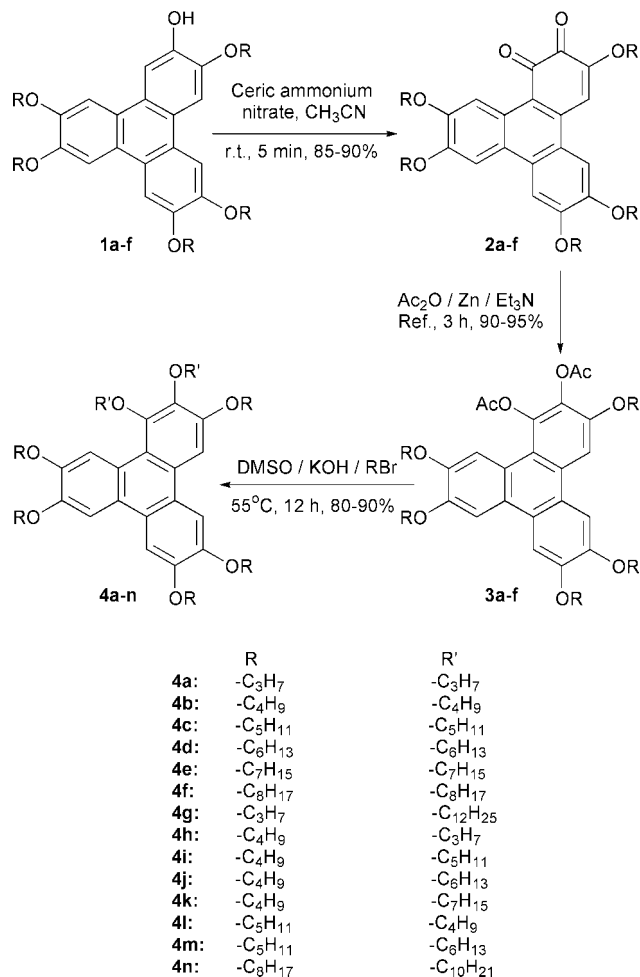
disymmetrical hexasubstituted triphenylenes with different alkyl chains in the periphery using a statistical approach to understand the effects of unsymmetrical chains in a triphenylene molecule. They found that an introduction of dissymmetric side-chains does not affect the nature of the Col_h phase but results in the reduction of the mesophase stability.¹⁴ This statistical approach to prepare unsymmetrical triphenylene derivatives gives a mixture of products which is very difficult to separate. An easy route to unsymmetrically substituted triphenylenes was recently reported using the so-called biphenyl route.³ Well-defined synthesis of unsymmetrical and low degree substituted triphenylenes has also been reported recently by using organometallic chemistry.¹² When one out of the six ether side chains in hexakis(alkoxy)triphenylenes was replaced by an ester group, the stability of the mesophase was enhanced significantly.¹⁵ A plastic columnar discotic phase is reported in these types of unsymmetric triphenylene derivatives.⁸ In another approach to prepare unsymmetrical triphenylenes and to induce molecular dipole, colour, etc., nitration and halogenation of hexakis(alkoxy)triphenylenes were performed.^{3,6} While the nitro or halogen group in these triphenylene derivatives could not be replaced by an alkylthio group by nucleophilic aromatic substitution,⁶ the reduction of the nitro group followed by acylation with various acid chlorides yielded "seven tail" triphenylene discotics.^{3d} However, because of the presence of the amide group, the clearing temperatures of these derivatives are high.

We prepared the heptakis(alkoxy)triphenylenes by two different methods. Oxidation of the 2-hydroxy-3,6,7,10,11-pentakis(butyloxy)triphenylenes **1a-f** (Scheme 1) with various oxidising agents such as chromium trioxide, nitric acid and ceric ammonium nitrate yielded the ring oxidised products 3,6,7,10,11-pentakis(alkoxy)triphenylene-1,2-diones **2a-f**. Reductive acetylation of these *o*-quinones with zinc and acetic anhydride in triethylamine results in the formation of diacetates **3a-f**. These diacetates were directly alkylated with various alkyl halides to produce symmetrical (having all the 7 chains identical) or unsymmetrical (two peripheral chains are different) heptakis(alkoxy)triphenylenes **4a-n** in very high yield (Scheme 1).

The heptakis(alkoxy)triphenylenes can also be prepared by phenyl-biphenyl coupling. Thus, when tetrakis(alkoxy)biphenyls **6** were reacted with tris(alkoxy)benzenes under oxidative coupling conditions using either $MoCl_5$ or $FeCl_3$, heptakis(alkoxy)triphenylenes formed in moderate yields (Scheme 2). Similarly, unsymmetrical heptakis(alkoxy)triphenylenes can also be prepared using the tetrakis(alkoxy)biphenyl and tris(alkoxy)benzene derivatives having different chains. However, it should be noted that the unsymmetrical heptakis(alkoxy)triphenylenes prepared from these two routes are different. The *o*-quinone route gives a unsymmetrical heptakis(alkoxy)triphenylene where two out of seven chains are different while the biphenyl route gives a product in which three out of seven chains are different. Reductive esterification of the *o*-diquinone with various acid chlorides yields 1,2-bis(alkanoyloxy)-3,6,7,10,11-pentakis(alkoxy)triphenylenes (Scheme 3). These mixed esters-ethers cannot be achieved from the biphenyl route as the phenyl-biphenyl coupling works only with highly electron rich precursors.

Thermal behaviour

The thermal behaviour of all the compounds was investigated by polarizing microscopy and by differential scanning calorimetry. In the case of materials which were mesomorphic, classical textures of columnar mesophases appeared upon cooling from the isotropic liquid. These textures are very similar to the known textures for the Col_h phases. Data obtained from the heating and cooling cycles of DSC are collected in Table 1. The peak temperatures are given in °C and

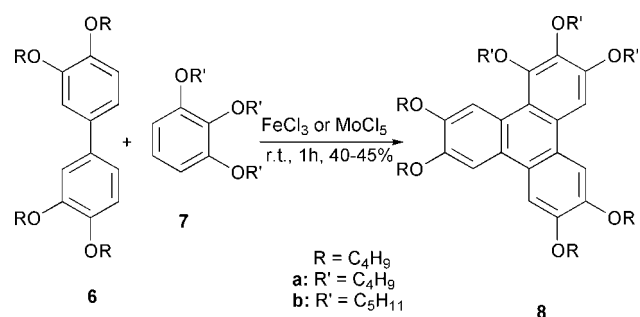


Scheme 1 Synthesis of heptakis(alkoxy)triphenylenes.

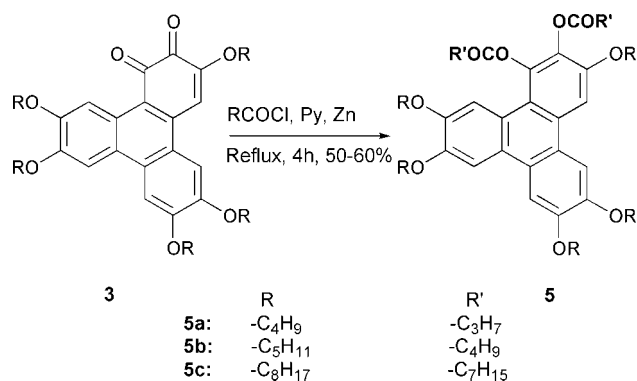
the numbers in parentheses indicate the transition enthalpy (ΔH) in $kJ\ mol^{-1}$.

All the heptakis-substituted triphenylene derivatives can be subdivided into three groups: (a) where chain length of all the seven peripheral tails is same and they are connected *via* ether linkages (compounds **4a-4f**), (b) where all the seven tails are connected through ether linkages as above but the length of two or three tails is different (compounds **4g-4n** and **8b**), and (c) where two of the peripheral chains are connected to the core *via* ester linkages and the other five *via* ether linkages (compounds **3a-3f**, **5a-5c**).

In group (a), the shortest chain member, *i.e.*, heptakis(propoxy)triphenylene is non liquid crystalline. It melts at about 92 °C on heating and crystallizes at 71 °C on cooling the isotropic melt. This is similar to the hexakis(propoxy)triphenylene derivative which has a melting point of 177 °C (this compound has recently been reported to be liquid crystalline on



Scheme 2 Synthesis of heptakis(alkoxy)triphenylenes *via* the biphenyl route.



Scheme 3 Synthesis of mixed ether-ether heptakisubstituted triphenylenes.

the basis of miscibility tests,¹⁶ however it has not been proved unambiguously). The decrease in melting point is expected because of the extra propyloxy chain. The higher homologues of heptakis(alkoxy)triphenylene, like hexakis(alkoxy)triphenylenes, are liquid crystalline. The melting and clearing temperatures do not alter significantly through the series. Highly reversible behavior is observed at the clearing point of all the compounds and only a very small hysteresis is observed over many heating and cooling cycles. Conversely, the melting transition was found to be irreversible. Upon cooling, all mesophases supercool to room temperature. None of the members of the series show any sign of crystallization upon keeping at room temperature for a long period. Therefore, it was necessary to use solvent crystallized materials to get the melting points. If the materials are heated above the melting points, they stay in the mesophase indefinitely. All the members of group (a) show two clear transitions on first heating. The first transition with a large ΔH in compounds **4b**, **4d**, **4e** and **4f** corresponds to crystal to melting transition. However, the enthalpy of this transition in compound **4c** is much less indicating that this could be perhaps a transition from a soft-solid to the mesophase. The second transition in all the compounds is from the mesophase to isotropic liquid. On cooling from the isotropic liquid, compound **4c** as well as all

other members of the group show only one transition corresponding to isotropic liquid to Col_h phase which is stable down to room temperature. Efforts have not been made to see transitions below the room temperature. Compared to hexakis(alkoxy)triphenylenes,² both the melting and clearing temperatures of heptakis(alkoxy)triphenylenes are very low. This could be due to the presence of the extra alkoxy chain and the steric hindrance caused by this chain.

In the mixed ethers group (b), increasing the size of two peripheral chains does not induce liquid crystallinity if the other chains are too short. Thus, compound **4g** with five propyloxy and two dodecyloxy chains, shows crystal to isotropic transition at 50.3 °C on heating and upon cooling it crystallises at room temperature. When five chains of a heptakis(alkoxy)triphenylene are of four carbon atoms which is essential for triphenylene derivatives to show mesomorphism, and the remaining two are of three carbon atoms, the compound **4h** shows a monotropic columnar phase. Compound **4h** shows crystal to isotropic transition at 74.3 °C on heating but on cooling it comes to a columnar mesophase at about 59 °C that crystallizes at about 48 °C. When the size of the two alkoxy chains is more than the remaining five alkoxy chains, there is a gradual decrease in the melting and clearing temperatures. Thus, bis(pentyloxy)pentakis(butyloxy)triphenylene **4i** shows the melting transition at 58.7 °C and the clearing transition at 69.3 °C. Compound **4j** having bis(hexyloxy) chains and five butyloxy chains has melting and clearing transitions at 56.2 and 59.1 °C respectively while compound **4k** with bis(heptyloxy) and pentakis(butyloxy) chains is a room temperature liquid crystalline material which precipitated out in the liquid crystalline form in organic solvents. It transforms from mesophase to isotropic phase at 47.6 °C. Compounds **4l**, **4m** and **4n** show similar behavior. Their melting and clearing temperatures are given in Table 1. Compound **8b** which has three pentyloxy and four butyloxy chains shows a melting transition at 60.6 °C and clearing transition at 73.5 °C. Similar to group (a) members, mesophases formed by group (b) members also supercool to room temperature and do not crystallize upon keeping at room temperature for a long period.

In the mixed ether-ester series, two types of materials were prepared; one having two of the shortest chain esters, *i.e.*

Table 1 Phase transition temperatures (peak temp.) and enthalpies of heptakis-substituted triphenylene derivatives. Cr = crystal, Col_h = hexagonal columnar liquid crystalline phase, Col_x = A yet to be identified columnar phase, I = isotropic

Compound	Thermal transitions /°C and enthalpy changes /kJ mol ⁻¹ (in parentheses)	
	Heating scan	Cooling scan
4a	Cr 92.3 (38.2) I	I 71.6 (29.0)
4b	Cr 65.8 (43.1) Col _h 70.1 (4.6) I	I 67.5 (5.9) Col _h
4c	Cr 45.7 (13.8) Col _h 75.0 (6.0) I	I 72.9 (6.1) Col _h
4d	Cr 44.6 (39.4) Col _h 69.5 (3.7) I	I 67.3 (3.6) Col _h
4e	Cr 46.6 (66.8) Col _h 71.8 (5.5) I	I 69.8 (5.0) Col _h
4f	Cr 44.3 (36.6) Col _h 68.7 (4.3) I	I 67.2 (4.3) Col _h
4g	Cr 50.3 (68.1) I	I ~ 30 Cr
4h	Cr 74.3 (29.8) I	I (58.9)(5.2) Col _h 47.8 (20.3) Cr
4i	Cr 58.7 (40.2) Col _h 69.3 (5.2) I	I 67.1 (5.2) Col _h
4j	Cr 56.2 (46.6) Col _h 59.1 (2.4) I	I 57.7 (3.5) Col _h
4k	Col _h 47.6 (3.6) I	I 45.8 (3.4) Col _h
4l	Cr 47.9 (35.7) Col _h 70.5 (4.9) I	I 68.9 (5.7) Col _h
4m	Cr 47.6 (47.3) Col _h 68.6 (3.1) I	I 65.2 (3.0) Col _h
4n	Col _h 63.9 (5.1) I	I 62.8 (4.4) Col _h
3a	Cr 152.0 (35.4) I	I 92.1 (9.7) Cr
3b	Cr 122.3 (21.3) I	I 87.2 (4.7) Col/Cr
3c	Cr 88.1 (1.6) Col _h 105.7 (9.6) I	I 101.5 (6.3) Col _h
3d	Cr 85.6 Col _h 90.0 I	I 86.2 (5.9) Col _h
3e	Cr 72.9 (12.9) Col _h 90.6 (7.9) I	I 87.4 (7.8) Col _h
3f	Cr 57.8 (15.5) Col _h 88.7 (7.7) I	I 85.5 (6.8) Col _h
5a	Col _x 97.4 (4.0) Col _h 121.1 (14.4) I	I 118.8 (14.3) Col _h 94.2 (0.8) Col _x
5b	Col _h 129.1 (13.8) I	I 127.2 (13.6) Col _h
5c	Cr 55.5 (20.6) Col _h 121.7 (9.3) I	I 120.2 (8.9) Col _h
8b	Cr 60.6 (22.6) Col _h 73.5 (4.4) I	I 71.1 (4.9) Col _h

acetate, and five alkoxy chains (compounds **3a–3f**) and the other having the same size of ether and ester chains (compounds **5a–5c**). Compound **3a** (1,2-diacetoxy)-3,6,7,10,11-pentakis(propoxy)triphenylene) on first heating, gives only one peak in the DSC at 152.0 °C with a large ΔH , corresponding to a transition from the crystalline solid state to the isotropic liquid state. Upon cooling from the isotropic liquid it starts crystallizing at about 92 °C. These crystals melt at about 99 °C on subsequent heating. Compound **3b**, on heating, gives a crystal to isotropic transition at 122.3 °C. On cooling from the isotropic liquid it comes to a metastable Col_h phase at about 87 °C which crystallizes slowly over a long period of time. The higher homologues **3c–3f** show a weak transition prior to the mesophase to isotropic transition but this transition is not discernible on cooling or on second heating. All these materials appear as a viscous mass (soft solid) at room temperature but do not show definite textures. Therefore, it is difficult to say that they stay in a liquid crystalline phase at room temperature. The first weak transition could be a soft-solid to mesophase transition and this may be the reason for a low ΔH for this transition than the usual crystal to mesophase transition. The pentakis(pentyloxy)-diacetyl **3c** has this weak transition at 88.1 °C and the mesophase to isotropic transition at 105.7 °C. Upon cooling it gives only one broad peak at 101.5 °C for the isotropic to mesophase transition and on subsequent heating it gives only one peak at 105.7 °C for mesophase to isotropic transition. Compound **3d** shows two broad peaks which are not well separated at 85.6 and 90.0 °C with total enthalpy of the transition 11.9 kJ mol⁻¹. On cooling from the isotropic liquid, it comes to a columnar phase at 86.2 °C which stays down to room temperature. On second heating it gives only one mesophase with an isotropic transition peak at 91.0 °C. Compound **3e** shows two transitions at 72.9 °C (ΔH , 12.9 kJ mol⁻¹) and at 90.6 °C (ΔH , 7.9 kJ mol⁻¹) on first heating and only one at 87.4 °C (ΔH , 7.8 kJ mol⁻¹) on cooling and at 91.6 °C (ΔH , 7.5 kJ mol⁻¹) on second heating indicating that the soft solid changes to Col_h phase at 72.9 °C and which transforms into the isotropic liquid at 90.6 °C. On cooling the isotropic liquid, the Col_h phase appeared at 87.4 °C which is stable until room temperature. Compound **3f** shows similar behavior and gives one very broad peak at 57.8 °C and another at 88.7 °C on first heating. The Col_h phase appeared at 85.5 °C on cooling.

Mixed ethers–esters with same chain length (compound **5a–c**) have relatively higher isotropic temperatures. When the peripheral chains are of four carbon atoms (compound **5a**), a transition from a highly ordered, yet to be identified, Col_x phase to Col_h phase is observed at 97.4 °C. The Col_h phase goes to an isotropic phase at 121.1 °C. Both these transitions are reversible. The Col_h phase appeared at 118.8 °C on cooling and changes to the Col_x phase at 94.2 °C. The higher homologue **5b** shows only one transition in the DSC corresponding to the mesophase to isotropic liquid at 129.1 °C. The Col_h phase which appears at 127.2 °C on cooling, stays until room temperature. On the other hand, compound **5c** melts at 55.5 °C and clears at 121.7 °C. On cooling the columnar phase stays down to ambient temperature.

X-Ray diffraction studies

For samples **4c**, **4e**, **4k**, **5b** and **5c** measurements were carried out at room temperature. A representative diffraction pattern obtained for the compound **5b** and its one-dimensional intensity vs. 2θ profile obtained by integrating over the entire χ (0–360°) range, are shown in Fig. 1. Qualitatively similar patterns were seen for the other compounds. In the low-angle region, four sharp peaks — one very strong and three weak reflections are seen whose d -spacings are in the ratio of 1 : 1/ $\sqrt{3}$: 1/ $\sqrt{4}$: 1/ $\sqrt{7}$. Identifying the first peak with the Miller index

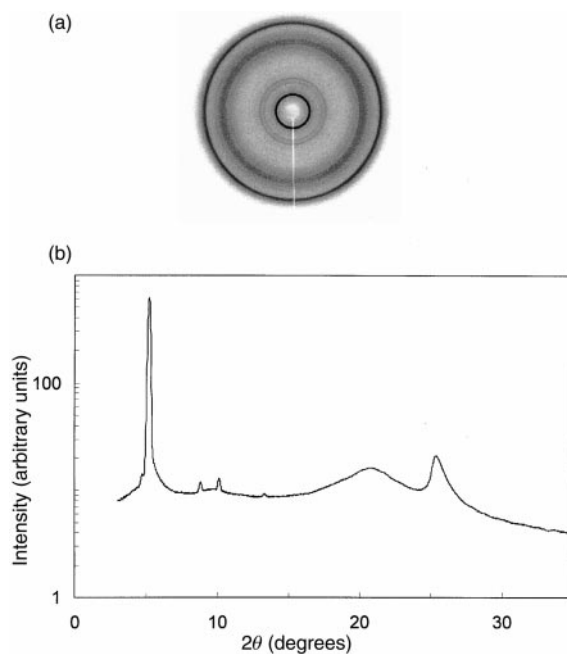


Fig. 1 (a) X-Ray diffraction pattern obtained for compound **5b** at room temperature. (b) χ -averaged one-dimensional intensity vs. 2θ profile. Four sharp peaks at low angles whose d -spacing values are in the ratio of 1 : 1/ $\sqrt{3}$: 1/ $\sqrt{4}$: 1/ $\sqrt{7}$ confronting to a two-dimensional hexagonal lattice. The first diffuse peak at $2\theta \sim 20^\circ$ is from the aliphatic chains, while the fairly sharp peak at higher angles is due to the stacking of the rigid cores within a column giving a core–core separation of 3.52 Å.

100, the ratios conform to the expected values from a two-dimensional hexagonal lattice. In the wide-angle region two diffuse reflections are seen. The broad one centered at about 4.3 Å corresponds to the liquid-like order of the aliphatic chains. The relatively sharper one seen at higher 2θ -values and well separated from the broad one is due to the stacking of the molecular cores one on top of another. As this is a diffuse peak it suggests that the stacking of the discs within each column is correlated over short distances only. All the above mentioned features are characteristic of the Col_h phase.

Table 2 summarizes the different spacings extracted by fitting each of the peaks in the one-dimensional profile to a Lorentzian form. Also shown is the correlation length for the intra-columnar packing arising out of the core–core interaction. It has been calculated using the FWHM of the sharper peak in the wide angle region and the Scherrer expression.¹⁷ For the sake of comparison, we have also given the data for two hexakis-substituted triphenylenes, viz., hexakis(pentyloxy) (H5TP) and hexakis(heptyloxy) (H7TP) triphenylenes obtained at 10 °C below the clearing point. For further discussion, we will divide the compounds for which X-ray studies have been made, into two groups: the ethers and the esters.

Table 2 Transition enthalpy ΔH for the Col_h to isotropic transformation, the disc diameter d_{100} , the core–core separation and the correlation length for the intra-columnar order in seven chain compounds

Compound	$\Delta H /$ kJ mol ⁻¹	d -spacing numbers / Å			Correlation length/Å
		d_{100}	$d_{\text{core-core}}$	$d_{\text{alkyl chain}}$	
4c	6.0	19.43	3.62	4.3	95
4e	5.5	21.91	3.61	4.36	92
4k	3.6	18.56	3.71	4.28	47
5b	13.8	19.70	3.52	4.28	147
5c	9.3	23.48	3.49	4.34	189
H5TP	8.2	19.00	3.54	4.55	125
H7TP	5.0	20.87	3.55	4.48	86

a) The ethers. The five compounds which belong to this group are the two hexakis(alkoxy)triphenylenes H5TP and H7TP and their seven chain counterparts, **4c** and **4e**, and the compound **4k**, which is a mixed chain material. Comparing the inter-columnar distance or equivalently the disc diameter, we see that the heptakis(alkoxy)triphenylenes with all the seven chains identical have a larger diameter than the corresponding six chain materials. The difference in the disc diameter between the corresponding heptakis- and hexakis-compounds increases as the number of carbon atoms per alkyl chain increases. Seen in the light of the fact that the chains adopt a liquid-like arrangement, this feature means that as the number of chains attached to the triphenylene core increases, the free volume available per chain decreases and therefore the chains try to stretch more. This effect is amplified as the number of carbon atoms per chain increases. In the case of the compound **4k**, there are two long chains with 7 methylene units and five shorter chains with 4 methylene units. As in the Col_h phase, the discs have the freedom to rotate about the column axis, one should expect the disc diameter to be decided by the longest of the seven chains. But from Table 2 we see that the disc diameter is much shorter; smaller than that for even the compound **4c**, with five methylene units. This is possible if the free volume available from the neighbouring shorter chains is so large that the longer chains curl up more, thus reducing the disc diameter.

The values obtained for disc stacking distance or the separation between the molecular cores within a column are typical of those seen in other systems exhibiting a Col_h phase.^{3–5} The correlation length for the intra-columnar packing, extracted from the sharper reflection at wide angles seems to have a direct correlation with the enthalpy of the Col_h to isotropic transition. For example, H5TP has the highest transition enthalpy in this group and exhibits a correlation length of 125 Å, while the mixed chain compound **4k** with the lowest transition enthalpy shows a correlation length of only 47 Å. Thus, one can infer that the number of molecules correlated within a column is about three times more in H5TP than in the compound **4k**.

b) The esters. The two materials (**5b** and **5c**) under this group are mixed chain compounds with two chains having ester linkages and the other five ether linkages. A comparison of the results for these compounds is possible only with the all-ether linkage materials as the six chain all-ester linkage materials with similar chain length are either non liquid crystalline or exhibit only rectangular columnar phases.¹⁸ It is seen that the value of the disk diameter obtained agrees with the trend described in the previous section, *viz.*, the seven chain materials have a larger value than the six chain ones. In fact, compared to the seven chain all-ether linkage compound **4c**, compound **5b** shows a slightly larger disc diameter, a smaller core–core separation and a higher correlation length. Such features indicate a better van der Waals interaction between the cores in the mixed ester–ether chain materials than in the all-ether linkage compounds. This is somewhat surprising, as it has been reported that the intra-columnar correlation is much weaker in the ester compounds than in ether compounds.¹⁸ One possible explanation could be that in the mixed ester–ether chain compounds, the molecules are arranged in such a way that the ester groups of the neighbouring cores are staggered with respect to each other, leading to a better packing and therefore a stronger interaction.

Conclusions

We have reported the synthesis of several heptakis-substituted triphenylene derivatives by two different routes. The methodology provides an easy, high yielding process for the preparation of various unsymmetrical, low clearing tempera-

ture, broad mesophase triphenylene discotics. It can be extended to other discotic cores.

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