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Unsymmetrical alkoxy-substituted triphenylenes: the dependence of mesomorphism on molecular shape

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Several series of unsymmetrical hexa-alkoxytriphenylenes have been prepared. For almost every series a maximum in the Col_h–I clearing point is found for the most symmetrical triphenylene, i.e. when all six alkoxy chains are of equal length. A similar trend is found for the melting points (T_m), although the effect is not so pronounced. A minimum length is required for formation of a columnar mesophase (Col_{hd}). After this critical value has been reached for short alkoxy chains, much lower Col_h–I temperatures are then observed for longer chains. Ordered hexagonal columnar phases required for efficient photoluminescence and electroluminescence have been found for several asymmetrical homologues with comparable T_{Col-I} to those observed for the symmetrical homologues, but also with lower T_m. This may facilitate the preparation of mixtures of triphenylenes with the desired ordered hexagonal columnar phases with a T_{Col-I} and a T_m below room temperature.

1. Introduction

Conjugated organic polymers exhibit a range of physical properties such as electrical conductivity [1], photoconductivity [2], charge storage [3], photoluminescence [4], electroluminescence [5], non-linear optical response [6], etc. of interest for a variety of electronic and optoelectronic applications such as semiconductors, sensors, display devices, telecommunications, etc. [7]. However, such polymers suffer from serious disadvantages such as structural defects, poor solubility and processability, polydispersity, etc. In contrast, low molar mass materials and oligomers with a high degree of conjugation and a propensity to self-assembly are of increasing interest for such applications due to their monodisperse character, flexibility of synthesis, good processability as thin solid films, etc. [7, 8]. An additional advantage is the improved properties observed due to the tendency of certain classes of these organic materials to self-organize in a supramolecular structure on the desired substrate surface [7, 8]. A serious drawback associated with some low molar mass materials and to a lesser extent oligomers is the tendency to form major defects due to crystallization.

However, further improvements over the whole physical property spectrum and especially conductivity could be expected if the one-dimensionality of these generally amorphous or partially ordered films could be extended to two dimensions with an increase in order and homogeneity in an organized structure, while avoiding crystal formation. Hence, columnar (discotic) liquid crystals with an aromatic central core [9–20], as opposed to an alicyclic core [21, 22], are of significant interest for such applications, especially as fast photoconductors for Xerography and laser printing applications [23–25]. Columnar liquid crystals generally consist of disc-shaped molecules or self-assembled aggregates organized in a supramolecular structure of nearly parallel columns of varying degrees of order in a two-dimensional lattice [9–11]. In the related nematic discotic phase formed by similar or even the same compounds at higher temperatures there is no regular columnar structure [9–20]. In columnar mesophases the molecular cores are organized above each other in columns separated by the peripheral aliphatic chains. Therefore, the intercolumnar distance (≈ 15–$40\,\text{Å}$) is much greater than the intracolumnar distance ($< 4 \cdot 5\,\text{Å}$) depending to some extent on the length and degree of conformational mobility of the aliphatic chains. The classification depends on the degree and type of order in the lattice (columnar hexagonal, Col_h; rectangular, Col_t; oblique, Col_{ob}, which are either ordered, e.g. Col_{ho} or disordered, e.g. Col_{hd}) [17–20]. The nature of columnar phases (especially those with hexagonal symmetry, Col_h), in which the aromatic cores of the molecules are arranged above each other in columns, allows exiton energy migration due to the overlap of the π-electron orbitals in the conjugated aromatic cores of neighbouring molecules [25].
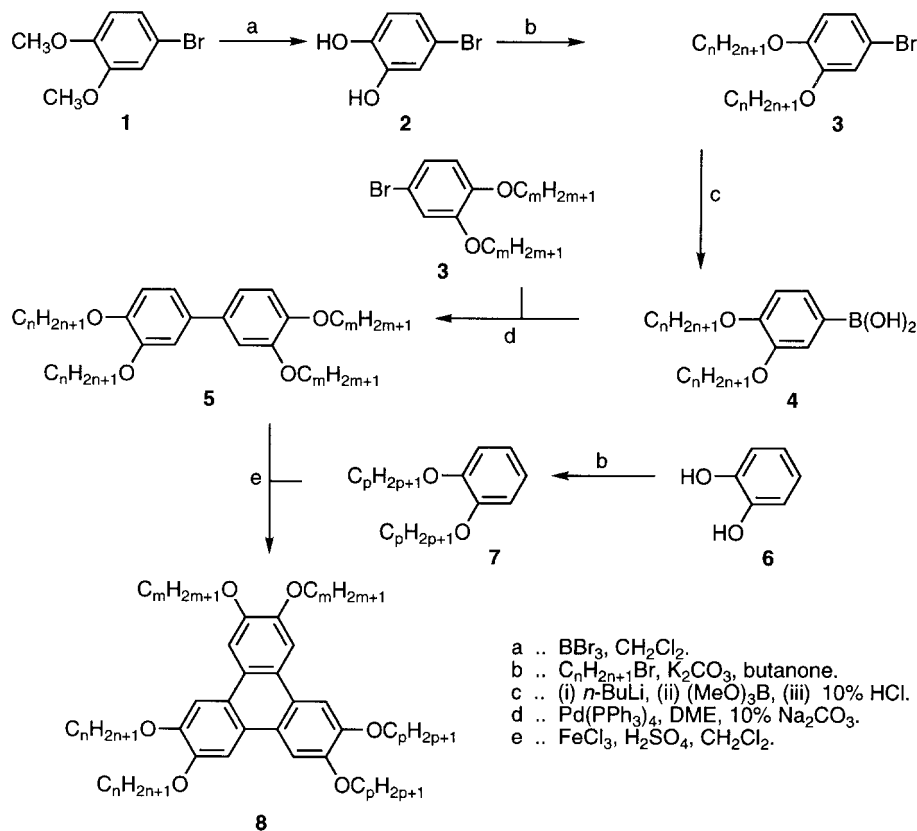
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It was recently discovered that triphenylenes [7, 26–31] and phthalocyanines [32] could exhibit large charge mobility in the pure, undoped state. The values obtained (e.g. for hexakis(*n*-alkoxy)triphenylenes and hexakis(*n*-alkylthio)triphenylenes [24, 31]) for the exiton mobility ($10^{-1} > \mu > 10^{-3}$ cm^2 V^{-1} s^{-1}) are intermediate between those observed for organic single crystals and inorganic semiconductors ($\mu \approx 1$ cm^2 V^{-1} s^{-1}) and those ($10^{-3} > \mu > 10^{-6}$ cm^2 V^{-1} s^{-1}) of amorphous polymers, e.g. poly(*N*-vinylcarbazole), PVK, used in commercial Xerography and laser-printer applications [2, 26–32]. The charge carrier mobility of such materials organized in self-assembled columnar liquid crystal phases renders them also of potential interest as organic semiconductors, e.g. in transistors [7], light-emitting diodes [7], photovoltaic cells [33], and optical data storage [34, 35]. Most of the compounds exhibiting columnar phases investigated for these applications have been triphenylene derivatives due to their high tendency to form the required columnar phases and the presence of the large conjugated aromatic molecular core with a large delocalized π-electron system. Standard methods [36] have now been replaced by more efficient methods of synthesis, which also allow unsymmetrical triphenylenes to be synthesized [36–40].

The materials prepared during the course of this work are currently being evaluated for photoconductor and light-emitting-polymer applications. This requires triphenylenes with a low melting point and a high clearing point so that mixtures with ordered hexagonal columnar phases with a high order parameter can be prepared and then evaluated at room temperature in order to facilitate the performance of physical measurements.

2. Synthesis

The unsymmetrical triphenylenes (**8**) were synthesized as described previously [40] (see the reaction scheme). Thus 4-bromoveratrole (1-bromo-3,4-dimethoxybenzene) (**1**) was demethylated to yield 1-bromo-3,4-dihydroxybenzene (**2**), which was then *O*-alkylated to produce the appropriate 1-bromo-3,4-*n*-dialkoxybenzenes (**3**) with various alkyl chains ($n = 4, 6, 8, 10, 12$). Compound (**3**) was then converted into the corresponding 3,4-di-*n*-alkoxyphenylboronic acid (**4**). A palladium-catalysed aryl–aryl cross-coupling reaction between the boronic acid (**4**) and the bromide (**3**) with various alkoxy chains provided a wide range of symmetrically and unsymmetrically substituted 3,4,3′,4′-tetraalkoxybiphenyls (**5**; $n, m = 4, 6, 8, 10, 12$; $n < m$). Reaction of the 1,2-di-*n*-alkoxybenzene (**7**; $p = 4, 6, 8, 10, 12$), produced from

a .. BBr$_3$, CH$_2$Cl$_2$.
b .. C$_n$H$_{2n+1}$Br, K$_2$CO$_3$, butanone.
c .. (i) *n*-BuLi, (ii) (MeO)$_3$B, (iii) 10% HCl.
d .. Pd(PPh$_3$)$_4$, DME, 10% Na$_2$CO$_3$.
e .. FeCl$_3$, H$_2$SO$_4$, CH$_2$Cl$_2$.

Scheme.

commercially available 1,2-dihydroxybenzene (**6**), with biphenyls (**5**; n, $m = 4$, 6, 8, 10, 12; $n < m$) [38, 40] selectively yielded the desired unsymmetrical 2,3,6,7,10,11-hexa-n-alkoxytriphenylenes (**8**; n, m, $p = 4$, 6, 8, 10, 12; $n < m < p$).

3. Phase characterization

3.1. *Phase characterization by thermal optical microscopy*

The observable mesophases of the unsymmetrical triphenylenes prepared in this work appear to be of the same columnar type and exhibit similar optical behaviour during optical microscopy. This hexagonal columnar phase (Col$_h$) is the same as that reported for symmetrical triphenylenes [41]. Birefringent dendrites or platelets are observed just below the clearing point on cooling from the isotropic liquid, see figure 1. These coalesce slowly in the bulk to form a homogeneous mosaic texture, see figure 2. These textures are typical of a hexatic columnar phase (Col$_{hd}$ or Col$_{ho}$). It is difficult to determine by optical microscopy whether the hexagonal phase observed is disordered or ordered, see § 3.2. However, this birefringent texture indicates that inhomogeneous domains of columns with hexagonal order were formed spontaneously, wherein the columnar axes were at a non-zero angle to the substrate normal or plane. X-ray studies are currently being carried out in order to determine the exact nature of the mesophase of the compounds prepared in this study. The observed hexagonal columnar mesophase is a viscous liquid which can be easily sheared between a microscope slide and a glass cover slip. On further cooling a non-shearable glass was formed or the sample recrystallized to form a solid (see § 3.2).

3.2. *Phase characterization by differential scanning calorimetry*

A typical heating thermogram for the 2,3,6,7,10,11-hexakis(alkoxy)triphenylenes (**8**) is shown in figure 3 for 2,3-didecyloxy-6,7,10,11-tetrahexyloxytriphenylene (**8**; $n = 10$; $m = p = 6$). It is clear from the enthalpy of the transitions (46·8 J g^{-1} and 2·2 J g^{-1}, respectively) for T_m and T_{Col-I} that both phase transitions are first order. A significant degree of supercooling at T_{Col-I} and below T_m can be observed. However, the peaks for the phase transitions are relatively sharp for columnar liquid crystals, indicating a high degree of purity for the materials (confirmed by the ^{1}H NMR data and HPLC). The clearing point enthalpies are relatively small in comparison with the melting enthalpies and the values measured are of a similar magnitude to those found for conventional liquid crystal systems which exhibit columnar to isotropic liquid transitions. The degree of supercooling observed for T_{Col-I} is not significant

compared with that found for T_m. These two factors indicate that the columnar phase observed for this compound is hexagonal disordered. There is no tendency for decomposition during the heating and cooling cycles, which are reproducible as shown in figure 4 for 2,3-dibutyloxy-6,7,10,11-tetradecyloxytriphenylene (**8**; $n = 4$; $m = p = 10$). However, the high enthalpy values observed for this homologue and the substantial degree of supercooling for T_m and T_{Col-I} indicate the presence of an ordered hexagonal columnar phase. These results will be verified by miscibility studies with standard triphenylenes of known morphology [38] as well as X-ray studies.

4. Discussion of the transition temperatures

The transition temperatures collated in table 1 for the unsymmetrical 2,3-di-n-alkoxy-6,7,10,11-tetramethoxy-triphenylenes (**8**; $n = 1$, 5, 6, 10, 12; $m = p = 1$) show clearly that a minimum chain length for all three alkoxy chains is required for columnar mesophase formation. Even though two of the chains can be long ($n = 12$), the methoxy chains at the other four positions are obviously too short. The melting points of the corresponding symmetrical hexakis(n-alkoxy)triphenylenes (**8**; $n = m = p = 1$–13) [17–20] decrease significantly from very high values for short chains ($n = m = p = 1$–3) as the length of the alkoxy chains increases. Therefore, it is impossible to state whether the three first members (**8**; $n = m = p = 1$–3) of the series of symmetrical triphenylenes exhibit monotropic mesomorphism or not. However, the next member of the series (**8**; $n = m = p = 4$) exhibits the highest observed clearing point of the series. The clearing point (Col$_{hd}$–I) then decreases regularly with increasing chain length. This suggests that chains of a minimum length are required to dilute the core-to-core interactions and introduce enough flexibility

Table 1. Transition temperatures (°C) for 2,3-di-n-alkyloxy-6,7,10,11-tetramethoxytriphenylenes (**8**; $n = 1$, 5, 6, 10, 12; $m = p = 1$).
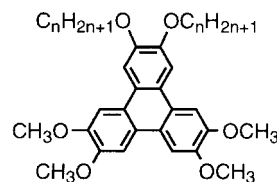
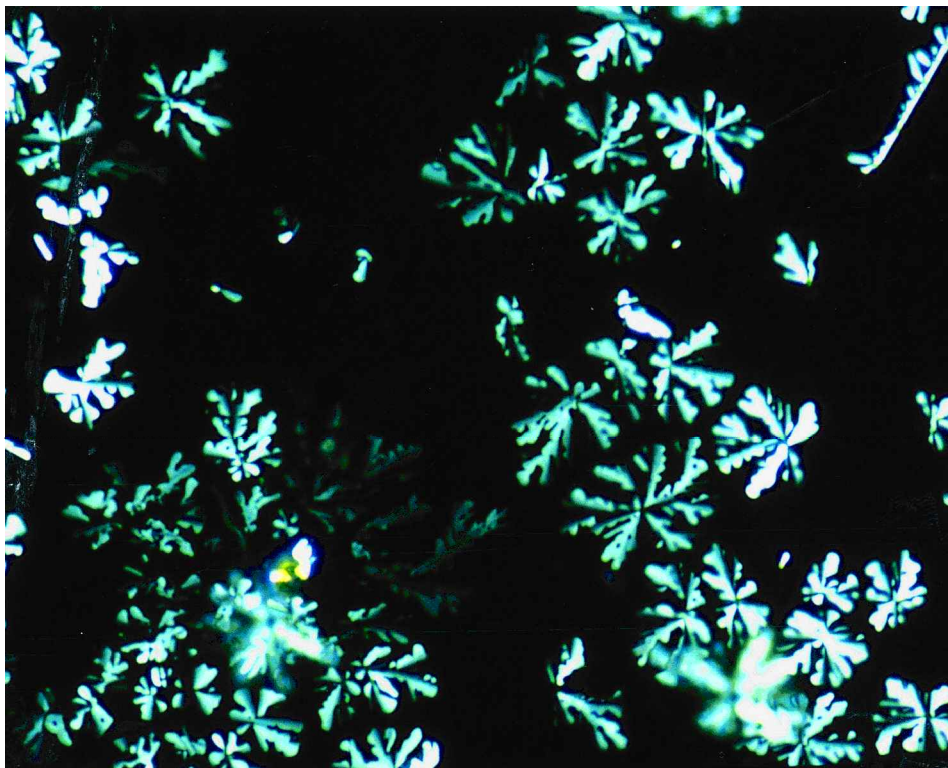| n	Cr		I	Reference
1	•	317	•	[17, 18]
5	•	80	•	
6	•	142·5	•	
10	•	74	•	
12	•	125	•	

Figure 1.   The dendrite or platelet texture of 2,3-dibutyloxy-6,7,10,11-tetradecyloxytriphenylene (**8**; $n = 4$; $m = 10$; $p = 10$) at 60°C, just below the clearing point, on a glass substrate ($\times 160$).
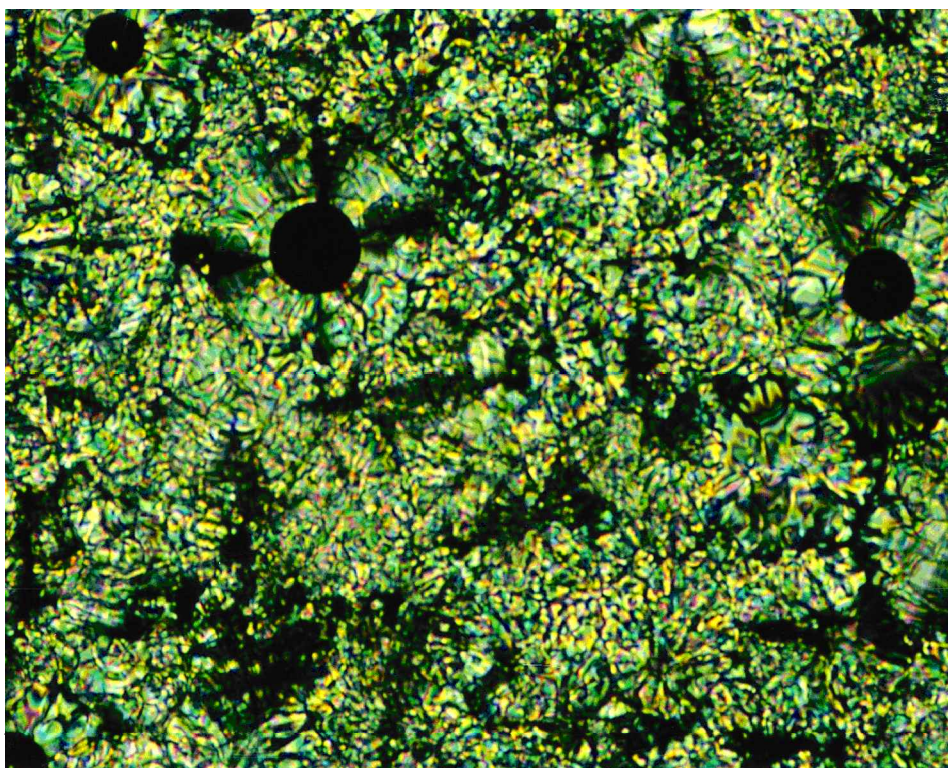
Figure 2.   The mosaic defect texture of 2,3-dibutyloxy-6,7,10,11-tetradecyloxytriphenylene (**8**; $n = 4$; $m = p = 10$) at 50°C on a glass substrate ($\times 160$).
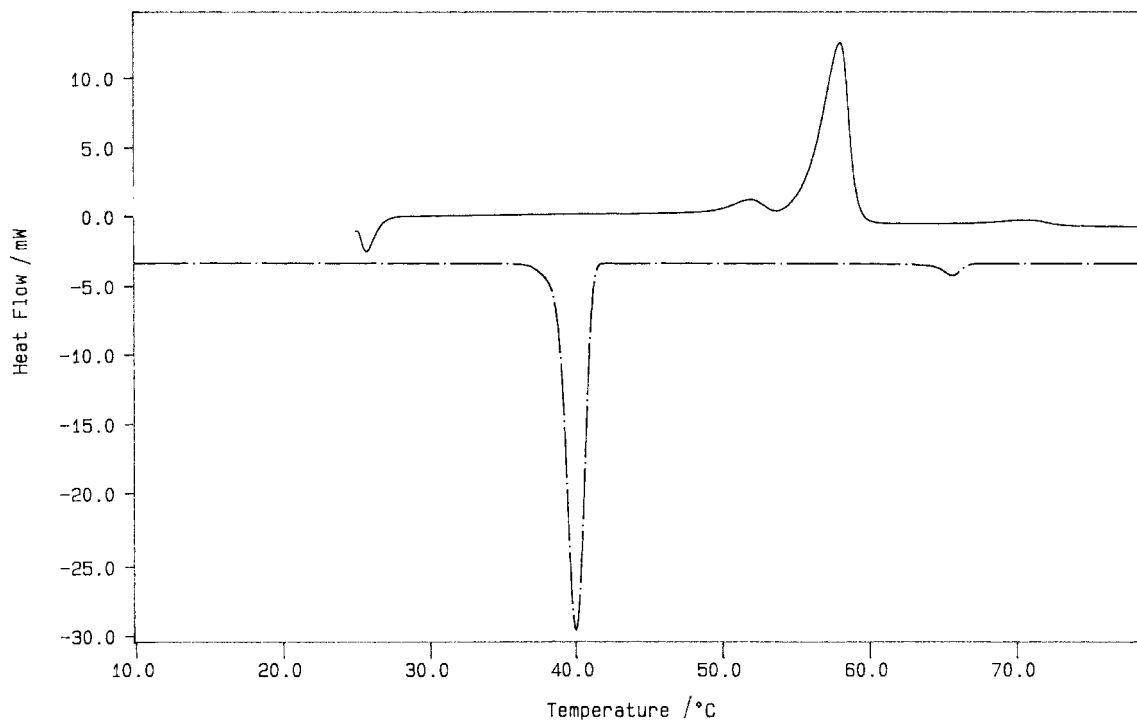
Figure 3. Differential scanning thermogram as a function of temperature for the first heating cycle for 2,3-didecyloxy-6,7,10,11-tetrahexyloxytriphenylene (**8**; $n = 10$; $m = p = 6$) scan rate 10°C min^{-1}.

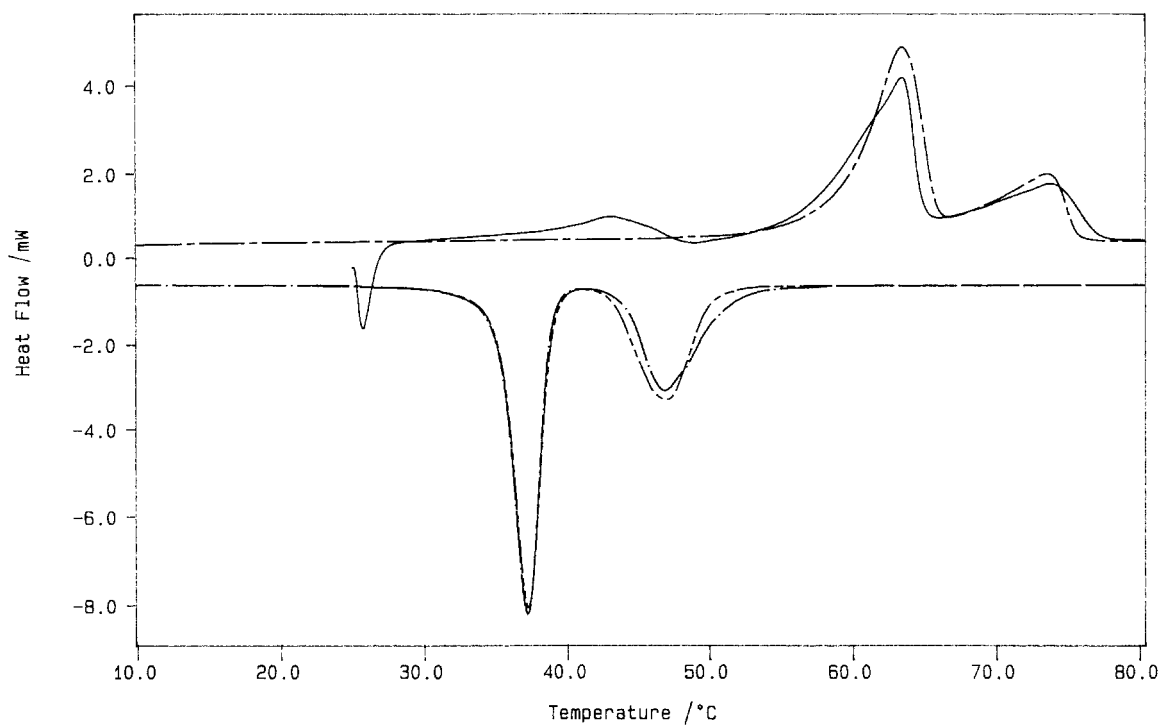Figure 4. Differential scanning thermogram as a function of temperature for the first and second heating and cooling cycles for 2,3-dibutyloxy-6,7,10,11-tetradecyloxytriphenylene (**8**; $n = 4$; $m = p = 10$) scan rate 10°C min^{-1}.

and conformational mobility into the molecular core to reduce intermolecular interactions sufficiently for formation of a columnar mesophase (Col_{hd}). However, after this critical value has been reached for short alkoxy chains ($n = m = p \leqslant 4$) this additional flexibility and the adoption of non-linear conformations of longer alkoxy chains lead to much lower Col_h–I temperatures as the number of possible non-linear conformations increases with chain length. It also becomes increasingly difficult to fill space efficiently as the breadth of the discs increases and the tendency to adopt a more spherical shape also increases.

These conclusions are reinforced by consideration of the data recorded in tables 2–5, where again four alkoxy chains are kept constant within a series as the two other chains increase in length. However, the length of the four chains of fixed length for each series of compounds collated in tables 2–5 is increased progressively from
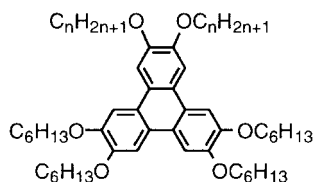
Table 2. Transition temperatures (°C) for 2,3-di-*n*-alkyloxy-6,7,10,11-tetrapentyloxytriphenylenes (**8**; $n = 1, 5, 9, 10, 11$; $m = p = 5$).
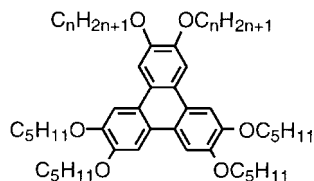
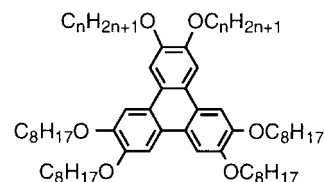| n	Cr		Col_h		I	Reference
1	•	80		—	•	
5	•	69	•	122	•	[17, 18]
9	•	54	•	74	•	
10	•	57	•	56[a]	•	
11	•	61		—	•	

[a] Monotropic transition.

Table 3. Transition temperatures (°C) for 2,3-di-*n*-alkyloxy-6,7,10,11-tetrahexyloxytriphenylenes (**8**; $n = 4, 6, 8, 10, 12$; $m = p = 6$).
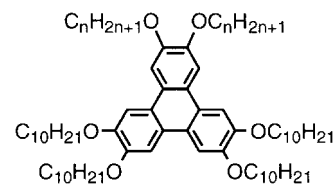

n	Cr		Col_h		I	Reference
4	•	59	•	90	•	
6	•	68	•	97	•	[17, 18]
8	•	47	•	84	•	
10	•	58	•	74	•	
12	•	64		—	•	

Table 4. Transition temperatures (°C) for 2,3-di-*n*-alkyloxy-6,7,10,11-tetraoctyloxytriphenylenes (**8**; $n = 4, 6, 8, 10, 12$; $m = p = 8$).

n	Cr		Col_h		I	Reference
4	•	60	•	67	•	
6	•	46	•	84	•	
8	•	67	•	86	•	[17, 18]
10	•	48	•	73	•	
12	•	51	•	61	•	

Table 5. Transition temperatures (°C) for 2,3-di-*n*-alkyloxy-6,7,10,11-tetradecyloxytriphenylenes (**8**; $n = 4, 5, 6, 10, 12$; $m = p = 10$).

n	Cr		Col_h		I	Reference
4	•	65	•	76	•	
5	•	61	•	63	•	[18]
6	•	44	•	72	•	
8	•	60	•	86	•	
10	•	58	•	69	•	[17, 18]
12	•	41	•	62	•	

table to table. A maximum in the Col_h–I temperature for almost every series is found for the symmetrical triphenylene, i.e. when all six alkoxy chains are of equal length (see figure 5). The Col_h–I temperature decreases on either side of this maximum with increasing or decreasing chain length. This shows clearly that an asymmetrical molecular shape is disadvantageous for columnar mesophase formation. The only exception is found in table 5, where three asymmetrical homologues possess a higher Col_h–I temperature than that of the symmetrical product. This casts some doubt on the literature value [17, 18] for the latter homologue. A similar trend is found for T_m, although the effect is not quite so regular as that for the Col_h–I transitions. The highest temperature for Col_h–I is found for relatively short *n*-alkoxy chains ($n = 5$ or 6), see tables 2 and 3. For longer alkoxy chains ($n = 8, 10$ and 12) a maximum Col_h–I temperature of 84–86°C is reached. There is a greater tendency for asymmetric triphenylenes with short
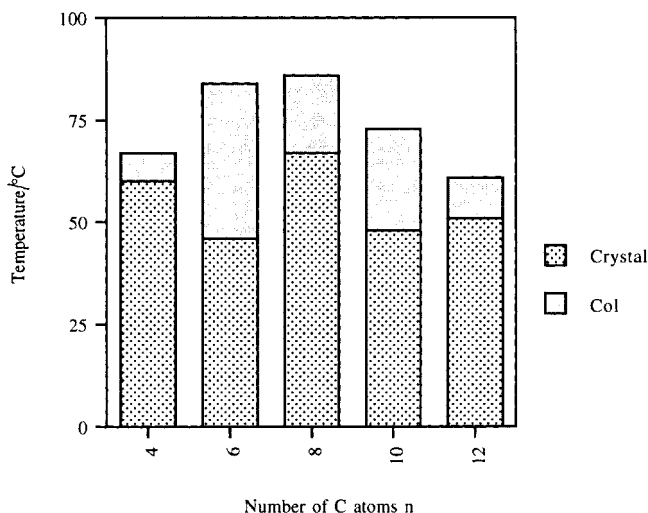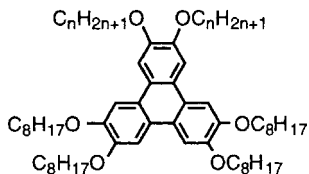
Figure 5. Plot of the liquid crystal transition temperatures against the number of carbon atoms (n) in the di-n-alkoxy chains of 2,3-di-n-alkoxy-6,7,10,11-tetraoctyloxytriphenylene ($\mathbf{8}$; $n = 4, 6, 8, 10, 12$; $m = p = 8$).

alkoxy chains to be non-mesomorphic (see tables 2 and 3).

When the three pairs of alkoxy chains are of different lengths maxima Col_h–I temperature and T_m are found for those members of the series where the chain lengths are most similar (see tables 6 and 7). The dependence of the Col_h–I temperature on chain length appears less
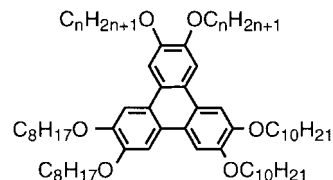
Table 6. Transition temperatures (°C) for 2,3-di-n-alkyloxy-6,7-dihexyloxy-10,11-dioctyloxytriphenylenes ($\mathbf{8}$; $n = 4, 6, 8, 10, 12$; $m = 6$; $p = 18$).
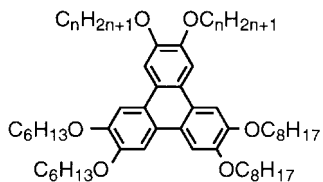
n	Cr		Col_h		I	Reference
4	•	48	•	72	•	
6	•	47	•	84	•	[18]
8	•	46	•	84	•	
10	•	47	•	75	•	
12	•	39	•	75	•	

Table 7. Transition temperatures (°C) for 2,3-di-n-alkyloxy-6,7-dioctyloxy-10,11-didecyloxytriphenylenes ($\mathbf{8}$; $n = 4, 6, 8, 10, 12$; $m = 8$; $p = 10$).

n	Cr		Col_h		I
4	•	36	•	46	•
6	•	48	•	75	•
8	•	54	•	78	•
10	•	60	•	86	•
12	•	47	•	65	•

sensitive when all three chains are different, but not too dissimilar (see tables 6 and 7). When all three chains are of quite dissimilar lengths no mesomorphism is observed, even when each of the chains is relatively long (e.g. $\mathbf{8}$; $n = m = 6$; $p = 12$) (see table 8). This is consistent with the trends observed for the other series studied.

5. Experimental
5.1. *Characterization*

The structure of each intermediate and final product was determined by ^{1}H NMR spectroscopy (JEOL JNM-GX 270 spectrometer; tetramethylsilane was used as the internal standard), mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer) and infrared spectroscopy (Perkin Elmer 457 grating spectrophotometer

Table 8. Transition temperatures (°C) for 2,3-di-n-alkyloxy-6,7-di-n-alkyloxy-10,11-didodecyloxytriphenylenes ($\mathbf{8}$; $n = 1, 4, 6, 8, 10$; $m = 1, 4, 6, 8, 10$; $p = 12$).
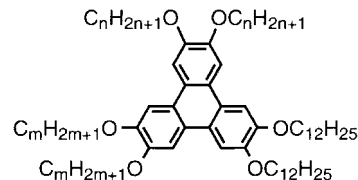
n	m	Cr		Col_h		I
1	1	•	125	—		•
1	4	•	88	—		•
4	4	•	79	—		•
4	8	•	52	—		•
6	6	•	64	—		•
6	8	•	39	•	75	•
6	10	•	43	•	51	•
8	10	•	47	•	65	•
10	10	•	41	•	62	•

or a Perkin-Elmer 1000 Fourier Transform FTIR spectrometer).

The purity of the compounds was determined by thin layer chromatography (TLC), high performance liquid chromatography (HPLC), gas chromatography (GC; Chrompack CP9001 gas chromatograph fitted with a 10 m CP-SIL 5CB/BP-1.0 column) and differential scanning calorimetry (DSC; Perkin Elmer DSC 7 PC system operating on 7 series/UNIX software). Aluminium backed precoated silica gel TLC plates (60 F254 Merck, Darmstadt, Germany) were utilized.

Column chromatography was carried out using silica gel 60 (230–400 mesh ASTM). Reaction solvents and liquid reagents were purified by drying or distillation shortly before use. Reactions were carried out under N_2.

Mesophase identification and the determination of transition temperatures of the ethers prepared were carried out by optical microscopy using either a Zeiss Universal or a Olympus BH-2 polarizing light microscope in conjunction with a Mettler FP 52 microfurnace and FP 5 Central Processor. Photomicrographs were obtained using a Nikon POH polarizing light microscope equipped with a Nikon AFM camera. The glass microscope slides were not buffed, as is usual for preparing aligned samples, but were used untreated so that many defects would be created when the liquid crystal formed on the surface of the slide on cooling from the liquid phase.

DSC was used to determine enthalpies of transition and to confirm the phase transition temperatures determined by optical microscopy. Differential scanning thermograms (scan rate $10°$ min^{-1}) were obtained and the results standardized with respect to indium (measured onset $156·68°C$, ΔH $28·47$ J g^{-1}, literature value $156·60°C$, ΔH $28·45$ J g^{-1}), nitrotoluene (measured onset $51·17°C$, ΔH $118·49$ J g^{-1}, literature value $51·63°C$, ΔH $122·58$ J g^{-1}) and benzil (measured onset $94·42°C$, ΔH $108·52$ J g^{-1}, literature value $94·87°C$, ΔH $92·68$ J g^{-1}).

Comparison of the transition temperatures determined by optical microscopy and DSC showed some discrepancies—up to about $3°C$ in some cases. This is due to two factors; firstly, the two methods used separate instruments which are calibrated in different ways, and secondly, and more importantly, columnar transitions are generally broad and typically exhibit a high degree of supercooling depending on the rate of cooling. This is most probably due to the high viscosity of the hexagonal columnar mesophase and the geometrical shape and size of discogens.

5.2. *Compound preparation*

5.2.1. *1-Bromo-3,4-dihydroxybenzene* (**2**)

A solution of boron tribromide (18 cm^3, $0·635$ mol) in dichloromethane (150 cm^3) was added to a solution of 1-bromo-3,4-dimethoxybenzene (4-bromoveratrole) ($45·93$ g, $0·212$ mol) in dichloromethane (150 cm^3) at $-80°C$. After the addition was complete the reaction mixture was allowed to warm to room temperature overnight with stirring. Water (100 cm^3) was added slowly to the reaction mixture followed by 36% aqueous hydrochloric acid ($pH < 4$). The reaction mixture was stirred until TLC showed that reaction was complete; the precipitated product was then filtered off and washed with dichloromethane. The aqueous layer was shaken with diethyl ether (3×300 cm^3). The combined organic layers were dried ($MgSO_4$) and then evaporated down to yield $40·0$ g (100%) of a pink solid with a purity (GC) of $95·3$%. ^{1}H NMR δ_H (270 MHz, DMSO): $9·0$–$8·0$ (2H, s, OH, hydrogen bonding), $6·88$–$6·68$ (3H, m, C_6H_3). IR (KBr) v_{max} cm^{-1}: 3420 (OH–, intramolec bonded OH, str), 3355 (OH–, intermolec bonded OH, str), 1608, 1594, 1494 (C=C, in-plane, str), 1440 (CH_3, CH_2, C–H def), 1380 (OH–, O–H bending), 1270, 1234 (Aryl–O asym str), 1178, 1110 (C–OH str), 888, 852, 802, 780, 770 (C–H, out-of-plane, bend), 638, 530 (C–Br, str). Ms *m/z*: 190 (M^+, 100%), 188 (M^+, 100%), 109, 81, 63, 43.

5.2.2. *1-Bromo-3,4-dihexyloxybenzene* (**3**; *m* = 6)

1-Bromohexane ($3·11$ g, $0·019$ mol) was added dropwise to a mixture of 1-bromo-3,4-dihydroxybenzene (**2**) ($0·89$ g, $0·0047$ mol), potassium carbonate ($6·51$ g, $0·047$ mol) and 2-butanone (50 cm^3) and the resultant mixture was heated under reflux for 24 h. The inorganic material was filtered off and the reaction mixture allowed to cool, poured into water (50 cm^3) and then shaken with diethyl ether (2×50 cm^3). The combined organic layers were dried ($MgSO_4$), filtered and then evaporated down. The resultant product was purified by column chromatography on silica gel with a 1 : 1 mixture of petroleum fraction (b.p. 40–$60°C$) and dichloromethane as eluent to yield $1·63$ g (97·0%) of a brown liquid with a purity (GC) of 96·96%. ^{1}H NMR δ_H (270 MHz, $CDCl_3$, Me_4Si): $7·0$ (2H, m, ArH), $6·75$ (1H, m, ArH), $3·96$ (4H, sex. $J = 6·75$ Hz, $ArOCH_2$), $1·8$ (4H, m, OCH_2CH_2 or $OCH_2CH_2CH_2CH_2$), $1·5$–$1·35$ (15H, m, CH_3 $(CH_2)_5$ and CH_2), $0·9$ (7H, m, CH_3 and CH_2CH_2). IR (film) v_{max} cm^{-1}: 2950 (CH_3, C–H asym str), 2935 (CH_2, C–H asym, str), 2860 (CH_2, C–H sym str), 1582, 1495 (C=C in-plane, str), 1460 (CH_3, C–H asym, bend), 1385 (CH_3, C–H sym, bend), 1248, 1218 (Aryl–O, asym, str), 1130 (Alkyl–O str), 940 (C–H, bend), 875, 835, 795 (trisub-, C–H, out-of-plane, bend), 725 (CH_2, rocking), 640, 578 (C–Br, str). Ms *m/z*: 358 (M^+), 356 (M^+), 274, 272, 190 (100%), 188 (100%), 85, 79, 69.

5.2.3. *3,4-Dihexyloxyphenylboronic acid* (**4**; *n* = 6)

A $2·5$M solution of *n*-butyllithium in hexane (2 cm^3, $0·0042$ mol) was added dropwise to a stirred solution

of 1-bromo-3,4-dihexyloxybenzene (**3**; $n = 6$) (1·5 g, 0·0042 mol) in tetrahydrofuran (40 cm^3) at $-78°$C. The reaction mixture was maintained at this temperature for 1 h (GC analysis confirmed complete reaction) before a previously cooled (0°C) solution of trimethyl borate (0·87 g, 0·0084 mol) in tetrahydrofuran (5 cm^3) was syringed into the reaction flask slowly at $-78°$C. The reaction mixture was allowed to warm to room temperature overnight, stirred for 1 h with 10% aqueous hydrochloric acid (50 cm^3), and then shaken with diethyl ether (2 × 100 cm^3). The combined organic layers were dried (MgSO$_4$), filtered and then evaporated. The resultant product was purified by column chromatography on silica gel with a 1:1 mixture of diethyl ether and petroleum ether (b.p. 40–60°C) as eluent to yield 0·55 g (47%) of a white solid with a purity (GC) of 94·5%. ^{1}H NMR δ_H (270 MHz, DMSO-d$_6$): 7·84 (2H, s, B(OH)$_2$), 7·35 (2H, m, ArH), 6·90 (1H, d, $J = 8·10$ Hz, ArH), 3·93 (4H, q, $J = 5·40$, CH$_2$OAr), 1·69 (4H, qn, $J = 6·82$, CH$_2$CH$_2$O), 1·43–1·30 (14H, m, C$_4$H$_8$ and C$_3$H$_6$), 0·87 (6H, m, CH$_3$). IR (KBr) v_{max} cm^{-1}: 3700–3080 (bonded, O–H, str), 2950 (CH$_2$, C–H asym str), 2910, 2855 (CH$_2$, C–H sym, str), 1590, 1514 (C=C, in-plane, str), 1464 (CH$_3$, C–H asym, bend; CH$_2$, C–H, bend), 1374, 1340 (B–O, str), 1255, 1230 (Aryl–O, asym, str), 1142, 1118, 1070 (Alkyl–O, sym, str), 1042 (Aryl–O, sym, str), 868, 822, 810, 795, 740, 728, 680 (trisub-, C–H, out-of-plane, bend). Ms m/z: 322 (M$^+$), 277, 194, 121, 110 (100%), 91, 85, 77, 69, 55, 43.

5.2.4. *3,4,3′,4′-Tetrahexyloxybiphenyl (5; n = m = 6)*

A mixture of 3,4-dihexyloxyphenylboronic acid (**4**; $n = 6$) (0·5 g, 0·0048 mol) in dimethyl sulphoxide (DMSO) (20 cm^3) was added to a stirred mixture of 1-bromo-3,4-dihexyloxybenzene (**3**; $m = 6$) (1·48 g, 0·0041 mol) and tetrakis(triphenylphosphine)palladium (0) (0·19 g, 0·16 mmol) in DMSO (30 cm^3) and 2M aqueous sodium carbonate (30 cm^3) at room temperature. The stirred mixture was heated under reflux until GC/TLC analysis revealed complete reaction (48 h). The reaction mixture was allowed to cool to room temperature, poured into water and then shaken with diethyl ether (2 × 50 cm^3). The combined ethereal extracts were washed with brine (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated. The resultant product was purified by column chromatography on silica gel using dichloromethane as eluent and by recrystallization from a 1:1 mixture of dichloromethane and methanol to yield 0·83 g (36·1%) of a white waxy solid. ^{1}H NMR δ_H (270 MHz, CDCl$_3$, Me$_4$Si): 7·1 (2H, m, ArH), 6·92 (1H, m, ArH), 4·04 (4H, m, CH$_2$OAr), 1·83 (4H, m, CH$_2$CH$_2$O), 1·49–1·35 (12H, m, C$_3$H$_6$), 0·92 (6H, m, CH$_3$). IR (KBr) v_{max} cm^{-1}: 2950, 2925 (CH$_2$, C–H asym str), 2870, 2855 (CH$_2$, C–H sym, str), 1595, 1570, 1505 (C=C, in-plane,

str), 1460 (CH$_3$, C–H asym, bend; CH$_2$, C–H, bend), 1385 (CH$_3$, C–H, sym, bend), 1254, 1218 (Aryl–O, asym, str), 1140 (Alkyl–O, sym, str), 1064, 1055, 1040 (Aryl–O, sym, str), 840, 795, 721 (trisub-, C–H, out-of-plane, bend). Ms m/z: 554 (M$^+$), 554 (100%), 470, 385, 301, 217, 188, 83, 55.

5.2.5. *1,2-Didecyloxybenzene (7; n = 10)*

This compound was prepared and purified in a similar way to that described for the 1-bromo-3,4-dihexyloxybenzene (**3**; $n = 6$) using commercially available 1,2-dihydroxybenzene (catechol) (**6**) (2·82 g, 0·026 mol), 1-bromodecane (22·65 g, 0·102 mol), potassium carbonate (35·4 g, 0·256 mol) and 2-butanone (150 cm^3) to yield 8·7 g (87%) of a white solid with a purity (GC) of 99·3%. ^{1}H NMR δ_H (270 MHz, CDCl$_3$, Me$_4$Si): 6·88 (4H, s, ArH), 3·99 (4H, t, $J = 6·75$ Hz, ArOCH$_2$), 1·81 (4H, m, OCH$_2$CH$_2$), 1·47–1·28 (28H, m, C$_7$H$_{14}$), 0·89 (6H, m, CH$_3$). IR (KBr) v_{max} cm^{-1}: 2955 (CH$_3$, C–H asym str), 2920 (CH$_2$, C–H asym, str), 1586, 1500 (C=C, in-plane, str), 1470 (CH$_3$, C–H asym, bend; CH$_2$, C–H bend), 1390 (CH$_3$, C–H sym, bend), 1255, 1222 (Aryl–O, asym, str), 1130, 1120 (Alkyl–O, str), 1050, 1030, 1020 (Aryl–O, sym, str), 740, 730 (disub-, C–H, out-of-plane, bend). Ms m/z: 390 (M$^+$), 110 (100%), 55.

5.2.6. *2,3-Didecyloxy-6,7,10,11-tetrahexyloxytriphenylene (8; n = m = 6; p = 10)*

A mixture of iron(III) chloride (1·76 g, 0·01 mol) and dichloromethane (20 cm^3) was added rapidly to a mixture of 1,2-didecyloxybenzene (**7**; $p = 10$) (1·41 g, 0·0036 mol), 3,4,3′,4′-tetrahexyloxybenzene (**5**; $n = m = 6$) (0·4 g, 0·0007 mol) and dichloromethane (20 cm^3). The resultant mixture was stirred for 2 h and then poured carefully into methanol (100 cm^3). The resultant precipitate was filtered off, washed with methanol, sucked dry and then purified by column chromatography on silica gel using a 2:1 mixture of petroleum ether (b.p. 40–60°C) and dichloromethane as eluent and by recrystallization from a 2:1 mixture of methanol and dichloromethane to yield 0·3 g (44·1%) of a light pink solid. ^{1}H NMR δ_H (270 MHz, CDCl$_3$, Me$_4$Si): 7·83 (1H, s, ArH), 4·23 (2H, t, $J = 6·75$ Hz, CH$_2$OAr), 1·94 (2H, qn, $J = 8·10$ Hz, CH$_2$CH$_2$O), 1·34–1·57 (16H, m, C$_3$H$_6$ and C$_5$H$_{10}$), 0·9 (3H, m, CH$_3$). IR (KBr) v_{max} cm^{-1}: 2950 (CH$_3$, C–H asym str), 2918 (CH$_3$, C–H sym, str), 2850 (CH$_2$, C–H sym, str), 1610, 1512 (C=C in-plane, str), 1460 (CH$_3$, C–H asym, bend; CH$_2$, C–H bend), 1430 (CH$_3$, CH$_2$, C–H def), 1380 (CH$_3$, C–H sym, bend), 1258 (Aryl–O asym str), 1170 (Alkyl–O str), 1068, 1048, 1030 (Aryl–O sym str), 838 (C–H out-of-plane bend). The unsymmetrical triphenylenes (**8**) collated in the tables 1–8 were prepared analogously.

6. Conclusions

A maximum in the Col$_h$–I transition temperatures for almost every series is found for the most symmetrical triphenylene of each series studied when all six alkoxy chains are of equal length. The Col$_h$–I temperature decreases on either side of this maximum with changing chain length. This shows that an asymmetrical molecular shape is disadvantageous for columnar mesophase formation. A similar trend is found for T_m, although the effect is not quite so pronounced. A minimum length is required for formation of a columnar mesophase (Col$_{hd}$). After this critical value has been reached for short alkoxy chains the adoption of non-linear conformations of longer alkoxy chains and the increasing difficulty of filling space efficiently leads to much lower Col$_h$–I temperatures. Ordered hexagonal columnar phases required for efficient photoluminescence and electroluminescence have been observed for several asymmetrical homologues with Col$_h$–I temperatures comparable to those observed for the symmetrical homologues, but which melt at lower temperatures. This may be of advantage for the preparation of mixtures of triphenylenes with ordered hexagonal columnar phases with a high clearing point and a melting point below room temperature.

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