

Microwave-assisted facile synthesis of liquid crystalline non-symmetrical hexaalkoxytriphenylenes containing a branched chain and their characterization

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Two novel series of liquid crystalline non-symmetrical hexaalkoxytriphenylenes containing a branched alkyl chain have been prepared using microwave dielectric heating. Series 1 contains 2-ethyl hexyloxy group as the branched chain whereas series 2 contains 3,7-dimethyl octyloxy as the branched chain along with five normal alkoxy chains. The number of carbon atoms varies from four to eight in the normal alkoxy chains. Mesophase behaviour of the compounds has been characterized by polarizing optical microscopy, differential scanning calorimetry and mesophase structure has been characterized by X-ray diffractometry. All the compounds show enantiotropic mesophase transitions with columnar hexagonal structure. In series 1 (4a–e) the mesophase range and transition temperatures of all the compounds are lowered as compared to the parent compounds whereas in series 2 (5a–e) the transition temperatures of all the compounds are lowered, mesophase range for lower members are decreased, however, higher members show more mesophase stability. Both melting and clearing temperatures of series 2 (5a–e) show strong odd–even effect. The intercolumnar distance increases as expected for compounds of both the series with increase in alkyl chain length with some degree of interdigitation of the alkyl chains. The intercolumnar distances for the compounds of the series 2 are slightly higher than the compounds of the series 1. Compound 4c displays homeotropic alignment without using any special technique for alignment of the columnar phase or application of any external force. Copyright © 2007 John Wiley & Sons, Ltd.

Keywords: discotic liquid crystals; triphenylenes; microwave; columnar phases

INTRODUCTION

Soon after the realization of thermotropic mesomorphism in pure disc-like molecules,^[1] triphenylene emerged as a potential novel discotic core.^[2] The non-covalent hierarchy, which leads to the formation of columnar mesophase, of the disc-like molecules is not only interesting to study energy and charge migration in self-organized molecular systems but also acts as potential functional material for many device applications such as one-dimensional conductors, photoconductors, light-emitting diode, photovoltaic solar cell, field effect transistor and gas sensors.^[3] Hitherto, triphenylene derivatives are probably the most widely synthesized and well-studied materials in the family of discotic liquid crystals (DLCs).^[4] This could be because triphenylene derivatives are thermally and chemically stable, their chemistry is fairly accessible and they show diverse mesophases such as helical, plastic, lamellar, columnar and nematic having interesting electronic properties.^[4]

Microwave-assisted high-speed chemical synthesis has attracted a considerable amount of attention in the past decade. This is not only due to the fact that almost all organic reactions proceed significantly faster and more selective than under thermal conditions but also because of the operational simplicity, high yield of products and cleaner reactions with easier work up. Though a large variety of organic molecules have been prepared using microwave dielectric heating, this technique has not been much explored for the synthesis of liquid crystalline materials.

A large number of review articles provide extensive coverage of the subject.^[5]

Since for any practical applications, discotic compounds should have lower melting points and wide mesophase range, there have been efforts to bring down the transition temperatures and stabilize the mesophases. In hexaalkoxytriphenylenes the strategy has been to use alkyl chains of different chain length. Tinh *et al.*,^[6] Allen *et al.*,^[7] and Paraschiv *et al.*^[8] prepared hexaalkoxy-substituted triphenylenes with different alkyl chain lengths to understand the effect of unsymmetrical chains on mesomorphism. They found that introduction of dissymmetric side-chains does not affect the nature of the columnar phase but results in reduction of mesophase stability by lowering the isotropic transition temperature. Similar results have been found in hepta-substituted triphenylenes.^[9] A number of research groups have recently demonstrated that when branching points are introduced into the aliphatic side chains of DLCs, the temperature range of the mesophase was widened and the transition temperatures were lowered without altering the nature

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of the mesophase.^[10] A similar strategy has been applied to phthalocyanines,^[11] hexabenzocoronenes,^[12] tricycloquinazolinolines,^[13] alkynylbenzenes^[14] and discotic transition metal complexes.^[15] In some of the cases, it has been possible to obtain room temperature DLCs with very broad range of mesophase.^[12–14] The decrease in the transition temperature could be due to the disorder caused by branched chains and stereo-heterogeneity. Here, we report microwave-assisted synthesis and characterization of two novel series of non-symmetric hexaalkoxytriphenylenes containing a branched alkyl chain (2-ethyl hexyl or 3,7-dimethyl octyl).

EXPERIMENTAL

General information

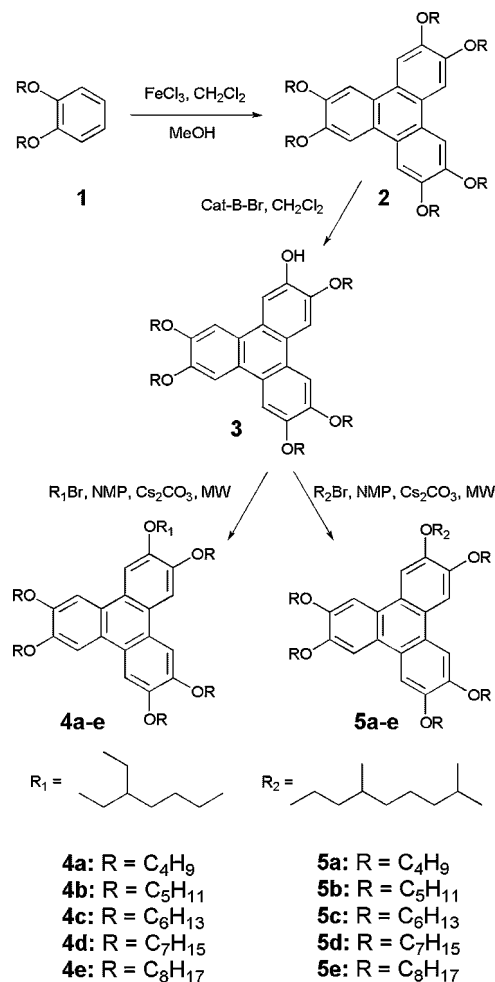
Microwave irradiation was performed in an unmodified household microwave oven. (LG, MS-192W). Column chromatographic separation was performed on silica gel (100–200 mesh). ¹H NMR spectra and ¹³C NMR spectra were recorded in CDCl₃ on a 400 MHz (Bruker AMX 400) spectrometer. All chemical shifts are reported in δ (ppm) units down field from tetramethylsilane and *J* values are reported in Hz. UV spectra were recorded in chloroform on a Hitachi U-3200 spectrophotometer. IR spectra were recorded as KBr discs on Shimadzu FTIR-8400. Elemental analysis was performed on Carlo-Erba Flash 1112 analyser. Transition temperatures were measured using a Mettler FP82HT hot stage and FP90 central processor in conjunction with an OLYMPUS BX51 polarizing microscope as well as by differential scanning calorimetry (Perkin-Elmer Model Pyris 1D). X-ray diffraction measurements were carried out using Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) generated from a 4 kW rotating anode generator (Rigaku Ultrax-18) equipped with a graphite crystal monochromator. Samples were filled in Hampton research capillaries (0.5 mm diameter), sealed and held on a heater. Samples were cooled 10 °C below the isotropic phase and diffraction patterns of the mesophase were recorded on a two-dimensional image plate (Marresearch). The synthesis of different triphenylene derivatives is outlined in Scheme 1. Compounds **1–3** and branched chain alkyl bromides were prepared as reported.^[11,16]

Synthesis of 4a–e and 5a–e

Monohydroxy-pentaalkoxytriphenylenes were prepared as reported.^[16] To a mixture of monohydroxy-pentaalkoxytriphenylene (0.15 mmol), cesium carbonate (0.3 mmol) and appropriate branched chain alkyl bromide (0.3 mmol) in a small glass vial was added few drops of NMP (0.2 ml). The vial was loosely covered with a rubber septum (Aldrich) and then irradiated under microwave for 30 seconds. The vial was taken out and again kept back after about 1 min. The process was continued 6–8 times until the reaction gets completed (monitored by TLC). The reaction mixture was cooled and worked up by adding water followed by extraction with dichloromethane. The crude product was purified by column chromatography (silica gel, ethyl acetate–petroleum ether 1:20) and crystallized from methanol in about 79–87% yield.

UV–Vis data

λ_{max} (CHCl₃) **4a**: 344, 305, 277, 266 nm; **5a**: 344, 304, 278, 269 nm. All the other derivatives give similar spectra.



Scheme 1. Synthetic route of asymmetric hexaalkoxy triphenylenes

IR data

(ν_{max}) **4a**: 3101, 2956, 2931, 2868, 2742, 1616, 1517, 1438, 1263, 1172, 1070, 1033, 960, 835, 599 cm^{−1}. **5a**: 3101, 2956, 2927, 2868, 1616, 1518, 1438, 1386, 1263, 1172, 1070, 1033, 962, 835, 599 cm^{−1}. All other derivatives give similar spectra.

¹H NMR data

4a: δ_{H} 7.84 (s, 6H, ArH), 4.25 (t, 10H, *J* = 6.2, ArOCH₂), 4.12 (d, 2H, *J* = 5.7, ArOCH₂), 1.9 (quintet, 12H, *J* = 6.5, CH₂CH₂CH₂), 1.7–1.4 (m, 17H, CH, CH₂), 1.1 (m, 18H, CH₃), 0.9 (t, 3H, *J* = 7, CH₃); **5a**: δ 7.84 (s, 6H, ArH), 4.24 (t, 12H, *J* = 6.4, ArOCH₂), 1.9 (quintet, 12H, *J* = 6.7, CH₂CH₂CH₂), 1.8–1.2 (m, 18H, CH, CH₂), 1.0 (m, 18H, CH₃), 0.9 (d, 6H, *J* = 6.6, CH₃). All other compounds give similar spectra having more number of hydrogens in the aliphatic region.

¹³C NMR data

4a: δ_{C} 149.1, 123.7, 107.6, 72.3, 69.5, 39.7, 31.5, 30.8, 29.2, 24.1, 23.1, 19.4, 13.9, 11.3. **5a**: 149.0, 123.7, 107.5, 69.4, 68.1, 39.3, 37.5, 36.4, 31.5, 30.0, 28.0, 24.8, 22.6, 19.8, 13.9. All other compounds give similar spectra.

Elemental analysis

4a, Found: C, 76.6; H, 9.7. $C_{46}H_{68}O_6$ requires C, 77; H, 9.6%; **4b**, Found: C, 77.5; H, 9.8. $C_{51}H_{78}O_6$ requires C, 77.8; H, 9.9%; **4c**, Found: C, 78.1; H, 10.6. $C_{56}H_{88}O_6$ requires C, 78.5; H, 10.4%; **4d**, Found: C, 78.7; H, 11.0. $C_{61}H_{98}O_6$ requires C, 79.0; H, 10.7%; **4e**, Found: C, 79.1; H, 10.9. $C_{66}H_{108}O_6$ requires C, 79.5; H, 10.9%; **5a**, Found: C, 77.0; H, 9.75. $C_{48}H_{72}O_6$ requires C, 77.4; H, 9.74%; **5b**, Found: C, 77.7; H, 10.5. $C_{53}H_{82}O_6$ requires C, 78.1; H, 10.1%; **5c**, Found: C, 78.3; H, 10.9. $C_{58}H_{92}O_6$ requires C, 78.7; H, 10.5%; **5d**, Found: C, 79.0; H, 11.2. $C_{63}H_{102}O_6$ requires C, 79.2; H, 10.7%; **5e**, Found: C, 79.2; H, 11.1. $C_{68}H_{112}O_6$ requires C, 79.6; H, 11.0%.

RESULTS AND DISCUSSION

Synthesis

Scheme 1 shows the general synthetic route of hexaalkoxytriphenylenes. Monohydroxy-functionalized pentaalkoxytriphenylenes were prepared as reported.^[16] The branched chain alkyl bromides were prepared from their corresponding alcohols using *N*-bromosuccinimide and triphenylphosphine.^[11] The non-symmetric hexaalkoxytriphenylenes have been prepared, as described in the Experimental Section, in very good yield within 3–4 min by using microwave dielectric heating which is simple, efficient, rapid and economic.

Thermal behaviour

The phase transition temperatures of all the compounds were initially established from the polarizing optical microscopy and then measured accurately by differential scanning calorimetry along with their associated enthalpy changes (Table 1). All the compounds exhibit enantiotropic liquid crystalline behaviour. These materials display characteristic defect textures for the columnar hexagonal mesophase, example of which is shown in Fig. 1. As a typical example the DSC thermogram of compound (**5c**) is shown in Fig. 2. The Cr-Col_h and Col_h-I transitions upon heating and I-Col_h transition upon cooling are seen. As can be seen from the Table 1, both the melting and clearing temperatures of all these materials are lower than their symmetrical counterparts.^[17] On an average about 15°C lowering in melting point and 25°C lowering in isotropic temperature was found for the compounds of series 1 (**4a–e**). In series 2 (**5a–e**) the melting

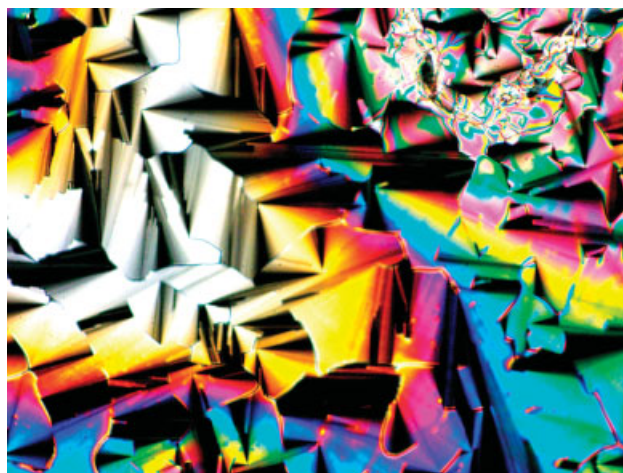


Figure 1. Optical texture of the compound **5d** under crossed polarizer at 75°C (magnification $\times 200$)

points of the compounds are lowered by about 25°C. This could be because of the disordering introduced by the branched alkyl chain into the periphery. The crystal to mesophase transition enthalpy increases as the chain length is increased in both the series. This could be due to the fact that with increase in chain length the molecules become more symmetric in shape and hence more favourable packing in the crystalline phase. The compounds **4c** and **5e** show sharp crystallization while cooling. It may be due to their symmetrical molecular shape but other members show slow crystallization. It should be noted that **5e** is the only member of that series which crystallizes but other members exhibit columnar mesophase down to room temperature. The transition enthalpies for mesophase to isotropic transition decreases with increase in chain length, this could be due to the extra steric crowding of the branched alkyl chains. Both **4b** and **5b** exhibit the highest mesophase range in their respective series where as H4TP exhibits the highest mesophase range in the symmetrical hexaalkoxytriphenylenes. This is due to the fact that H4TP forms a highly ordered plastic columnar phase.^[18] It is interesting to note that both melting and clearing temperatures for the compounds **5a–e** show very strong odd–even effect (Fig. 3). The members containing odd number of carbon atoms in their periphery (except the branched chain)

Table 1. Phase transition temperatures (°C, peak temperatures) and enthalpies (kJ/mol, in parentheses) of triphenylene derivatives **4a–e** and **5a–e**. Cr = crystal, Col_h = hexagonal columnar, I = isotropic

Compound	Heating scan	Cooling scan
4a	Cr 71.6 (28.8) Col _h 95(8.4) I	I 93.5 (8.4) Col _h 40.2 (22.6) Cr
4b	Cr 54.3 (32.5) Col _h 88.1(6.4) I	I 86.7 (6.3) Col _h 29.8 (27) Cr
4c	Cr 53.3 (37.4) Col _h 74.5 (4.7) I	I 72.6 (4.6) Col _h 35.1 (36.3) Cr
4d	Cr 48.7 (51.5) Col _h 68.8 (4.4) I	I 67.2 (4.4) Col _h 32 (45.2) Cr
4e	Cr 51 (43.5) Col _h 58.5 (3.2) I	I 56.6 (3.3) Col _h 33.5 (46.8) Cr
5a	Cr 51.8 (28.9) Col _h 80.1 (6.1) I	I 78.4 (6.2) Col _h
5b	Cr 39.7 (30.8) Col _h 88.6 (6.8) I	I 86.7 (6.5) Col _h
5c	Cr 44 (36.8) Col _h 84.4 (5.5) I	I 82.9 (5.4) Col _h
5d	Cr 42.7 (47.2) Col _h 86.3 (5.3) I	I 84.4 (4.9) Col _h
5e	Cr 51.7 (57) Col _h 80.5 (4.9) I	I 78.1 (4.6) Col _h 32.8 (50.3) Cr

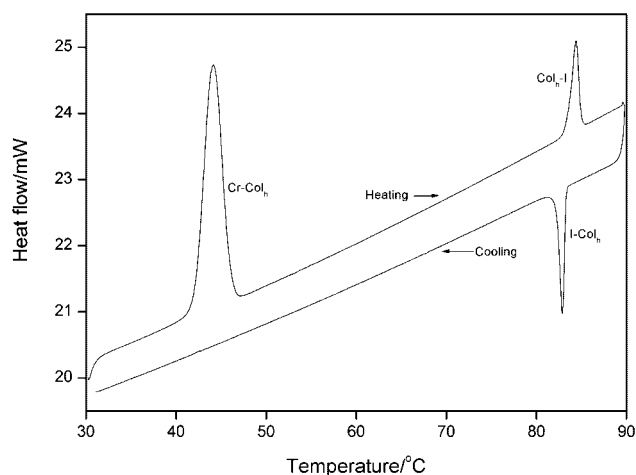


Figure 2. DSC thermogram of the compound **5c** on heating and cooling cycles (scan rate 5°C/min)

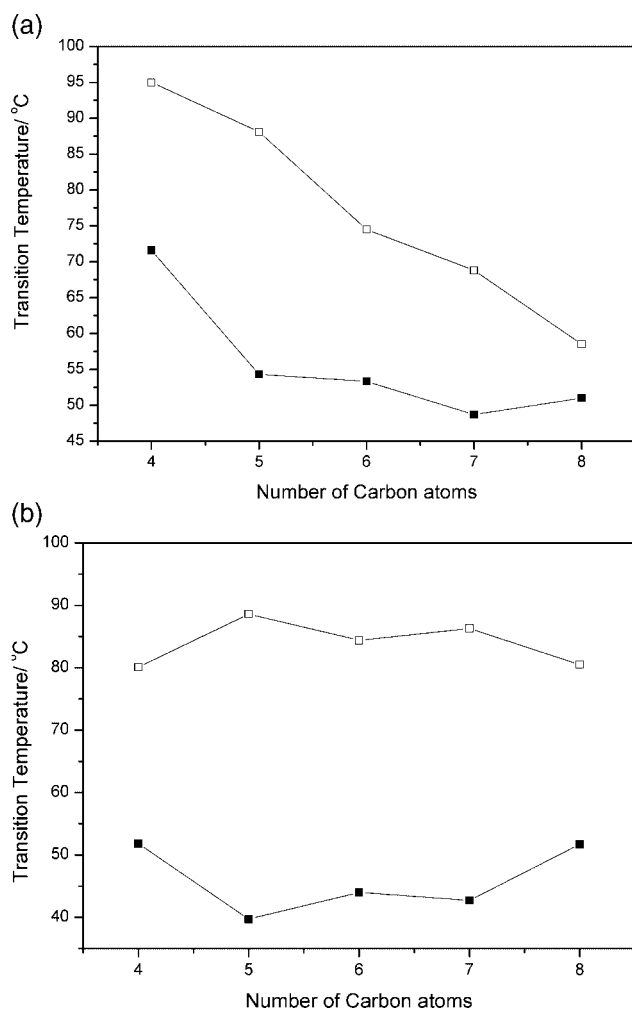


Figure 3. Variation of melting and clearing temperatures with number of carbon atoms in the alkyl chains. (a) Melting (■) and clearing (□) temperatures of the series 1. (b) Melting (■) and clearing (□) temperatures of the series 2

exhibit lower melting points than having even number of carbon atoms in their periphery which is reverse to the clearing temperatures. This could be due to favourable packing of the molecules containing even number of carbon atoms in their crystalline state where as the packing of the molecules is favourable in the mesophase in case of the members containing odd number of carbon atoms in the alkoxy chains. The members **5c–e** display broader mesophase range than their symmetrical counter parts though their clearing temperatures are less than the symmetrical ones. This is because the melting transition temperatures are lowered more as compared to the clearing temperatures for these compounds and hence resulting broad mesophase range. The mesophase stability for the series **4a–e** is less than the series **5a–e** (Fig. 3). This could be because of the more proximity of the ethyl group to the aromatic core of the discotic molecules and hence making unstacking of the molecules in the columns easy.

X-ray diffraction studies

X-ray diffraction patterns for all the compounds were recorded in the columnar phase 10°C below the isotropic temperature while cooling from the isotropic phase. A representative diffraction pattern obtained for the compound **4a** (Fig. 4) and its one-dimensional intensity vs. 2θ profile obtained by integrating over the entire χ (0–360°) range are shown in Fig. 5. Qualitatively similar patterns were obtained for the other compounds. The overall features observed are consistent with the structure of the col_h phase. 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 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 centred at 4.66 Å corresponds to the liquid-like order of the aliphatic chains. The relatively sharper one seen at higher 2θ value and well separated from the broad one is due to the staking of the



Figure 4. X-ray diffraction pattern of the compound **4a**

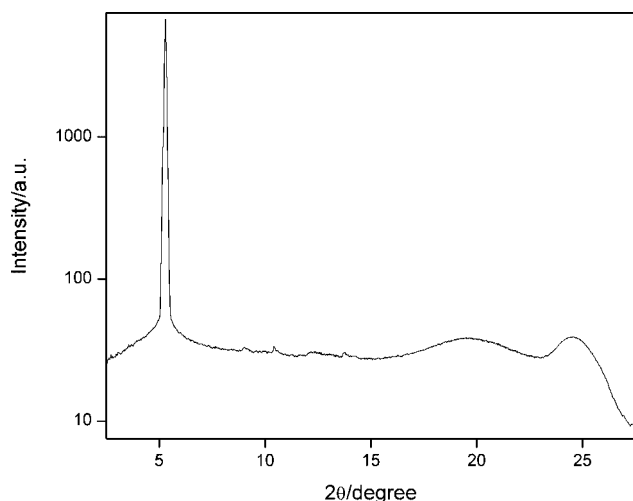


Figure 5. Intensity- 2θ graph derived from the above pattern of the compound **4a**

molecular cores one on top of the other. As it is a diffuse peak it suggests that the staking of the discs within each column is correlated over short distances only. The average staking distance (core–core separation) was found to be 3.64 Å and falls in the range observed for a number of materials exhibiting the columnar phase. It should be noted here that H4TP forms a highly ordered plastic columnar phase^[18] but the compounds **4a** and **5a** form normal hexagonal columnar phase. The intercolumnar distance for H4TP is 18.59 Å^[19] where as this distance is 19.26 and 19.74 Å, respectively for **4a** and **5a**. This could be because of the interdigitation of the long branched chain alkoxy groups which restricts the molecular rotation within the column and hence destroy the plastic columnar phase. The hexagonal columnar structure of the compounds is corroborated by the appearance of six symmetrically positioned spots (Fig. 6) in the diffraction pattern of the compound **4c** without any pretreatment for alignment of the columnar phase or application of any external force. This type of pattern can be obtained from aligned samples by passing the X-ray beam along the column axis in the

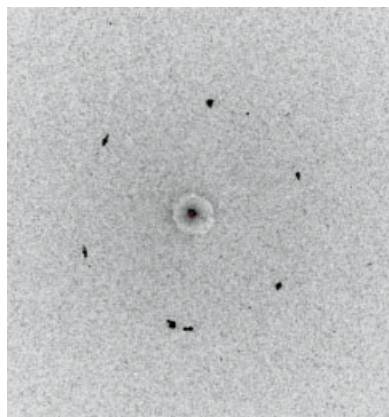


Figure 6. X-ray diffraction pattern of the compound **4c**. Note that no special technique was used for the alignment of the sample. This figure is available in colour online at www.interscience.wiley.com/journal/poc

Table 2. Layer spacing and intercolumnar distances for the mesophase of series **4a–e** and **5a–e**, deduced from X-ray measurements

Compound	<i>d</i> -Spacing (Å)	Intercolumn distance (Å)	Interdisc distance (Å)
4a	16.68	19.26	3.64
4b	17.65	20.38	3.67
4c	18.01	20.79	3.67
4d	19.31	22.29	3.67
4e	20.01	23.10	3.66
5a	17.10	19.74	3.64
5b	17.72	20.46	3.65
5c	18.73	21.62	3.66
5d	19.57	22.59	3.63
5e	20.33	23.47	3.64

columnar mesophase. So, this could be because of formation of large homeotropic domains by branched chain discotic compounds as found earlier.^[11] The miller indices of 100 reflections (d_{100}) and the corresponding intercolumnar distances along with the interdisc distances (intracolumnar) for all the compounds are listed in Table 2. The intercolumnar spacing for a hexagonal lattice is obtained by division of d_{100} by $(\cos 30^\circ)$. As can be seen from Table 2, for compounds of both the series the intercolumnar distances increase monotonically with increase in the chain lengths. As expected the compounds of the series **2** show slightly higher intercolumnar distances (Fig. 7) than the compounds of the series **1** because the 3, 7-dimethyl octyloxy chain is longer than the 2-ethyl hexyloxy chain. The intercolumnar distances are intermediate between their symmetrical counterparts and their fully extended all-*trans* structure which suggests some degree of interdigitation of the alkyl chains.^[20] The compounds **4c** (20.79 Å) and **5e** (23.47 Å) have intercolumnar distances similar to H6TP (21.17 Å)^[8] and H8TP (23.4 Å)^[20] suggesting there is little interdigitation of the alkyl chains in this two compounds. This

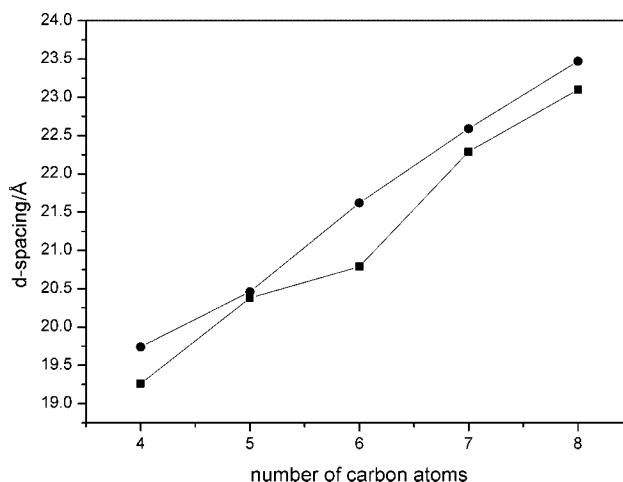


Figure 7. Variation of intercolumnar distances with number of carbon atoms (■) intercolumnar distance of the series **1** (●) intercolumnar distance of the series **2**

could be due to their relatively more symmetrical structure than the other compounds.

CONCLUSIONS

In summary, we have prepared two novel series of triphenylene-based DLCs having a branched-alkyl chain and five normal alkyl chains using microwave dielectric heating. Mesophase behaviour of the compounds has been characterized by polarizing optical microscopy, differential scanning calorimetry and mesophase structure has been characterized by X-ray diffractometry. The introduction of branched-alkyl chain produces materials having low clearing temperature ($<100^{\circ}\text{C}$) and wide mesophase range. From X-ray studies, it was observed that these compounds have a tendency of homeotropic alignment without any pretreatment for alignment of the columnar phase or application of any external force. The manipulation of the molecular architecture provides the opportunity to obtain homeotropically aligned films of self-assembled materials with low clearing temperature and wide mesophase range which is essential for the implementation of these kinds of materials in electronic devices like organic light-emitting diodes, photovoltaic solar cells, gas sensors, etc. We are looking forward to study charge transport in the columnar mesophase and the fabrication of devices incorporating these materials.

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