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Liquid Crystals

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Online publication date: 11 November 2010

To cite this Article Kumar, Sandeep and Naidu, Jaishri J.(2010) 'Novel hexasubstituted triphenylene discotic liquid crystals having three different types of peripheral substituent', *Liquid Crystals*, 29: 7, 899 – 906

To link to this Article: DOI: 10.1080/02678290210145148

URL: <http://dx.doi.org/10.1080/02678290210145148>

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Novel hexasubstituted triphenylene discotic liquid crystals having three different types of peripheral substituent

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(Received 28 December 2001; accepted 27 February 2002)

The synthesis and mesomorphic properties of a variety of novel hexasubstituted triphenylene derivatives having three different types of peripheral substitutions are described. Monobromination of 2,3,6,7-tetrakis(pentyloxy)triphenylene **4**, prepared by Suzuki coupling of 2-iodo-3',4,4',5-tetrakis(pentyloxy)biphenyl **2** and phenylboronic acid followed by cyclization, yields 10-bromo-2,3,6,7-tetrakis(pentyloxy)triphenylene **5**. Nucleophilic aromatic displacement of the bromine with the potassium salt of pentanethiol, followed by bromination, yields 2-bromo-6,7,10,11-tetrakis(pentyloxy)-3-(pentylsulphonyl)triphenylene **7** having a bromo, thioalkyl and alkoxy-substituted periphery of the triphenylene nucleus. The reaction of **7** with copper(I) cyanide gives the cyanotriphenylene derivative **8**, while palladium-copper catalysed alkylation of **7** results in the synthesis of the substituted alkyne derivative **9**. The deprotected alkyne **10** was converted to dimer **11** where two molecules of a monothioalkyl-tetra-alkoxytriphenylene are connected via a rigid π -conjugated diacetylene bridge. Compounds **7**, **8**, **9**, **10** form hexagonal columnar phases while the dimer **11** shows a discotic nematic phase.

1. Introduction

Molecular structure and molecular order play a key role in the formation of liquid crystals—the intermediate state between true liquids and solid crystals. Depending upon their structural features, thermotropic liquid crystals (LCs) can be broadly divided into calamitic (rod-like) and discotic (disk-like). Generally, substitution of sites on rigid aromatic cores with flexible aliphatic chains results in the formation of LCs. The nature of these outer substituents has a great influence on the mesophase structure and its stability. Numerous rod-like molecules with a variety of peripheral substitutions are known to exhibit various types of mesophase [1]. However, probably because of synthesis problems, such a rich variety of peripheral substitutions are uncommon in discotic LCs. A large proportion of discotic LCs is formed by the symmetrically substituted hexaethers, thioethers, esters or benzoates of various flat or nearly flat, rigid aromatic cores such as benzene, triphenylene, truxene, phthalocyanine, etc. [2, 3].

Triphenylene derivatives are the most widely synthesized and extensively studied of discotic LCs. A variety of triphenylene-based discotic LCs have been studied for their one-dimensional conducting [4], photoconducting [5], one-dimensional energy migration [6], mechanism of charge transport [7], electroluminescence [8], ferro-

electric switching [9], and other properties. In order to understand the structure–property relationship, several efforts have recently been made to effect architectural changes in different parts of the discotic molecules, e.g. core modification [10–12], mixed peripheral aliphatic chains [10 *b*, 10 *c*, 13–19], chiral chains [9, 20], fluorinated side chains [21], introduction of hetero atoms in the tails [22], lateral substitution [23], etc. The influences of these changes depend on the structure of the core, flexible chains, linking group, position of the substitution, etc., and generalizations are difficult.

Hexaesters of triphenylene form rectangular and hexagonal columnar mesophases [3]. On the other hand, the hexabenzoate esters form discotic nematic phases [3]. Hexaphenylacetylene derivatives of triphenylene also exhibit discotic nematic phases [3]. The potential applications of discotic nematic LCs in wide viewing angle display devices have recently been described [24]. Symmetrical substituted hexaether derivatives of triphenylene having 5 to 13 carbon atoms in the aliphatic chains form single hexagonal columnar Col_h mesophase [3]. However, it has been recently reported that in hexabutyloxytriphenylene (4 carbon atoms in the aliphatic chains) the intracolumnar order is higher than in the Col_h phase and this is referred to as a columnar plastic Col_p phase [18 *a*]. It should be noted that hexabutyloxytriphenylene has previously been reported to exhibit the Col_h phase only. Mononitrohexabutyloxytriphenylene [10 *e*] and several other unsymmetrical triphenylene

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derivatives, prepared by replacing one of the six peripheral alkoxy chains of a hexaalkoxytriphenylene by bulky ester groups, have also been reported to form Col_p mesophases [18]. Charge carrier mobility up to an order of magnitude higher than Col_h phase is observed in the Col_p phase [5d].

An exceptional mesophase structure with helical order has been demonstrated in hexahexylthiotriphenylene. In the three-dimensionally ordered helical phase of this compound, charge carrier mobility comparable to organic single crystals ($10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) has been reported [5d]. Clearly the degree of molecular order has a significant effect on the efficiency of charge migration in columnar liquid crystalline materials. It is expected that an increase in the orbital overlap area will lead to higher charge mobility. With this in mind, discotic LCs with larger cores such as dibenzopyrene [25], hexabenzotrinaphthalene [26], hexabenzocoronene [27], etc. have been prepared, and the Warman group has recently observed remarkably high charge carrier mobility (up to $0.38 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in the LC phase and $1.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the crystalline phase of hexabenzocoronenes [28].

The recognition of triphenylene-based discotic LCs for their potential application in various devices has fostered numerous efforts to improve the synthesis of triphenylene-based discotics. The traditional method of preparing alkoxytriphenylene starting from veratrol [29] has been replaced by direct trimerization of the dialkoxybenzene using FeCl_3 [30], MoCl_5 [31] or VOCl_3 [32] as oxidizing agent followed by reductive work-up with methanol. Unsymmetrical peripheral substitution affects the phase behaviour markedly. The symmetry of a discoid molecule can be reduced in different ways; like for example by core asymmetric substitution or by introducing an extra group or alkyl chain in a triphenylene molecule, or by side chain asymmetry by attaching alkyl chains of different length in the periphery, or by changing the mode of attachment of the peripheral chains, e.g. mixed ether-ester derivatives. Several methods are now available for the preparation of a variety of unsymmetrically substituted triphenylene derivatives [10–19]. Further, mono- and di-hydroxy functional triphenylenes are required for the preparation of LC dimers, oligomers, polymers and elastomers. A number of synthetic methods have been developed to prepare these monomers [33], which have been utilized to prepare a variety of triphenylene-based dimers, oligomers and polymers. Moreover triphenylene derivatives having two different types of functional group, such as nitro-hydroxy have also been prepared and converted to nitro-functionalized triphenylene discotic dimers and trimers [34].

Almost all the triphenylene derivatives prepared so far have either a single type of peripheral substitution pattern, or two types of peripheral substitution such

as alkoxy-nitro, alkoxy-bromo, alkoxy-cyano, alkoxy-alkanoyloxy, etc. Little effort has so far been made to prepare discotic LCs having more than two types of peripheral substituent. In this paper we report the synthesis of various novel triphenylene derivatives having three different types of peripheral substitution.

2. Experimental

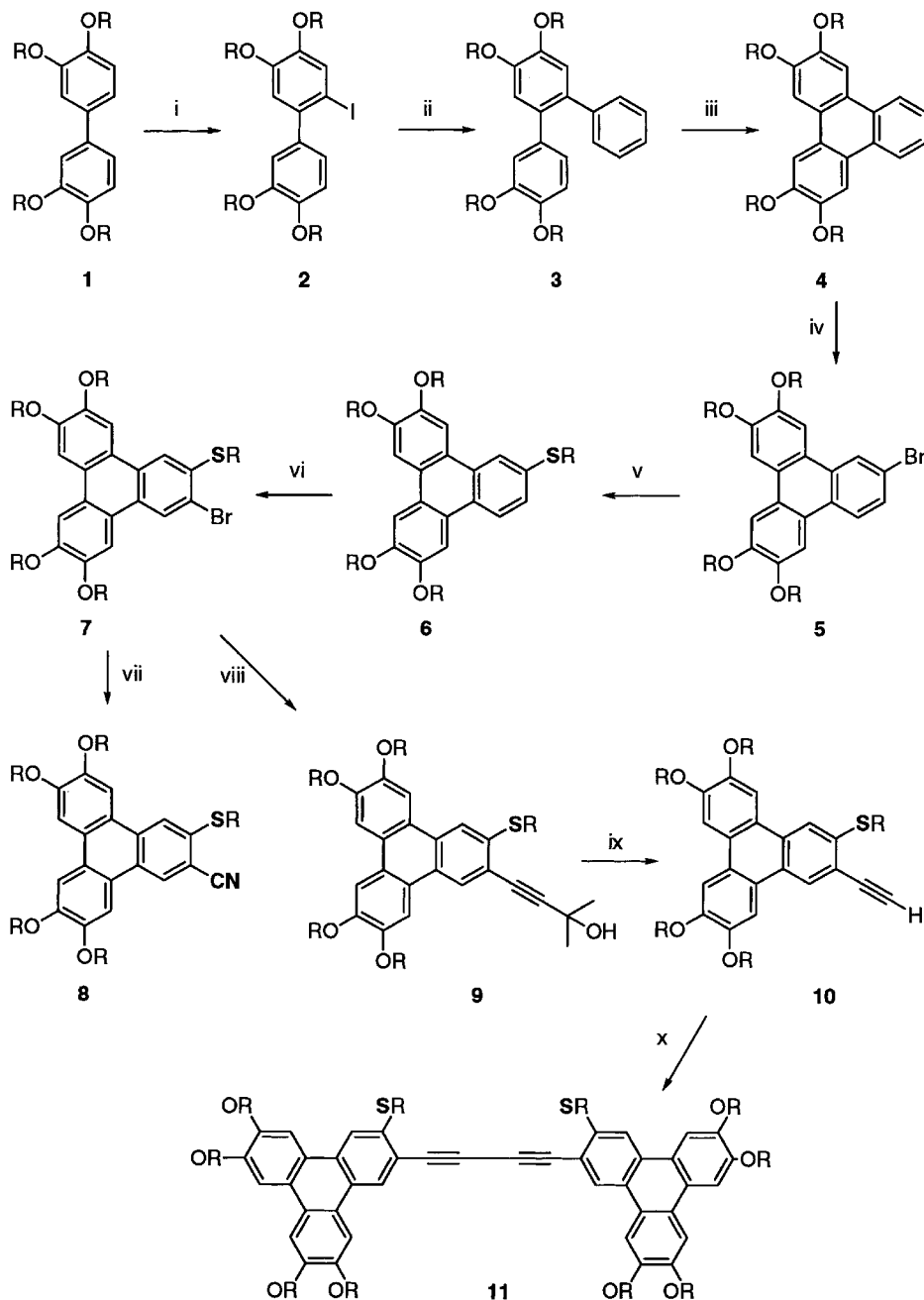
Chemicals and solvents (AR quality) were used without any purification. Column chromatographic separations were performed on silica gel (230–400 mesh) and neutral aluminium oxide. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). HPLC analysis was performed on a Merck-Hitachi LaChrom 2000 machine using a UV detector and Merck LiChrospher Si 60 ($5 \mu\text{m}$) column. Mass spectra were recorded on a JEOL J600H spectrometer in FAB⁺ mode using *m*-nitrobenzyl alcohol (NBA) matrix. NMR spectra were recorded on a 200 or 400 MHz machine (Bruker). All chemical shifts are reported in δ units downfield from Me_4Si , 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). The synthesis of different triphenylene derivatives is outlined in the scheme. The tetrapentyloxybiphenyl **1** was prepared following classical Ulman reaction conditions [35].

2.1. 2-Iodo-3',4,4',5-tetrakis(pentyloxy)-1,1'-biphenyl (**2**)

A solution of tetrapentyloxybiphenyl (**1**, 498 mg, 1.0 mmol) in dichloromethane (3 ml) and acetic acid (15 ml) was heated to reflux and iodine added (448 mg, 1.7 mmol). After about 10 min, iodic acid (155 mg, 0.9 mmol) in 1 ml water was added dropwise. The reaction mixture was heated at reflux for 7 h and then cooled to room temperature, poured into water (20 ml) and extracted with chloroform ($3 \times 20 \text{ ml}$). The combined extracts were washed with 10% aqueous NaOH followed by water and dried over anhydrous sodium sulphate; the solvent was removed under vacuum and the crude product purified by column chromatography over silica gel. Elution of the column with hexane yielded compound **2** (280 mg, 45%). About 50% of the starting material was also recovered from the reaction. ¹H NMR (200 MHz, CDCl_3): δ 7.33 (s, 1H), 6.8 (m, 4H), 3.96 (m, 8H), 1.8 (m, 8H), 1.4 (m, 16H), 0.9 (m, 12H).

2.2. 2-Phenyl-3',4,4',5-tetrakis(pentyloxy)-1,1'-biphenyl (**3**)

To a solution of compound **2** (2.6 g, 4.17 mmol) in dry deoxygenated THF (25 ml), was added tetrakis(triphenylphosphine)palladium(0) (100 mg, 0.087 mmol),



Scheme. Reagents and conditions (i) iodine/iodic acid, CH_2Cl_2 -AcOH, reflux, 45%; (ii) $\text{C}_6\text{H}_5\text{B}(\text{OH})_2$, $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Pd}$, Na_2CO_3 , THF, reflux, 41%; (iii) CH_2Cl_2 , VOCl_3 , r.t., 80%; (iv) Br_2 , CH_2Cl_2 , 60%; (v) $\text{C}_5\text{H}_{11}\text{SK}$, NMP, $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Pd}$, 73%; (vi) Br_2 , CH_2Cl_2 , 28%; (vii) CuCN , NMP, reflux, 35%; (viii) 2-methyl-3-butyn-2-ol, CuI , $\text{PdCl}_2(\text{PPh}_3)_2$, Et_3N , 60–70°C, 40%; (ix) KOH , toluene, reflux, 98%; (x) $\text{Cu}(\text{Ac})_2$, $\text{THF}-\text{C}_5\text{H}_5\text{N}-\text{CH}_3\text{OH}$, reflux, 18%.

aqueous sodium carbonate (2%, 10 ml) and benzenboronic acid (1.27 g, 10.4 mmol in about 2 ml EtOH). The solution was purged with nitrogen for 2 minutes. The reaction was brought to reflux under an atmosphere of nitrogen and stirred at reflux for 15 h. The mixture was then cooled to room temperature, water added and the mixture extracted with ether. The combined extracts were washed with water and brine and dried over

anhydrous sodium sulphate. The dried crude organic phase was purified by column chromatography (silica gel, hexane: dichloromethane 90:10) to give 1.0 g (41%) of compound **3**. MS m/z 574.7. ^1H NMR (200 MHz, CDCl_3): δ 7.15 (m, 5H), 6.93 (m, 2H), 6.75 (br s, 2H), 6.51 (br s, 1H), 4.05 (m, 8H), 3.95 (t, $J=6.7$ Hz, 4H), 3.61 (t, $J=6.7$ Hz, 4H), 1.9–1.2 (m, 16H), 0.9 (m, 12H).

2.3. 2,3,6,7-Tetrakis(pentyloxy)triphenylene (4)

To a solution of compound **3** (500 mg, 0.87 mmol) in dry dichloromethane (10 ml), VOCl_3 (377 mg, 2.17 mmol) was added drop-wise. The reaction mixture was stirred at room temperature for 10 min under N_2 . The reaction was quenched with methanol (5 ml) and the mixture poured over ice-water (20 ml) and extracted with CH_2Cl_2 (4×20 ml). The crude product was purified by column chromatography over silica gel, eluting with 10–15% CH_2Cl_2 in hexane to furnish 398 mg (80%) of compound **4**. MS m/z 572.7. ^1H NMR (200 MHz, CDCl_3): δ 8.5 (m, 2H), 8.02 (s, 2H), 7.8 (s, 2H), 7.57 (m, 2H), 4.25 (m, 8H), 1.96 (m, 8H), 1.5 (m, 8H), 0.98 (t, $J = 7.1$ Hz, 12H).

2.4. 10-Bromo-2,3,6,7-tetrakis(pentyloxy)triphenylene (5)

Compound **4** (572 mg, 1.0 mmol) was dissolved in 10 ml of dichloromethane. Bromine (320 mg, 2.0 mmol) dissolved in 2 ml of dichloromethane was added drop-wise, and the reaction mixture was stirred for 10 min at room temperature. It was then diluted with dichloromethane and washed with 5% aqueous sodium thiosulphate. The organic layer was dried over anhydrous sodium sulphate, and the solvent removed under vacuum. The crude product was chromatographed through silica with 30:70 dichloromethane; hexanes to give 390 mg of compound **5** as a white solid (60%). MS m/z 652.7. ^1H NMR (200 MHz, CDCl_3): δ 8.55 (d, $J = 1.94$ Hz, 1H), 8.31 (d, $J = 8.8$ Hz, 1H), 7.93 (s, 1H), 7.87 (s, 1H), 7.81 (s, 2H), 7.64 (dd, $J = 8.8, 1.94$ Hz, 1H), 4.24 (m, 8H), 1.96 (m, 8H), 1.5 (m, 8H), 0.94 (t, $J = 7.2$ Hz, 12H).

2.5. 2,3,6,7-Tetrakis(pentyloxy)-10-(pentylsulphanyl)triphenylene (6)

Pentanethiol (1.04 g, 10 mmol) was added to a solution of potassium-*t*-butoxide (1.12 g, 10 mmol) in 1-methyl-2-pyrrolidinone (25 ml). After the solution was heated at 80°C for 10 min, compound **5** (651 mg, 1 mmol) and a catalytic amount of tetrakis(triphenylphosphine)-palladium(0) (20 mg) were added. The reaction mixture was stirred at 80°C for 6 h under N_2 and then 1-bromopentane (755 mg, 5 mmol) was added. The reaction mixture was left to react overnight, and after addition of water, the product was extracted using dichloromethane. The crude product was purified by column chromatography over silica gel, eluting with hexane to afford 494 mg (73%) of compound **6** as a light yellow solid. MS m/z 674.7. ^1H NMR (200 MHz, CDCl_3): δ 8.41 (d, $J = 1.7$ Hz, 1H), 8.37 (d, $J = 8.8$ Hz, 1H), 7.95 (s, 2H), 7.81 (s, 2H), 7.54 (dd, $J = 8.8, 1.7$ Hz, 1H), 4.24 (m, 8H), 3.06 (t, $J = 7.2$ Hz, 2H), 1.96 (m, 8H), 1.5 (m, 22H), 0.97 (t, $J = 7.2$ Hz, 15H).

2.6. 2-Bromo-6,7,10,11-tetrakis(pentyloxy)-3-(pentylsulphanyl)triphenylene (7)

2,3,6,7-Tetrakis(pentyloxy)-10-(pentylsulphanyl)triphenylene **6** (700 mg, 1.04 mmol) was dissolved in 10 ml dichloromethane and cooled to 0°C . Bromine (200 mg, 1.25 mmol) dissolved in 2 ml of dichloromethane was added drop-wise. The reaction was stirred for 10 min at 0°C . The reaction mixture was diluted with dichloromethane and washed with 5% aqueous sodium thiosulfate. The organic layer was dried over anhydrous sodium sulphate, and the solvent was removed under vacuum. The crude product was chromatographed through silica with 5:95 dichloromethane; hexanes to give 215 mg (28%) of a white solid **7**. MS: m/z 752.9. ^1H NMR (400 MHz, CDCl_3): δ 8.60 (s, 1H), 8.33 (s, 1H), 7.90 (s, 1H), 7.83 (s, 1H), 7.80 ($2 \times$ s, 2H), 4.22 (m, 8H), 3.11 (t, $J = 7.2$ Hz, 2H), 1.96 (m, 8H), 1.5 (m, 22H), 0.95 (m, 15H). ^{13}C NMR (100 MHz, CDCl_3): 150.1, 150.0, 149.4, 149.2, 134.9, 128.4, 128.3, 127.0 \times 2, 124.6, 124.2, 123.5, 122.5, 122.4, 122.3, 107.0 \times 2, 106.7, 69.6, 69.5, 34.0, 31.4, 29.2, 28.4, 22.6, 22.4, 14.1.

2.7. 6,7,10,11-Tetrakis(pentyloxy)-3-(pentylsulphanyl)-2-cyanotriphenylene (8)

Compound **7** (50 mg, 0.07 mmol) and an excess of copper(I) cyanide (100 mg, 1.1 mmol) were combined in 2.0 ml of *N*-methylpyrrolidinone. The reaction mixture was stirred at reflux for 16 h and then cooled to room temperature and poured into water. The resultant aqueous suspension was extracted with three equal portions of dichloromethane. The combined extracts were dried over anhydrous sodium sulphate, and the solvent removed under vacuum. The crude product was chromatographed through silica with 10–15% of dichloromethane in hexanes to give 35 mg of the product as a pale yellow solid (35%). MS: m/z 699.6. ^1H NMR (400 MHz, CDCl_3): δ 8.74 (s, 1H), 8.49 (s, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 7.80 (s, 2H), 4.25 (m, 8H), 3.15 (t, $J = 7.4$ Hz, 2H), 1.98 (m, 8H), 1.8–1.3 (m, 22H), 0.98 (t, $J = 7.2$ Hz, 12H), 0.98 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 151.2, 150.4, 149.8, 149.4, 135.3, 132.0, 129.6, 127.3, 126.0, 124.4, 122.0, 121.6, 118.4, 112.3, 107.6, 107.0, 106.6, 106.4, 69.7, 69.5, 35.3, 31.0, 29.1, 28.4, 22.6, 22.3, 14.1.

2.8. 2-Methyl-4-[6,7,10,11-tetrakis(pentyloxy)-3-(pentylsulphanyl)-2-triphenylenyl]-3-butyne-2-ol (9)

A solution of compound **7** (500 mg, 0.66 mmol), dichlorobis(triphenylphosphine)palladium(II) (100 mg, 0.14 mmol), 2-methyl-3-butyne-2-ol (550 mg, 6.6 mmol), triphenylphosphine (200 mg, 0.76 mmol) and copper(I) iodide (100 mg, 0.52 mmol) in dry deoxygenated triethylamine (20 ml) was stirred at 60 – 70°C under argon for 15 h. Triethylamine was removed *in vacuo* and the residue

was purified by column chromatography over silica gel eluting with 10% ethyl acetate in hexane to yield 200 mg (40%) of the product **9**. MS: m/z 756.6. ^1H NMR (200 MHz, CDCl_3): δ 8.48 (s, 1H), 8.30 (s, 1H), 7.89 (s, 2H), 7.80 (s, 2H), 4.24 (m, 8H), 3.13 (t, $J = 7.3$ Hz, 2H), 1.98 (m, 8H), 1.8–1.3 (m, 22H), 0.95 (m, 15H). ^{13}C NMR (100 MHz, CDCl_3): 150.2, 149.7, 149.5, 149.2, 136.2, 129.1, 127.5, 126.7, 125.1, 124.0, 122.9, 122.7, 120.9, 107.4, 107.2, 107.1, 106.8, 99.1, 81.0, 69.8, 69.7, 69.6, 69.5, 66.0, 33.5, 31.5, 31.4, 29.7, 29.1, 28.9, 28.4, 22.5, 22.4, 14.1.

2.9. *2-Ethynyl-6,7,10,11-tetrakis (pentyl oxy)-3-(pentylsulphanyl)triphenylene (10)*

Compound **9** (100 mg, 0.13 mmol) was dissolved in 5 ml of toluene and powdered KOH (18 mg, 0.32 mmol) in about 0.5 ml of methanol was added. The reaction mixture was boiled for 30 minutes, cooled to room temperature and diluted with water. The organic portion was extracted with ethyl acetate (3×20 ml). The combined extracts were dried over anhydrous sodium sulphate, the solvent removed under vacuum and the crude product purified by column chromatography over silica gel. Elution of the column with 5–10% ethyl acetate in hexane yielded compound **10** (90 mg, 98%). MS: m/z 700.8. ^1H NMR (200 MHz, CDCl_3): δ 8.60 (s, 1H), 8.35 (s, 1H), 7.91 (s, 1H), 7.90 (s, 1H), 7.80 (s, 2H), 4.24 (m, 8H), 3.53 (s, 1H), 3.15 (t, $J = 7.3$ Hz, 2H), 1.93 (m, 8H), 1.8–1.3 (m, 22H), 0.95 (m, 15H). ^{13}C NMR (50.3 MHz, CDCl_3): 150.2, 149.7, 149.5, 149.2, 136.2, 129.1, 127.5, 126.7, 125.1, 124.0, 122.9, 122.7, 120.9, 107.4, 107.2, 107.1, 106.8, 99.1, 81.0, 69.8, 69.7, 69.6, 69.5, 66.0, 33.5, 31.5, 31.4, 29.7, 29.1, 28.9, 28.4, 22.5, 22.4, 14.1.

2.10. *2,3,6,7-Tetrakis (pentyl oxy)-10-(pentylsulphanyl)-11-{4-[6,7,10,11-tetrakis (pentyl oxy)-3-(pentylsulphanyl)triphenylenyl]-1,3-butadiynyl}-triphenylene (11)*

To a solution of compound **10** (100 mg, 0.14 mmol) in THF/pyridine/methanol (5 ml each) was added copper(II) acetate (85 mg, 0.42 mmol), and the reaction mixture was heated under reflux for 24 h under nitrogen. The precipitate obtained on pouring the reaction mixture into water was filtered and chromatographed on neutral alumina (30% dichloromethane in hexane) and recrystallized from ether (yield 18%). MS: m/z 1395.5. ^1H NMR (200 MHz, CDCl_3): δ 8.68 (s, 2H), 8.33 (s, 2H), 7.91 (s, 2H), 7.88 (s, 2H), 7.78 (s, 4H), 4.25 (m, 16H), 3.19 (t, $J = 7.3$ Hz, 4H), 2.0–1.56 (m, 40H), 0.97 (m, 30H). ^{13}C NMR (100.6 MHz, CDCl_3): 150.4, 149.7, 149.6, 149.1, 136.8, 129.6, 129.3, 126.8, 125.3, 124.0, 122.7, 122.4, 120.3, 107.4, 107.3, 106.9, 106.5, 82.1, 79.2, 69.8, 69.6, 69.4, 34.0, 31.3, 29.1, 28.9, 28.4, 22.5, 22.3, 14.0.

3. Results and discussion

The sulphur atom is slightly larger and more polarizable than the oxygen atom, which may significantly affect molecular packing in the columnar phase. Mixed alkoxy-alkylthio-substituted triphenylene derivatives have recently been proposed as interesting candidates for various physical studies. Praefcke and co-workers have postulated that triphenylene derivatives having a single thio- or selino-alkyl chain may form more stable, ordered, wider range columnar mesophases, and they unsuccessfully attempted the synthesis of monoalkylthio-hexaalkoxytriphenylene **s** [12]. We have previously reported the synthesis of symmetrical mixed alkoxy/alkylsulphanyl derivatives of triphenylene [10c]. We now felt that the incorporation of a third type of peripheral substituent such as cyano, bromo, alkyne, etc., into the mixed alkoxy/alkylsulphanyl triphenylene system would provide another new group of discotic liquid crystals with interesting properties.

The synthesis of various triphenylene derivatives having three different types of peripheral substitution is outlined in the scheme. A palladium-catalysed coupling of benzenboronic acid with 2-iodo-3,3',4,4'-tetrakis(pentyl oxy)-1,1'-biphenyl **2**, obtained from the monoiodination of tetraalkoxybiphenyl **1**, afforded the terphenyl **3**. Oxidative cyclization of this terphenyl using VOCl_3 [32] gave the 2,3,6,7-tetrakis(pentyl oxy)triphenylene **4**. The bromination of **4** using two equivalents of Br_2 in methylene chloride gave a mixture of monobrominated and dibrominated products from which the desired monobrominated compound **5** could be isolated by column chromatography in moderate yield. The mixed alkoxy/alkylsulphanyl derivative **6** was prepared by the treatment of the 10-bromo-2,3,6,7-tetrakis(pentyl oxy)-triphenylene **5** with the potassium salt of pentanethiol in *N*-methylpyrrolidinone. Use of a catalytic amount of tetrakis(triphenyl)phosphine Pd(0) improves the yield of the product. Bromination of **6** afforded the mesogenic 2-bromo-6,7,10,11-tetrakis(pentyl oxy)-3-(pentylsulphanyl)-triphenylene **7** in good yield. Reaction of **7** with copper(I) cyanide gave the cyanotriphenylene **8**. Palladium/copper-catalysed alkylation of **7** can be accomplished with compound **9**. Treatment of **9** with base gave free acetylene **10** in high yield. The alkyne **10** was easily dimerized to compound **11** using copper acetate [36]. All the compounds were fully characterized from their ^1H NMR, ^{13}C NMR and mass analysis. The HPLC purity of all the compounds was found to be 99+ %.

4. Thermal behaviour

The thermal behaviour of all the compounds was investigated by polarizing optical microscopy and by differential scanning calorimetry. Phase transition temperatures and enthalpy measurements were carried out

on 2–3 mg samples using a Perkin-Elmer DSC7 with heating and cooling rates of $10^{\circ}\text{C min}^{-1}$. Data from heating and cooling cycles are collected in the table. The peak temperatures are given in $^{\circ}\text{C}$ and the numbers in parentheses indicate the transition enthalpy (ΔH) in kJ mol^{-1} .

Like pentaalkoxytriphenylene [10b] the penta-substituted mixed alkoxy/alkylsulphanyl derivative, 2,3,6,7-tetrakis(pentyloxy)-10-(pentylsulphanyl)triphenylene **6** was found to be non-mesogenic, indicating that the polar nature of the sulphur atom alone is insufficient to induce mesogenicity. The bromination of this compound affords the mesogenic 2-bromo-6,7,10,11-tetrakis(pentyloxy)-3-(pentylsulphanyl)triphenylene **7**. The crystalline compound **7** melts at about 75°C and changes to isotropic liquid at about 145°C . On cooling, the columnar phase appears at about 142°C and supercools to room temperature. On second heating, DSC shows no crystal to melting transition, but gives only a mesophase to isotropic transition at 144.6°C . Dipolar interactions of the bromine atom and/or filling the vacant space on the pentasubstituted core could be responsible for the mesogenic nature of this compound. Similar behaviour has been observed with pentaalkoxytriphenylene [10b].

Cyanobiphenyls are the most important calamitic LCs used in optoelectronic devices. The use of cyano substitution to enhance the mesophase range in discotic liquid crystals has recently been demonstrated by Boden *et al.* [11d]. Cyanation of **7** with copper(I) cyanide produces the cyano-substituted mixed alkoxy/alkylsulphanyl triphenylene derivative **8** having a strong dipole moment in the plane of the molecule. This compound shows melting and clearing transitions at 121 and 193.8°C , respectively, in the DSC heating run. Upon cooling, the columnar phase appears at about 192°C , crystallizing at about 80°C .

The alkyne derivatives **9** and **10** form similar columnar phases. Their transition temperatures are given in the table. The free acetylene derivative **10** was found to be unstable and decomposes on heating above the isotropic temperature, but the protected acetylene derivative **9** is stable in the scanning calorimeter. The optical textures

of all the above mixed triphenylenes **7**, **8**, **9** and **10** are very similar to the hexagonal columnar Col_h phase shown by several well characterized discotic LCs [37]. Figure 1 shows two representative examples of such photomicroscopic pictures of compound **7** and **9**, obtained on cooling from the isotropic liquid.

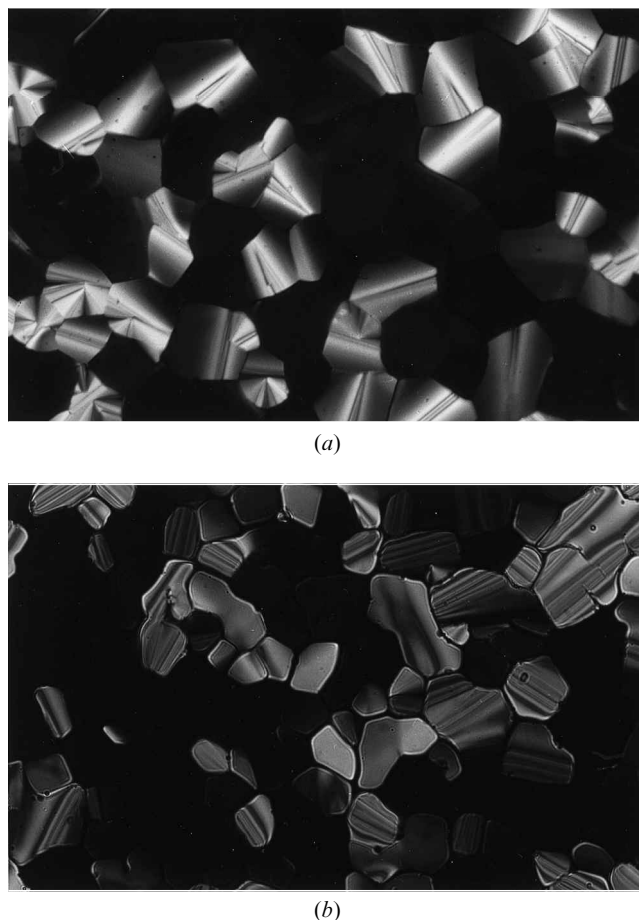


Figure 1. (a) Optical textures of compound **7** obtained on cooling from the isotropic liquid at 114°C (crossed polarizers, magnification $\times 100$). (b) Optical textures of compound **9** obtained on cooling from the isotropic liquid at 103°C (crossed polarizers, magnification $\times 100$).

Table. Phase transition temperatures ($^{\circ}\text{C}$) (peak temp.) and enthalpies (kJ mol^{-1}) of new triphenylene derivatives. Cr = crystal, Col_h = hexagonal columnar liquid crystalline phase, N_D = discotic nematic phase, I = isotropic.

Compound	Thermal transitions, and enthalpy changes (in parentheses)	
	Heating scan	Cooling scan
7	Cr 75.6 (18.6) I Col_h 144.8 (6.8) I	I 142.4 (6.4) Col_h
8	Cr 121.0 (30.0) Col_h 193.8 (3.3) I	I 191.5 (2.9) Col_h 80.3 (31.0) Cr
9	Cr 81.8 (23.8) Col_h 167.8 (5.8) I	I 163.0 (5.8) Col_h
10	Cr 57.7 (24.3) Col_h 125.4 (2.8) I	
11	Cr 182.5 (11.2) N_D 196.3 (0.8) I	I 193.4 (0.8) N_D 174.7 (9.9) Cr

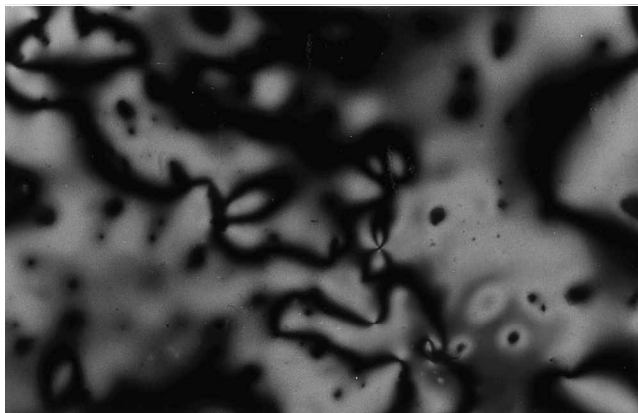


Figure 2. Optical textures of compound **11** obtained on cooling from the isotropic liquid at 185°C (crossed polarizers, magnification $\times 200$).

On the other hand, the dimer **11** displays a typical schlieren texture (figure 2) and high fluidity characteristic of the N_D phase. It melts at 182.5°C on heating to the nematic phase, transforming to isotropic liquid at 196.3°C on further heating. The nematic phase reappears at 193.4°C on cooling and crystallization takes place at 174.7°C. We have recently shown [38] that two discotic molecules linked via a short rigid spacer may experience some steric hindrance due to overlapping or interdigitating aliphatic side chains and a weak distortion of the planarity of the core. This may reduce the strong π - π interactions responsible for the formation of ordered columnar mesophases. The rigid dimer molecules may stay in a more or less parallel position having orientational order but losing their long range translational order and, therefore, are likely to form discotic nematic phase.

5. Conclusion

We have shown that triphenylene-based discotic LCs having three different types of peripheral substitution can be prepared. Such examples are rare in literature. The methodology allows us to prepare a variety of functionalized triphenylene derivatives. Efforts are now in hand to synthesize a series of new mixed-tail triphenylene discotics, which may be interesting for various physical studies.

We are grateful to Professor S. Chandrasekhar for many helpful discussions. Mr Sanjay K. Varshney is thanked for his technical assistance.

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