Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A columnar mesophase with high lateral order from a triphenylene-hexa(3,5-dialkoxy)benzoate

Arkadiusz Kotlewski[ab]; Wolter F. Jager[ac]; Eduardo Mendes[a]; Stephen J. Picken[a]
[a] NanoStructured Materials, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, NL2628 BL Delft,, The Netherlands [b] Novel Aerospace Materials, Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands [c] Nano-Organic Chemistry, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

To cite this Article Kotlewski, Arkadiusz , Jager, Wolter F. , Mendes, Eduardo and Picken, Stephen J.(2010) 'A columnar mesophase with high lateral order from a triphenylene-hexa(3,5-dialkoxy)benzoate', Liquid Crystals, 37: 5, 579 — 586
To link to this Article: DOI: 10.1080/02678291003710466
URL: http://dx.doi.org/10.1080/02678291003710466

Liquid Crystals,
Vol. 37, No. 5, May 2010, 579–586

Taylor & Francis
Taylor & Francis Group

A columnar mesophase with high lateral order from a triphenylene-hexa(3,5-dialkoxy)benzoate

Arkadiusz Kotlewski[a,b], Wolter F. Jager[a,c], Eduardo Mendes[a] and Stephen J. Picken[a]*

[a]*NanoStructured Materials, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, NL2628 BL Delft, The Netherlands;* [b]*Novel Aerospace Materials, Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands;* [c]*Nano-Organic Chemistry, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands*

(*Received 14 January 2010; final version received 17 February 2010*)

This paper describes the synthesis of triphenylene-2,3,6,7,10,11-hexayl hexakis(3,5-dialkoxy)benzoates, bearing hexyloxy (**1a**) and dodecyloxy tails (**1b**). These benzoate esters were synthesised in high yields by employing a DCC coupling of the (3,5-dialkoxy) benzoic acid to 2,3,6,7,10,11-hexahydroxytriphenylene. The 3,5-dihexyloxy benzoate **1a**, forms a highly ordered columnar mesophase with extensive lateral and very limited columnar order, whereas no mesomorphic phases were observed for the 3,5-didodecyloxy benzoate **1b**. In contrast with most benzoate esters of triphenylene, nematic mesophases were not observed for **1**.

Keywords: discotic liquid crystals; triphenylene; benzoate esters

1. Introduction

Triphenylenes are a well-known and frequently studied class of thermotropic discotic liquid crystalline materials [1–3]. Owing to π–π interactions of the rigid aromatic cores, triphenylene derivatives self-organise in stacks and form long columns, which are ordered in a two-dimensional pattern. In most cases, highly ordered columnar phases such as the hexagonal columnar phases (Col_h) are observed over a wide temperature range. Most columnar discotic liquid crystals exhibit one-dimensional charge-carrier migration [4] along the stacks and may find application in molecular electronics [5]. For obtaining high charge-carrier mobility, the distance between aromatic disks in a column and the tilt angle are crucial elements. Improvement of the short-range intracolumnar order will drastically influence electronic overlap of aromatic cores and thus the associated conductivity. It is known that a significant rise of charge-carrier mobility is observed at the transition from a columnar hexagonal disordered to a columnar hexagonal ordered phase [6]. In the case of a columnar hexagonal disordered phase, such an increase is observed even within the mesophase range by decreasing the temperature.

Mesophases of lower order, such as the nematic discotic (N_D) and the columnar discotic (N_{Col}) phases, are not commonly reported for triphenylenes [7]. Such mesophases, however, are generally observed for more flexible discotics such as phenylethynyl substituted benzenes [8, 9]. For these compounds, the rotational freedom of the ethynyl linkers results in non-planar conformations, which reduce interdisc interactions and efficient stacking of the discs, thus preventing the formation of columnar phases. Nematic discotic materials are used as compensating films that find application for improving the viewing angle of liquid crystalline displays [10].

Benzoate esters of 2,3,6,7,10,11-hexahydroxytriphenylene are well-known compounds possessing interesting properties [11]. In most cases these compounds exhibit a discotic nematic phase, and in some cases these are accompanied by hexagonal or rectangular columnar mesophases [11]. For example, it has been reported that 4-alkoxy benzoates of triphenylene exhibit discotic nematic phases [12]. It has also been observed that small methyl substituents at the *para* position on the benzoate moieties depress mesophase transition temperatures, broaden liquid crystal windows and influence phase sequences of these compounds [13, 14]. Based on acrylated benzoate esters of 2,3,6,7,10,11-hexahydroxytriphenylene, stable anisotropic films have been obtained by photopolymerisation [15, 16]. It is also known that introduction of large bulky substituents causes thickening of the molecules and weakens the face-to-face interactions. This suppresses columnar phases, while the nematic phase remains relatively unaffected [17, 18]. Broadening of the mesophase range is mostly achieved by frustrating the crystallisation process, thus specifically lowering the melting temperature. The extreme case of such broadening is demonstrated for triphenylene benzoate esters with a chlorine or nitro group in the *meta* position [19].

Here we report on the synthesis and mesophase behaviour of triphenylen-2,3,6,7,10,11-hexayl hexakis(3,5-dialkoxybenzoates **1a** and **1b** (Figure 1). In contrast to other benzoate esters, the symmetric 3,5-dihexyloxy benzoate **1a** exhibits an unusual columnar

---

*Corresponding author. Email: s.j.picken@tudelft.nl

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678291003710466
http://www.informaworld.com

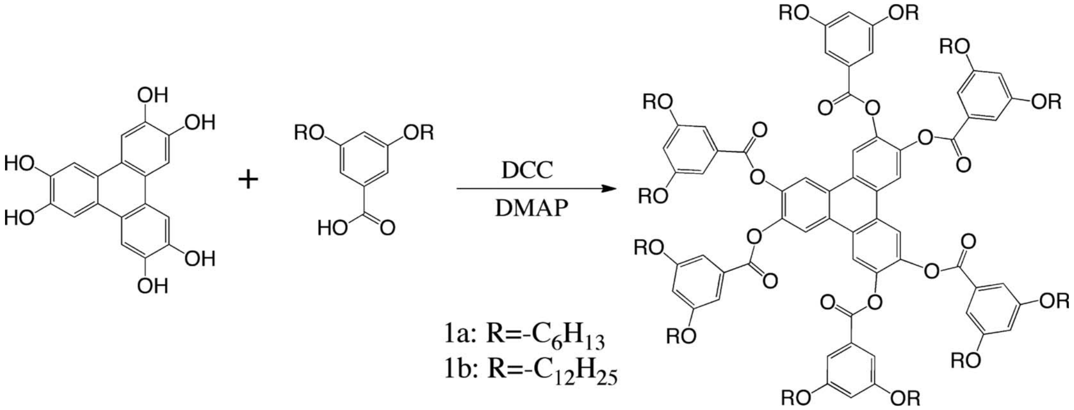


Figure 1. Synthetic route for the preparation of **1a** and **1b**.

mesophase, which is highly ordered in the lateral direction and highly disordered in the columnar direction. In our view such a mesophase, with extensive lateral and very limited columnar order, may be regarded as an additional type of discotic phase, structurally distinct from the N_D phase observed in most benzoate esters, and the Col_h phases observed in alkyloxy substituted triphenylenes.

2. Results and discussion

2.1 *Synthesis*

Compounds **1a** and **1b** have been prepared as shown in Figure 1. The starting materials, 3,5-dialkoxybenzoic acids [20] and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) [13, 18, 21–23], have been synthesised as reported previously. Symmetric benzoate esters of triphenylene have been synthesised by reacting an acid chloride with 2,3,6,7,10,11-hexahydroxytriphenylene in the presence of pyridine or triethylamine. However, the reaction of 3,5-dialkoxybenzoyl chloride with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) did not result in acceptable isolated yields of **1a** and **1b**. Therefore the desired liquid crystalline materials were prepared by applying a Steglich esterfication. In this reaction the carboxylic acid reacts with N,N′-dicyclohexylcarbodiimide (DCC) to an O-acyl isourea derivative, which is more reactive than the free acid. In the next step this intermediate reacts instantly with phenol, giving dicyclohexylurea and the corresponding ester. This route increases the reaction yield significantly and simplifies the purification. The 4-dimethylaminopyridine (DMAP) is used as an acyl transfer-reagent since 1,3-rearrangement of the O-acyl intermediate to a N-acyl urea can take place. The yields for **1a** and **1b** using DCC/DMAP esterfication were 97% and 70%, respectively.

2.2 *Optical characterisation and thermal analysis*

The thermal properties of **1a** and **1b** have been investigated by differential scanning calorimetry (DSC) (Figure 2). The thermograms show that compound **1a** exhibits two phase transitions upon heating, a crystal to columnar at 77.8°C and a columnar to isotropic at 187.6°C. On cooling the sample shows a 10° hysteresis and becomes liquid crystalline at 173.9°C. Crystallisation sets in at 68.6°C. Compound **1b** shows only a broad melting peak on the first heating. During subsequent DSC scans the sample appeared to be amorphous with no indication of a glass transition.

Optical polarisation microscopy (OPM) results show that only **1a** exhibits mesomorphic behaviour. Compound **1b** appears amorphous and even extensive annealing did not result in liquid crystal texture formation. Crystallisation was also strongly suppressed and the sample required a few weeks to initiate the growth of crystals. The slow crystallisation and the lack of mesophase formation found for **1b** may be due to the large size of the molecule, which may result in slow dynamics and thus prevent formation of mesophases on a reasonable timescale.

Compound **1a** shows various unusual optical textures, whose appearance was strongly affected by the cooling rate and the sample thickness. The cooling experiment at the standard rate of 10°C/min gave a feather-like texture along with extensive dark areas, see Figure 3(A). Initially, this texture was not assigned as belonging to a columnar mesophase, but a closer examination of the birefringent defects in the dark areas (Figure 3(B)) revealed large ‘dendritic-like’ monodomains [24]. Existence of these features suggests a homeotropic alignment of columns in the dark parts of the image, and a planar or tilted alignment in feather-like textures. Faster cooling rates (>>10°C/min) resulted in fine, distorted fan-shaped textures (see

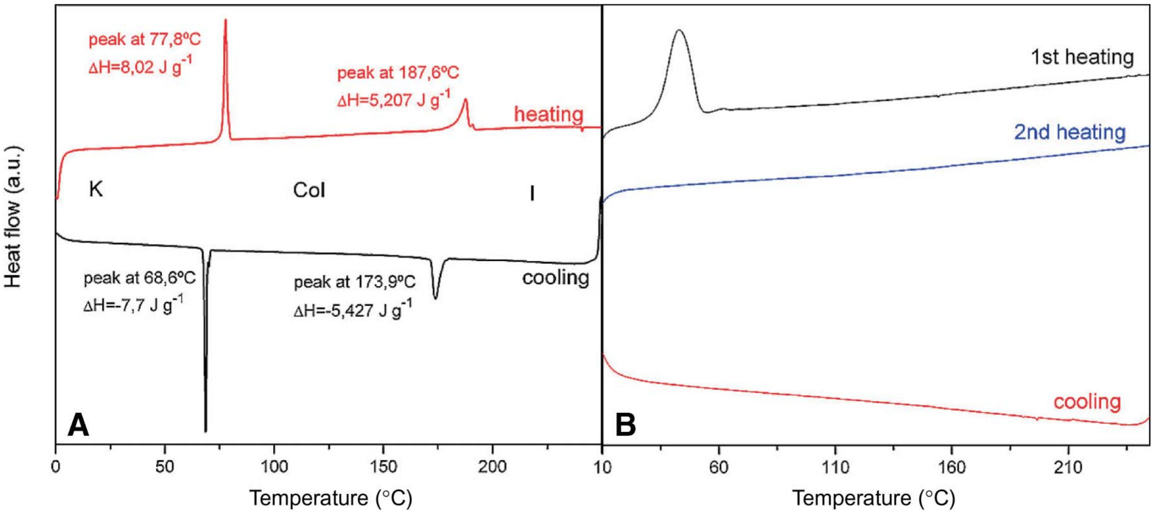


Figure 2. Differential scanning calorimetry traces showing the mesophase behaviour of (A) **1a** and (B) **1b**.

Figure 3(C)), which are typical for columnar order. Visualisation of the crystallisation was possible only when the λ plate was used (Figure 3(D)). This was observed by the formation of small cracks in the liquid crystalline material. Crystallisation could be suppressed by fast cooling from the columnar phase down to temperatures far below the Col to K transition.

Long anisotropic textures with soft edges could be obtained when cooling was stopped just below the isotropic to liquid crystalline phase transition temperature for about 30min (Figure 4(A)). The maximum birefringence was observed in the entire texture at ±45° alignment of the needle-like texture. These findings are in favour of planar organisation of columns in large monodomains, while the black part shows homeotropic organisation.

It is known that mechanical shear applied to a columnar phase can induce orientation, forming a birefringent texture aligned along the shearing direction. Upon shear of thin samples (Figure 5(A)) an unusual thread-filiform-like texture (Figure 5(B)) is formed with 'threads' perpendicular to the shearing direction. The observed texture indicates that the flow gives rise to a periodic variation in the director alignment, and the overall dark appearance indicates that most of the sample is homeotropic. Thicker samples with needle-like textures could also be partially aligned as indicated by Figure 4(B). In addition to the aforementioned arguments, the high viscosity of the samples was in favour of a columnar phase.

2.3 *Wide-angle X-ray scattering*

The formation of a columnar mesophase was clearly confirmed by wide-angle X-ray scattering (WAXS) measurements. Figure 6 shows 2D X-ray diffraction patterns and Figure 7 represents X-ray equatorial scans of **1a** recorded upon cooling.

At 230°C the sample shows a diffuse diffraction pattern typical for an isotropic liquid. Upon cooling, the development of multiple reflections (in the small angle region) with high intensity was observed. Cooling was stopped at 100°C, the temperature at which the sample is in the columnar mesophase. The broad diffuse scattering in the wide-angle region remains unchanged even after 200min at 100°C.

Amplification of the wide-angle region (Figure 7) shows that there are two broad peaks at 2Θ equal to 24° and 19°. They roughly correspond to the π–π distance of triphenylene cores in a column (24°) and a diffuse peak which typically comes from scattering of alkyl tails (18°). It is worth mentioning that the sample did not reveal the typical relationship of hexagonal packing ($1{:}\ \sqrt{3}{:}\ 2{:}\ \sqrt{7}\ldots$). Upon further cooling crystallisation sets in at around 29°C and it is accompanied by development of additional reflections in the wide-angle region. The broad halo at 26° comes from the integration procedure, because at wide angles part of the scattered beam falls outside the detector grid.

The 2D images reveal that on very slow cooling of the sample in the X-ray capillary, partial alignment of domains was obtained. Figure 8 depicts a 2D pattern where most of the columns are nearly parallel to the X-ray beam and perpendicular to the long axis of the capillary. Rotation of the capillary around its long axis changed the apparent orientation of columns in the sample.

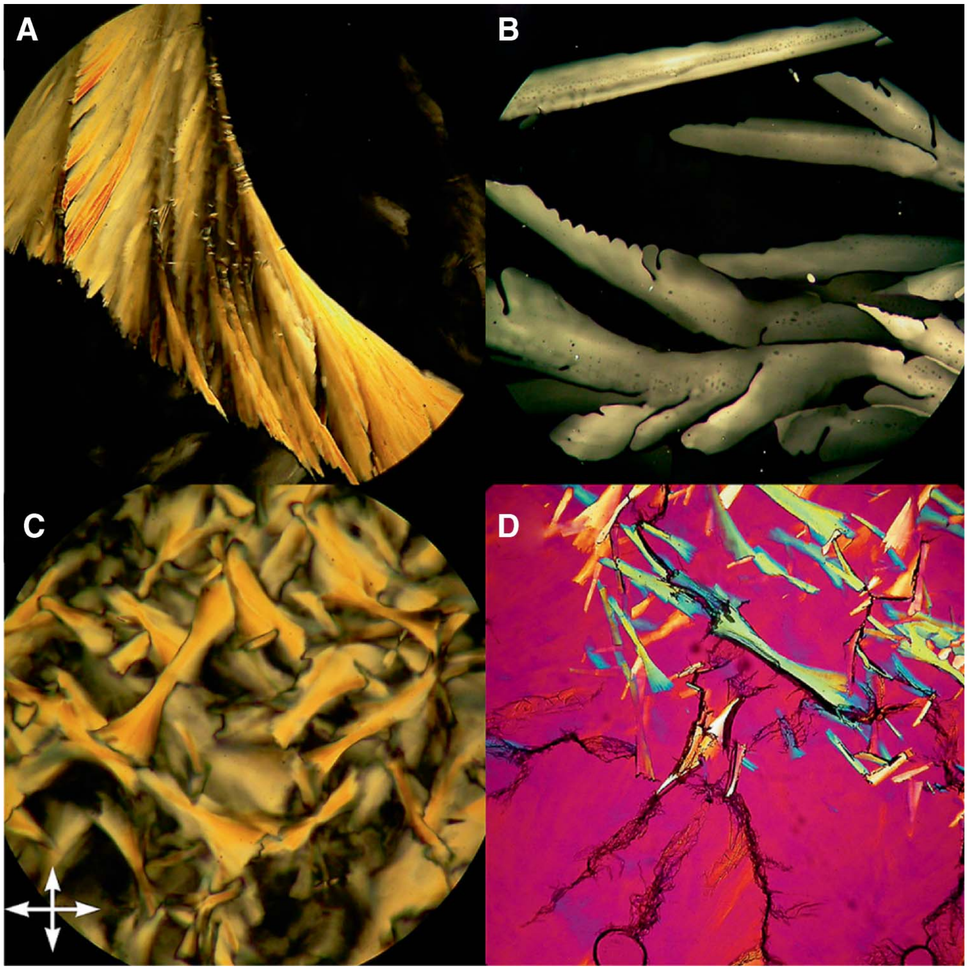


Figure 3. Optical textures of **1a** obtained on cooling: (A) and (B) at 10°C/min, (C) at >>10°C/min, (D) crystallisation with an additional lambda plate.

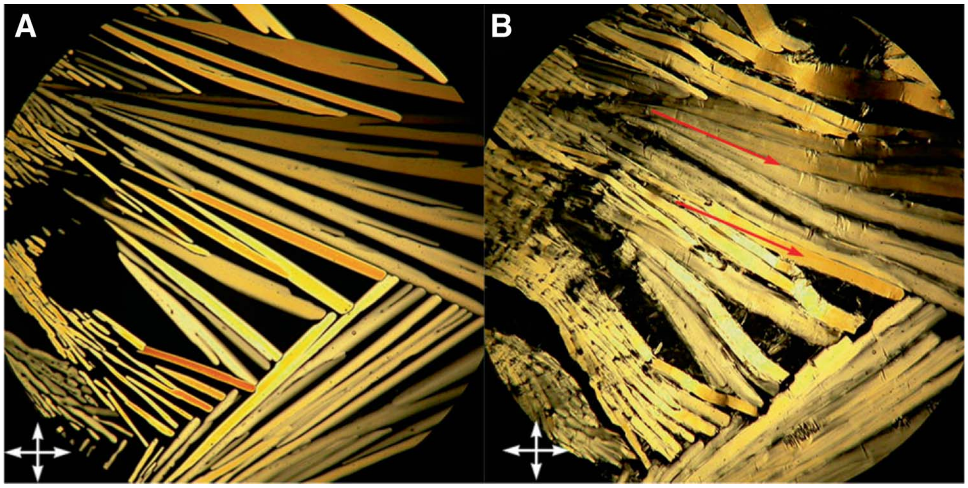


Figure 4. Optical textures of the columnar mesophase of a thick sample of **1a**: (A) without shearing, (B) after shearing, arrows indicate direction.

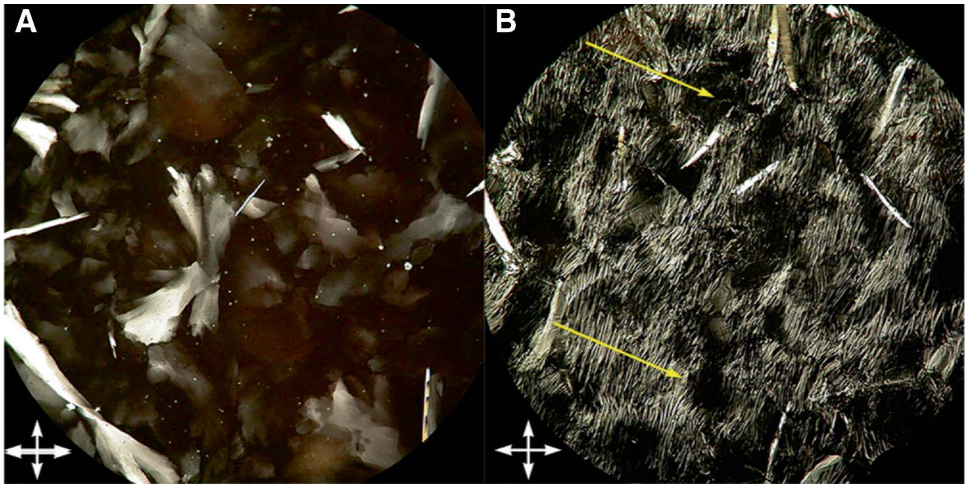


Figure 5. Optical textures of the columnar mesophase of a thin sample of **1a**: (A) without shearing, (B) after shearing, arrows indicate direction.

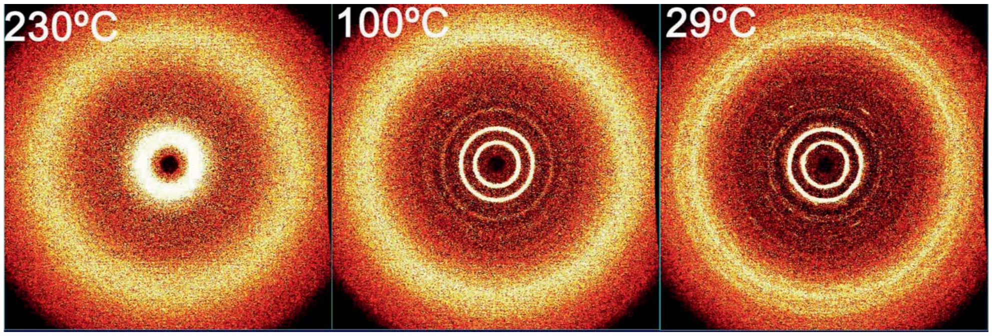


Figure 6. Two-dimensional X-ray diffraction patterns of **1a** – isotropic at 230°C, columnar at 100°C, crystalline at 29°C.

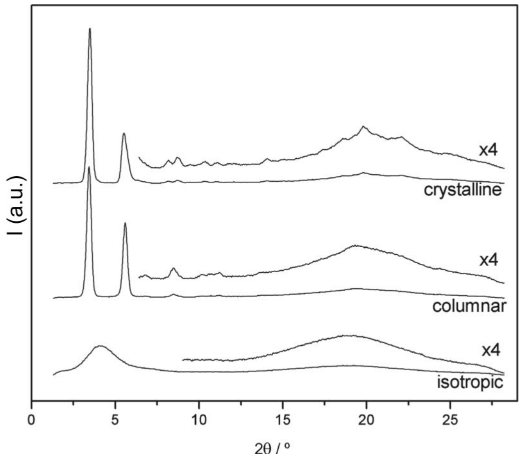


Figure 7. Normalised radial scans of wide-angle X-ray diffraction patterns of **1a**: isotropic at 230°C, columnar at 100°C and crystalline phase at 29°C (wide-angle area was magnified 4×).

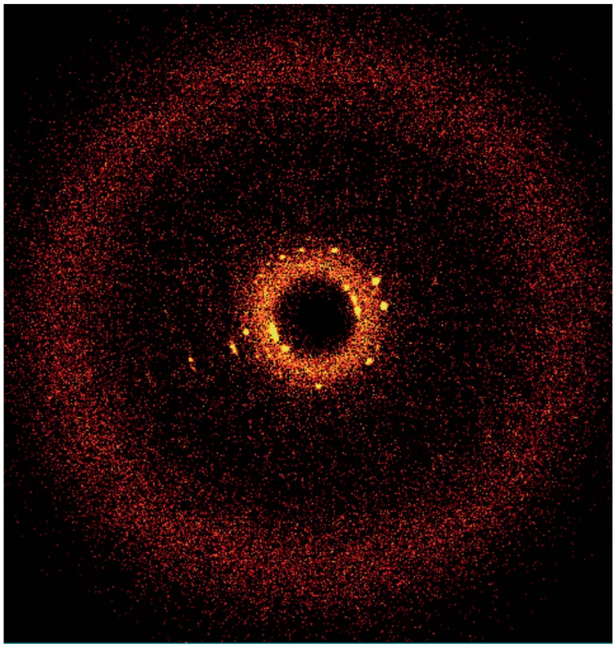


Figure 8. The two-dimensional diffraction pattern of a partially aligned sample of **1a** at 184°C.

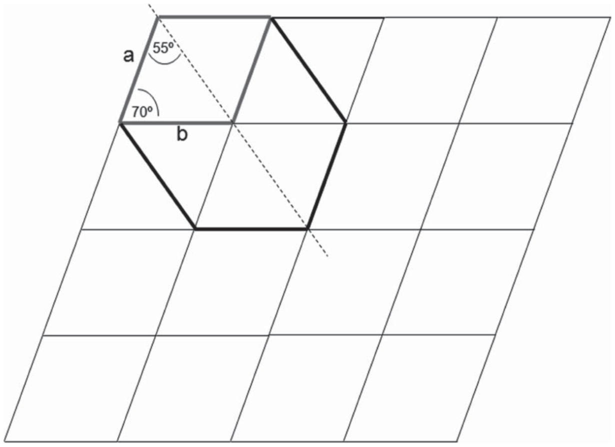


Figure 9. Schematic representation of the monoclinic cell.

Indexing of the 2D lattice of the columnar phase at 100°C gave a monoclinic cell with approximate cell parameters $a = 26.8$, $b = 27.3$, $c = 4.75$ and the angle between a and b equal to 70° (see Figure 9). This should give peaks at azimuthal angles of 70° and 55°.

In our experimental azimuthal scans multiple peaks with several angles occurring rather frequently were observed. These reflections and a table with average distances between them are shown in Figure 10. This again is a clear indication that the phase is not hexagonal, as otherwise only 60° or multiples thereof would be found. The peak locations, however, do not reveal the expected 70° and 55° values; this may be due to the difference in temperature, as the indexing was performed on a sample at 100°C while azimuthal scans were recorded at 184°C. Unfortunately at 184°C the number of visible peaks is insufficient to accurately determine the columnar lattice parameters. Differences may also arise from defects in domains and a tilt of the molecules in the column, which additionally complicates the analysis of these results.

3. Discussion and conclusions

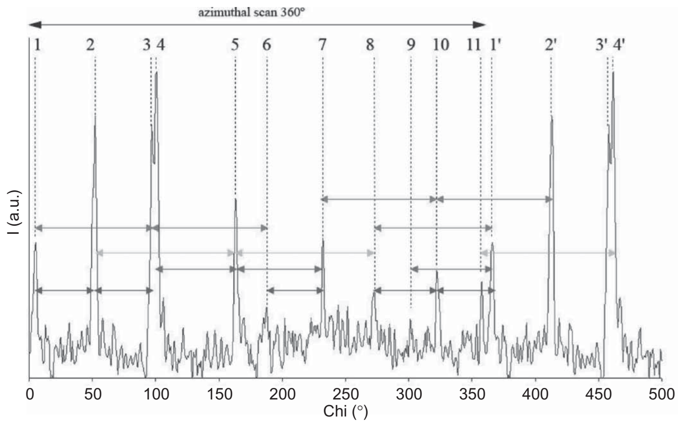
We have synthesised **1a** and **1b**, the first triphenylenes substituted with symmetric 3,5-dialkoxy benzoates, in high yields by a Steglich esterification. Only compound **1a** exhibits mesomorphic behaviour, but in contrast to most benzoate substituted triphenylates, this compound does not exhibit a nematic discotic (N_D) phase. Instead, a distorted hexagonal columnar phase with angles of 55° and 70° was observed. The most striking characteristic of this mesophase, in comparison with the commonly observed columnar hexagonal (Col_h) phase, was a strongly increased lateral order. Along with the increased lateral order, a very low order in the columnar direction was found. The observed 4.75 Å disc–disc distance is indicative of tilting of the aromatic cores with respect to the columnar axis, which is very commonly observed for triphenylenes in the crystalline state [25, 26], but has not been reported frequently for columnar discotic triphenylenes [18, 25]. The increased lateral intercolumnar order leads to formation of unusual textures in OPM and development of multiple reflections in WAXS measurements. Such features would be normally assigned to the crystalline phase. In this case, however, the disks are mobile and highly disordered in the columnar direction, which was also demonstrated by the flow behaviour and the absence of a 001 reflection in WAXS investigations.

4. Experimental details

The mesomorphic behaviour of liquid crystalline materials has been examined by a combination of various techniques listed bellow.

4.1 Optical polarisation microscopy

Identification of optical textures and related transition temperatures were analysed by a Nikon Eclipse E600



Average distance [°]	Between reflections
50	1-2
	2-3
	6-7
	8-10
	10-1'
60	4-5
	5-7
	9-1'
100	1-3
	3-6
	7-10
	10-2'
	8-1'
110	2-5
	5-8
	11-4'

Figure 10. X-ray azimuthal scan of d110 = 15.6Å reflection and a table with average distances between reflections.

optical polarisation microscope with a Nikon Coolpix 4500 digital camera and using a Mettler FP 82HT hot stage with Mettler FP80 controller. Samples have been placed between two glass slides. Prior to measurement each sample was heated above the clearing temperature. All photographs of liquid crystalline textures shown in this paper were made upon cooling.

4.2 *Differential scanning calorimetry*

The thermal properties of materials were investigated by a Perkin-Elmer DSC 7 differential scanning calorimeter in a nitrogen atmosphere at a heating and cooling rate of 10°C/min. The transition temperatures were determined as the maximum or minimum of the exotherm or endotherm.

4.3 *Wide-angle X-ray scattering*

Measurements were performed on a Bruker-Nonius D8-Discover setup with a 2D detector. Monochromatic CuKα radiation with a wavelength of 0.154 nm was used. Samples were placed in standard glass 0.7 mm X-ray capillaries and the temperature was controlled in a small graphite tube heating element which was mounted between the polecaps of the magnet (10 mK stability, 20–350°C range, up to 100°C/min heating and cooling rate). The broad halo at 26° comes from the integration procedure because at wide angles part of the scattered beam falls outside the detector grid.

4.4 *Triphenylen-2,3,6,7,10,11-hexayl hexakis (3,5-didodecyloxy)benzoate, 1b*

The N,N′-dicyclohexylcarbodiimide (0.9 g; 4.37 mmol) was added to a stirred mixture of 2,3,6,7,10,11-hexahydroxytriphenylene (0.1g; 0.309 mmol), 3,5-didodecyloxybenzoic acid (1g; 1.85 mmol) and 4-dimethylaminopyridine (0.45 g; 3.68 mmol) in dry THF at room temperature. Stirring was continued overnight. The solvent was then removed and the residue was extracted with ethyl acetate and washed with water. After removing the ethyl acetate, the ethanol was added followed by an excess of hydrazine hydrate (10×). The reaction mixture was slowly heated to 70°C and refluxed overnight. The crude product, a yellow oil, was filtered through the short silica gel column (CH_2Cl_2) and purified on the chromatography column (silica gel, CH_2Cl_2/petroleum ether 80:20) yielding 0.67 g of pure **1b** (70%).

^{1}H NMR (300MHz, $CDCl_3$): δ0.89 (t, CH_3, 36H); 1.28-1.63 (m, CH_2, 144H); 3.62 (s, OCH_2, 24H); 6.47 (s, ArH, 6H); 6.98 (s, ArH, 12H); 8.39(s, ArH, 6H) ppm.

4.5 *Triphenylen-2,3,6,7,10,11-hexayl hexakis (3,5-dihexyloxy)benzoate, 1a*

1a was prepared in the same way as **1b** using 3,5-dihexyloxybenzoic acid, yielding 0.65 g (97%) of pure product.

^{1}H NMR (300MHz, $CDCl_3$): δ0.90 (t, CH_3, 36H); 1.31-1.62 (m, CH_2, 96H); 3.58 (s, OCH_2, 24H); 6.44 (s, ArH, 6H); 6.96 (s, ArH, 12H); 8.35(s, ArH, 6H) ppm.

^{13}C NMR (75MHz, $CDCl_3$): δ14.6 (CH_3); 22.64-31.74 (CH_2); 68.05 (OCH_2); 107.49 (d, Ar-H, benzene), 118.90 (Ar-H, triphenylene), 127.51 (Ar-Ar, triphenylene), 130.37 (Ar-(C=O), benzene) 142.20 (ArO, triphenylene), 159.86 (ArO, benzene) 164.24 (C=O) ppm.

References

[1] Kumar, S. *Liq. Cryst.* **2004**, *31*, 1037–1059.

[2] Kumar, S. *Chem. Soc. Rev.* **2006**, *35*, 83–109.

[3] Kumar, S. *Liq. Cryst.* **2005**, *32*, 1089–1113.

[4] Adam, D.; Schuhmacher, P.; Simmerer, J.; Haussling, L.; Siemensmeyer, K.; Etzbach, K.H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141–143.

[5] Bushby, R.J.; Donovan, K.J.; Kreouzis, T.; Lozman, O.R. *Opto-Electr. Rev.* **2005**, *13*, 269–279.

[6] Warman, J.M.; Schouten, P.G. *J. Phys. Chem.* **1995**, *99*, 17181–17185.

[7] Bisoyi, H.K.; Kumar, S. *Chem. Soc. Rev.* **2010**, *39*, 264–285.

[8] Praefcke, K.; Kohne, B.; Singer, D. *Angew. Chem. Int. Ed.* **1990**, *29*, 177–179.

[9] Kouwer, P.H.J.; Jager, W.F.; Mijs, W.J.; Picken, S.J. *Macromolecules* **2000**, *33*, 4336–4342.

[10] Kumar, S.; Varshney, K.S. *Angew. Chem. Int. Ed.* **2000**, *39*, 3140–3142.

[11] Demus, D.; Goodby, J.W.; Gray, G.W.; Spiess, H.W.; Vill, V. *Handbook of Liquid Crystals, Four Volume Set*; Wiley-VCH: Weinheim, 1998.

[12] Tinh, N.H.; Gasparoux, H.; Destrade, C. *Mol. Cryst. Liq. Cryst.* **1981**, *68*, 101–111.

[13] Hindmarsh, P.; Hird, M.; Styring, P.; Goodby, J.W. *J. Mater. Chem.* **1993**, *3*, 1117–1128.

[14] Phillips, T.J.; Jones, J.C.; Mcdonnell, D.G. *Liquid Crystals* **1993**, *15*, 203–215.

[15] Favre-Nicolin, C.D.; Lub, J. *Macromolecules* **1996**, *29*, 6143–6149.

[16] Favre-Nicolin, C.D.; Lub, J.; van der Sluis, P. *Adv. Mater.* **1996**, *8*, 1005–1008.

[17] Hindmarsh, P.; Watson, M.J.; Hird, M.; Goodby, J.W. *J. Mater. Chem.* **1995**, *5*, 2111–2123.

[18] Zniber, R.; Achour, R.; Zoubair Cherkaoui, M.; Donnio, B.; Gehringer, L.; Guillon, D. *J. Mater. Chem.* **2002**, *12*, 2208–2212.

[19] Heppke, G.; Kruerke, D.; Lohning, C.; Lotzsch, D.; Moro, D.; Muller, M.; Sawade, H. *J. Mater. Chem.* **2000**, *10*, 2657–2661.

[20] Pickaert, G.; Ziessel, R. *Synthesis* **2004**, *16*, 2716–2726.

[21] Beattie, D.R.; Hindmarsh, P.; Goodby, J.W.; Haslam, S.D.; Richardson, R.M. *J. Mater. Chem.* **1992**, *2*, 1261–1266.

[22] Boden, N.; Bushby, R.J.; Cammidge, A.N. *J. Chem Soc., Chem. Commun.* **1994**, 465–466.

[23] Krebs, F.C.; Schmidt, N.C.; Batsberg, W.; Bechgaard, K. *Synthesis* **1997**, *11*, 1285–1290.

[24] Dierking, I. *Textures of Liquid Crystals*; Wiley-VCH: Weinheim, 2003.

[25] Takabatake, M.; Iwayanagi, S. *Jap. J. Appl. Phys.* **1982**, *21*, 685–686.

[26] Boden, N.; Bushby, R.J.; Jesudason, M.V.; Sheldrick, B. *J. Chem Soc., Chem. Commun.* **1988**, 1342–1343.