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## Liquid Crystals

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# Columnar liquid crystals derived from ester-substituted tetraphenylenes

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We report the synthesis and liquid crystalline properties of novel ester-substituted tetraphenylenes obtained from octamethoxytetraphenylene by demethylation and esterification. The target compounds display focal-conic textures typical for columnar mesophases, which are either rectangular or hexagonal columnar in nature, depending on the alkyl chain length.

## 1. Introduction

Tetraphenylenes and their derivatives provide an interesting scaffold for both supramolecular chemistry and material science, due to their saddle shape [1], the high tendency to form inclusion complexes [2], and the various possibilities to functionalize the four aromatic rings [3]. Recently, we have reported that octaalkyloxy-substituted tetraphenylenes form columnar and smectic mesophases, depending on the alkyloxy chain length [4]. Based on these results the question arose whether the replacement of alkyloxy groups by ester functions would have a major influence on the mesomorphic properties of the tetraphenylenes. When comparing ether and ester derivatives of a particular mesogen, strikingly different results have been reported in the literature. Whereas esters of flat columnar systems such as triphenylene and rufigallol display a significant increase of both melting and clearing points, in comparison with the corresponding ethers, cone-shaped columnar systems behaved completely differently. For example, the replacement of ether groups by ester moieties in tribenzocyclononatrienes and tetrabenzocyclododecatetraenes caused the increase of clearing points only, while the melting points remained almost constant, thus resulting in an overall increase of the mesophase width [5]. Therefore, we have turned our attention to the synthesis and mesomorphic properties of ester-substituted tetraphenylenes and here we report the results of our investigations.

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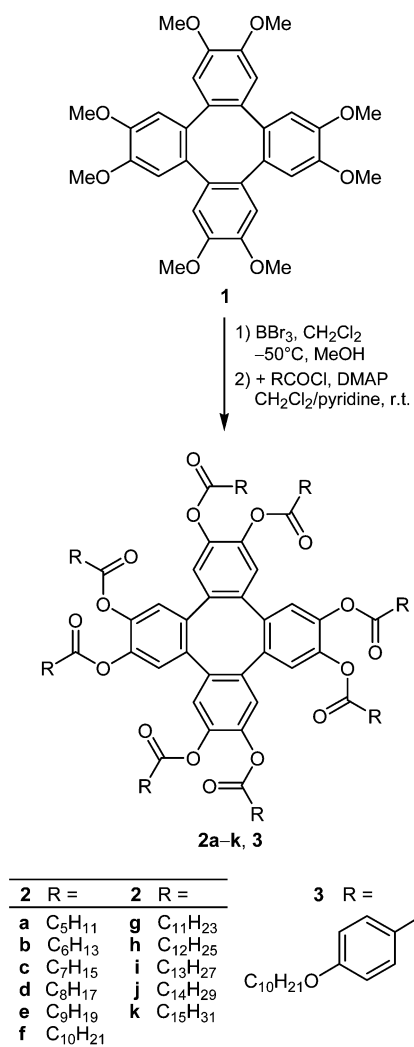
## 2. Experimental

### 2.1. Characterization

DSC was performed using a Mettler Toledo DSC822, and polarizing microscopy using an Olympus BX50 polarizing microscope combined with a Linkam LTS350 hot stage and a Linkam TP93 central processor. X-ray experiments were performed with Ni-filtered  $\text{CuK}_\alpha$  radiation (wavelength 1.5418 Å). Small angle scattering data from unaligned samples (filled into Mark capillary tubes of 0.7 mm diameter) were obtained using a Kratky compact camera (A. Paar) equipped with a temperature controller (A. Paar) and a one-dimensional electronic detector (M. Braun). Aligned samples were exposed in a home-made flat film camera and the 2D diffraction patterns recorded with an imaging plate detector (Fuji BAS SR). In the flat film camera, the sample was placed in a small hole in a brass block, whose temperature was controlled by a Lakeshore controller and kept in a 1.5 T magnetic field for alignment.

### 2.2. Synthesis

A 1 M solution of  $\text{BBr}_3$  in  $\text{CH}_2\text{Cl}_2$  (1.05 mmol) was added to compound **1** (1 mmol) (see scheme 1) at  $-50^\circ\text{C}$  under inert gas atmosphere. After stirring at room temperature for 1 h, the reaction mixture was evaporated at  $60^\circ\text{C}$  under vacuum (10 mbar) and then hydrolysed with absolute degassed MeOH ( $5\text{ ml mmol}^{-1}$  **1**). After removal of all volatile materials at  $60^\circ\text{C}$  under vacuum (10 mbar), the residue was dissolved in abs. degassed  $\text{CH}_2\text{Cl}_2$ /pyridine (5 ml each)



Scheme 1. Synthesis of octaalkyloxytetraphenylenes **2a–k**.

and added to the respective acid chloride (0.5 mmol) and catalytic amounts of DMAP. The reaction mixture was stirred under inert gas atmosphere at r.t. for 12 h and hydrolysed with a 2 M aqueous solution of HCl. The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 ml). The combined organic layers were washed with a satd solution of NaHCO<sub>3</sub> and water, dried (MgSO<sub>4</sub>) and concentrated. The crude products were purified by chromatography on SiO<sub>2</sub> with hexanes/ethyl acetate (15/1) as eluent.

**2a**: yield 35%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 7.03 s (8H, Ph–H); 2.49 t (16H, CH<sub>2</sub>); 1.74–1.68 m (16H, CH<sub>2</sub>); 1.41–1.31 m [48H, (CH<sub>2</sub>)<sub>3</sub>]; 0.91 t (24H, CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): 13.9 (CH<sub>3</sub>); 22.3, 24.6, 31.3, 34.1 (CH<sub>2</sub>); 124.5, 137.8, 141.5 (Ph); 170.7 (CO). IR (neat)  $\nu_{\max}/\text{cm}^{-1}$ : 2931 (s), 2859 (s), 1763 (vs), 1508 (m), 1489 (m), 1465 (s), 1381 (s), 1269 (m),

1226 (m), 1131 (vs), 928 (s), 727 (m), 604 (m). Anal: calcd for C<sub>72</sub>H<sub>96</sub>O<sub>16</sub> C 71.03, H 7.95; found C 70.99, H 7.88%.

**2b**: yield 34%. Anal: calcd for C<sub>80</sub>H<sub>112</sub>O<sub>16</sub> C 72.26, H 8.49; found C 72.18, H 8.47%.

**2c**: yield 57%. Anal: calcd for C<sub>88</sub>H<sub>128</sub>O<sub>16</sub> C 73.30, H 8.95; found C 73.55, H 8.99%.

**2d**: yield 52%. Anal: calcd for C<sub>96</sub>H<sub>144</sub>O<sub>16</sub> C 74.19, H 9.34; found C 74.24, H 9.35%.

**2e**: yield 55%. Anal: calcd for C<sub>104</sub>H<sub>160</sub>O<sub>16</sub> C 74.96, H 9.68; found C 75.01, H 9.72%.

**2f**: yield 47%. MS (ESI-Tof) *m/z*: 912.14 [M+2 Na<sup>+</sup>]. Anal: calcd for C<sub>112</sub>H<sub>176</sub>O<sub>16</sub> C 75.63, H 9.97; found C 75.52, H 9.96%.

**2g**: yield 45%. Anal: calcd for C<sub>120</sub>H<sub>192</sub>O<sub>16</sub> C 76.23, H 10.24; found C 76.31, H 10.11%.

**2h**: yield 41%. MS (ESI-Tof) *m/z*: 1024.26 [M+2 Na<sup>+</sup>]. Anal: calcd for C<sub>128</sub>H<sub>208</sub>O<sub>16</sub> C 76.75, H 10.47; found C 76.59, H 10.54%.

**2i**: yield 48%. MS (ESI-Tof) *m/z*: 1080.32 [M+2 Na<sup>+</sup>]. Anal: calcd for C<sub>136</sub>H<sub>224</sub>O<sub>16</sub> C 77.22, H 10.67; found C 77.36, H 10.72%.

**2j**: yield 36%. MS (ESI-Tof) *m/z*: 1136.39 [M+2 Na<sup>+</sup>]. Anal: calcd for C<sub>144</sub>H<sub>240</sub>O<sub>16</sub> C 77.65, H 10.86; found C 77.83, H 10.90%.

**2k**: yield 20%. MS (ESI-Tof) *m/z*: 1192.45 [M+2 Na<sup>+</sup>]. Anal: calcd for C<sub>152</sub>H<sub>256</sub>O<sub>16</sub> C 78.03, H 11.03; found C 78.22, H 11.11%.

**3**: yield 10%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 7.99 d (16H, Ph–H); 7.37 s (8H, Ph–H); 6.83 d (16H, Ph–H); 3.97 t (16H, OCH<sub>2</sub>); 1.80–1.75 m (16H, CH<sub>2</sub>); 1.47–1.41 m (16H, CH<sub>2</sub>); 1.34–1.27 m [96H, (CH<sub>2</sub>)<sub>6</sub>]; 0.88 t (24H, CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): 14.1 (CH<sub>3</sub>); 22.7, 26.0, 29.3, 29.4, 29.6, 31.9 (CH<sub>2</sub>); 68.3 (OCH<sub>2</sub>); 114.2, 121.0, 124.7, 132.4, 138.1, 142.2, 163.5 (Ph); 163.6 (CO). IR (neat)  $\nu_{\max}/\text{cm}^{-1}$  2921 (s), 2852 (s), 1733 (s), 1510 (m), 1467 (m), 1395 (m), 1246 (vs), 1167 (vs), 1131 (vs), 1065 (vs), 1006 (m), 844 (m), 760 (s), 689 (m), 658 (m). MS (ESI-Tof) *m/z*: 1280.23 [M+2 Na<sup>+</sup>]. Anal: calcd for C<sub>160</sub>H<sub>208</sub>O<sub>24</sub> C 76.40, H 8.33; found C 76.65, H 8.42%.

### 3. Results and discussion

As shown in the scheme, octamethoxytetraphenylene (**1**) which is accessible in a three-step reaction from 4-bromoveratrol, according to our previous procedure, serves as starting material. Demethylation was achieved by treatment of **1** with BBr<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at –50°C. Subsequent esterification with the respective acid chlorides in the presence of catalytic amounts of DMAP gave the octaesters **2a–k** in 30–60% yield. The 4-decyloxybenzoate **3** was prepared by analogy from **1** in 10% yield (not optimized).

The mesomorphic properties of tetraphenylenes **2a–k** and **3** were studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The results of the DSC experiments are summarized in table 1.

Whereas the pentyl-substituted ester **2a** displayed only a crystal to crystal transition at 106°C and isotropic melting at 112°C on heating, for the corresponding derivatives **2b–k** two endothermic peaks were observed, i.e. a melting transition into the mesophase and a clearing transition. Both melting and clearing transition show substantial supercooling (table 1). In the case of esters **2d–k** an additional endothermic crystal to crystal transition was detected. The phase transition was enantiotropic. Crystal to crystal transitions were not visible during the cooling cycles. POM reveals focal-conic textures typical for columnar mesophases for all derivatives **2b–k** as well as **3** on cooling from the isotropic phase. Some characteristic examples of textures are shown in figures 1–4.

The structures of the mesophases in **2b**, **2e**, and **2i** were investigated by small angle X-ray scattering (SAXS). In the case of the higher homologues **2e** and **2i**, two distinct scattering peaks were observed, the  $d$ -spacings of which accurately match the characteristic ratio of  $1 : 1/\sqrt{3}$  of the (10) and (11) reflections in 2D hexagonal columnar mesophases ( $\text{Col}_h$ ,  $P_6 2/m 2/m$ ).

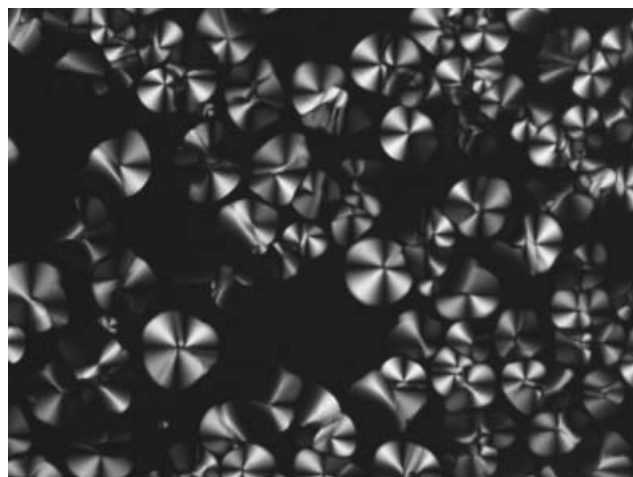


Figure 1. Mesophase texture of derivative **2b** at 62°C, on cooling from the isotropic phase ( $0.5 \text{ K min}^{-1}$ , magnification  $100\times$ ).

Further details concerning the  $\text{Col}_h$  phases of **2e** and **2i** are listed in table 2.

In the case of the homologue **2b** with a shorter alkyl chain the situation is different. We now observe three incommensurate small angle reflections with  $d$ -values of 18.5, 16.2 and 12.9 Å (figure 5). The ratios 1:1.14:1.43 of these  $d$ -values together with the splitting of the leading small angle reflection into a doublet are incompatible

Table 1. Transition temperatures (°C) and associated enthalpies ( $\text{kJ mol}^{-1}$ ) of ester-substituted tetraphenylenes **2a–k**. Cr=crystal, Col=columnar mesophase, I=isotropic liquid.

Compound	Cr <sub>1</sub>	Cr <sub>2</sub>	Col	I	Cycle (first)
<b>2a</b>	• 106 (0.99)	• 112 (14.2)	—	•	heating
<b>2b</b>	• 45 (32.0)	—	• 75 (7.52)	•	heating
<b>2c</b>	• 67 (103.1)	—	• 88 (3.66)	•	heating
	—	• 30 (−46.6)	• 85 (−8.31)	•	cooling
<b>2d</b>	• 44 (51.9)	• 52 (44.8)	• 89 (11.0)	•	heating
	—	• 8 (−17.1)	• 84 (−9.99)	•	cooling
<b>2e</b>	• 15 (9.09)	• 58 (121)	• 93 (12.2)	•	heating
	—	• 29 (−84.7)	• 92 (−11.4)	•	cooling
<b>2f</b>	• 11 (9.58)	• 59 (128)	• 93 (11.8)	•	heating
	—	• 28 (−90.7)	• 92 (−12.3)	•	cooling
<b>2g</b>	• 62 (81.3)	• 63 (31.7)	• 95 (11.9)	•	heating
	—	• 42 (−131.7)	• 93 (−12.3)	•	cooling
<b>2h</b>	• 45 (28.0)	• 67 (130)	• 93 (13.9)	•	heating
	—	• 40 (−126)	• 93 (−13.3)	•	cooling
<b>2i</b>	• 20 (34.3)	• 77 (158)	• 89 (11.9)	•	heating
	—	• 48 (−162)	• 91 (−11.8)	•	cooling
<b>2j</b>	• −10 (63.6)	• 75 (138)	• 93 (14.9)	•	heating
	—	• 50 (−158)	• 91 (−14.1)	•	cooling
<b>2k</b>	• −10 (115)	• 80 (154)	• 88 (12.0)	•	heating
	—	• 57 (−223)	• 86 (−12.7)	•	cooling
<b>3</b>	• 109 (23.4)	—	• 134.7 (23.4)	•	heating
	—	• 114.6 (−31.0)	• 124.9 (−23.2)	•	cooling



Figure 2. Mesophase texture of derivative **2e** at 93°C, on cooling from the isotropic phase ( $5 \text{ K min}^{-1}$ , magnification  $100\times$ ).

with a hexagonal structure and clearly indicate the formation of a less symmetrical mesophase. In order to clarify the symmetry of this phase we further studied the 2D X-ray scattering of a **2b** sample aligned in a magnetic field. A typical diffraction pattern obtained at 70°C is shown in figure 6. The difference in the azimuthal scattering directions of adjacent small angle reflections in figure 6 varies between  $58^\circ$  and  $62^\circ$ , thereby showing only minor deviations from a perfect six-fold symmetry where  $60^\circ$  is expected. We therefore assume that the mesophase of **2b** has a distorted pseudo-hexagonal structure of rectangular symmetry ( $\text{Col}_r, P 2_1/a$ ). Further details on this phase are found in table 2. The possibility of a rectangular columnar phase



Figure 3. Mesophase texture of derivative **2i** at 85°C, on cooling from the isotropic phase ( $0.5 \text{ K min}^{-1}$ , magnification  $100\times$ ).

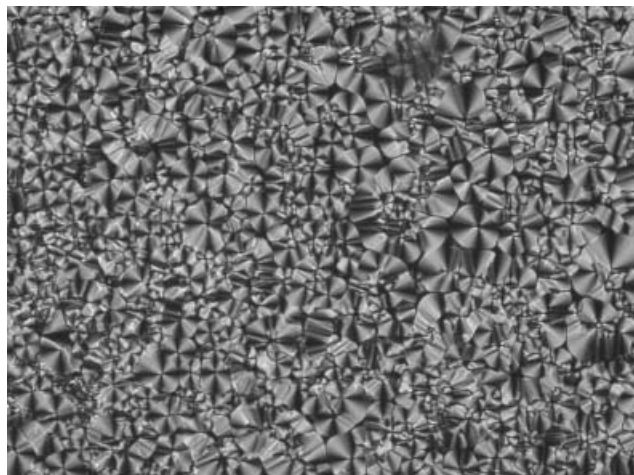


Figure 4. Mesophase texture of derivative **3** at 134°C on cooling from the isotropic phase ( $1 \text{ K min}^{-1}$ , magnification  $200\times$ ).

with the even lower symmetry  $P 2/a$  is excluded through the absence of, for example, (11) and (20) reflections with  $d$ -values higher than  $18.5 \text{ \AA}$  (see, for example, [6]).

In conclusion, mesogenic ester-substituted tetraphenylenes **2a–k** and **3** with alkyl chains of varying lengths have been prepared. All the derivatives, except **2a** display columnar mesophases. The X-ray investigations indicate a crossover from rectangular at short chain lengths to hexagonal columnar mesophases at longer alkyl chain lengths. A similar crossover has been observed in several columnar systems with increasing side chain lengths [7, 8].

In the case of C9–C16 alkyl chain length, an additional crystal to crystal transition was observed. In comparison with the previously reported tetraphenylene ethers, increased melting points and slightly increased

Table 2. Lattice parameters for the mesophases of **2b**, **2e** and **2i**.  $I$  is the intensity of the diffraction signal (vs: very strong, s: strong, w: weak);  $d_{\text{obs}}$  and  $d_{\text{calcd}}$  denote the observed and the calculated diffraction spacings, respectively;  $hk$  is the indexation of the 2D lattice with symmetry and lattice parameters  $a$ ,  $b$  listed in the last column.

Compound	$T/^\circ\text{C}$	$d_{\text{obs}}/\text{\AA}$	$I$	$hk$	$d_{\text{calcd}}/\text{\AA}$	Mesophase and lattice parameters
<b>2b</b>	57	18.5	vs	(20)	18.5	$\text{Col}_r, P 2_1/a$ $a=37.0 \text{ \AA}$ $b=18.0 \text{ \AA}$
		16.2	s	(11)	16.2	
		12.9	w	(21)	12.9	
<b>2e</b>	80	19.4	vs	(10)	19.3	$\text{Col}_h, P_6 2/m 2/m$ $a=22.3 \text{ \AA}$
		11.2	w	(11)	11.2	
<b>2i</b>	85	22.2	vs	(10)	22.2	$\text{Col}_h, P_6 2/m 2/m$ $a=25.6 \text{ \AA}$
		12.8	w	(11)	12.8	

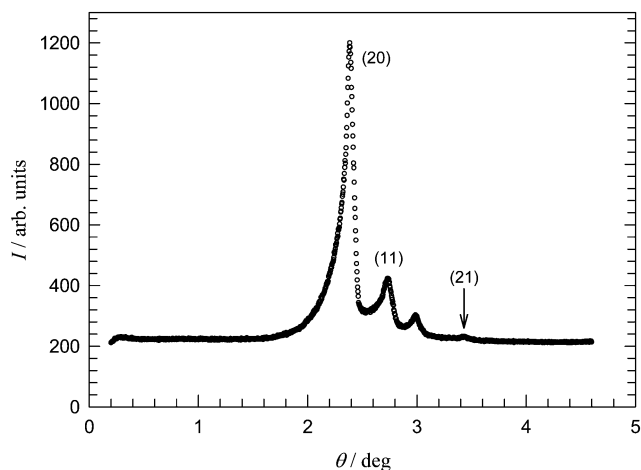


Figure 5. SAXS profile from the  $\text{Col}_r$  mesophase of the derivative **2b** at  $57^\circ\text{C}$  showing (20), (11) and (21) reflections due to the long range intercolumnar ordering. The remaining scattering maximum at  $\theta \approx 3^\circ$  is a satellite peak of the strong (20) reflection which originates from parasitic  $\text{FeK}_\alpha$  radiation.

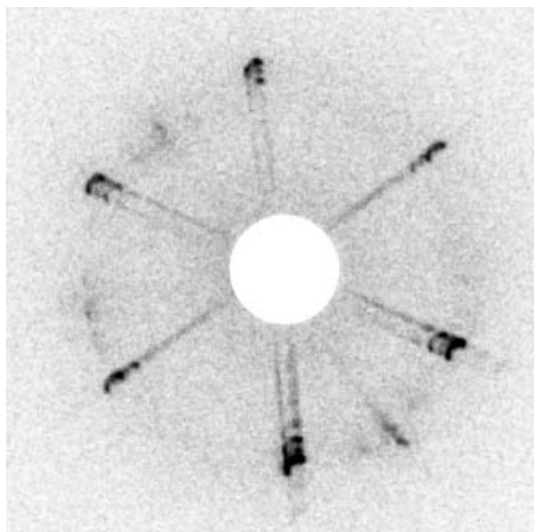


Figure 6. 2D diffraction pattern of the small angle scattering from the columnar mesophase of **2b** ( $70^\circ\text{C}$ ) showing a slightly distorted pseudo-hexagonal symmetry. The sample was aligned by a magnetic field applied in a vertical direction.

clearing points of the corresponding esters **2b–k** were observed. Thus, the overall mesophase width was reduced on exchanging ethers by esters.

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