Saddle-shaped tetraphenylenes with peripheral gallic esters displaying columnar mesophases

Eugen Wuckert¹, Constanze Hägele², Frank Giesselmann², Angelika Baro¹ and Sabine Laschat*¹

Abstract

Tetraphenylenes 2 with eight peripheral gallic esters were prepared in two steps from octamethoxytetraphenylenne 1 in 19–72% yield. Investigation of the mesomorphic properties of 2 by DSC, POM and X-ray diffraction revealed that derivatives 2a–d with short alkoxy chain lengths (C₅–C₈) did not show any mesomorphic properties, whereas compounds 2e–i with C₉–C₁₃ chains displayed rectangular columnar mesophases and compounds 2j–l with C₁₄–C₁₆ chains displayed hexagonal columnar mesophases. Furthermore an anomalous odd-even effect of the clearing points of compounds 2e–l versus chain length was detected.

Introduction

Columnar liquid crystals have received increasing interest during the last decade due to their 1D charge transport and self-healing properties, which make them particularly promising candidates for organic field effect transistors, organic photovoltaic devices and light emitting diodes [1-3]. Tetraphenylenes, whose saddle-shaped conformation is caused by the anti-aromatic character of the corresponding central flat 8-membered ring [4-6], are suitable building blocks for supramolecular chemistry, asymmetric catalysis and formation of inclusion complexes [3-28]. We have shown that tetraphenylenes with eight peripheral alkoxy or alkanoate chains display thermotropic columnar and smectic mesophases [29,30]. Furthermore, anomalous odd-even effects were discovered for these discotic tetraphenylenes, i.e. the ascending and descending transition temperatures with increasing numbers of methylene groups in the side chain exhibit an inversion of this alternation between \( n = 12 \) and \( n = 14 \) homologues [31]. In order to explore whether this anomalous odd-even effect is a more general phenomenon, the corresponding gallic ester-substituted tetraphenylenes were prepared and their liquid crystalline properties were investigated. In addition, we were curious about the mesophase types, because tetraphenylenes with peripheral alkoxy or alkanoate
chains displayed smectic mesophases in addition to columnar phases, whereas the corresponding tetraphenylenes with $p$-alkoxybenzoate substituents displayed only columnar mesophases even with long chain lengths [29-31]. Thus, we anticipated that the presence of the sterically demanding gallic esters in the periphery of the tetraphenylene can be accommodated much better by columnar packing as compared to a smectic layer structure. The results are discussed below.

**Results and Discussion**

The synthesis started from the known octamethoxytetraphenylene 1 [4,19,20,29-31], which was demethylated with boron tribromide in CH$_2$Cl$_2$ at $-50$ °C to room temp. followed by hydrolysis with MeOH (Scheme 1). Subsequent treatment with gallic acid chlorides in the presence of catalytic amounts of DMAP in pyridine/CH$_2$Cl$_2$ yielded after aqueous workup and chromatographic purification the desired gallic ester-substituted tetraphenylenes 2a-l in 19–72%. In some cases purification turned out to be rather tedious resulting in decreased yields.

Mesomorphic properties of compounds 2 were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (WAXS, SAXS). The DSC results are summarized in Table 1.

While compounds 2a–d with chain lengths up to C$_8$ showed only crystal to crystal transitions and isotropic melting, tetraphenylenes 2e–i with chain lengths between C$_9$ and C$_{16}$ displayed enantiotropic mesomorphism. For compounds 2e,f additional crystal to crystal transitions were detected. A typical DSC curve is shown in Figure 1. Thus tetraphenylene 2h with dodecyl chains displays a melting transition at 3 °C and a clearing transition at 36 °C upon second heating. Upon cooling an isotropic to mesophase transition at 33 °C and a crystallization peak at 0 °C were detected. The hysteresis phenomena observed for some compounds are probably due to supercooling, which is common for such highly viscous materials.

POM investigations revealed focal conic and fan-shaped textures typical for columnar mesophases (Figure 2).

However, clear evidence was possible only by XRD data, which are summarized in Table 2. While rectangular columnar mesophases were observed for tetraphenylenes 2e–i with shorter chains ($n=9–13$) (shown for 2f in Figure S1 in the Supporting Information), hexagonal columnar mesophases were found for the long chain derivatives 2j–l ($n=14–16$) (shown for 2j in Figure S2 in the Supporting Information). Indeed, as expected the columnar mesophase seems to accommodate the eight bulky gallic esters much better than the smectic layer structure.

**Scheme 1: Synthesis of tetraphenylenes 2.**

| 2   | a | b | c | d | e | f | g | h | i | j | k | l |
|-----|---|---|---|---|---|---|---|---|---|---|---|---|
| $n$ | 5 | 6 | 7 | 8 | 9 | 10| 11| 12| 13| 14| 15| 16|
| yield [%] | 28 | 72 | 65 | 28 | 69 | 68 | 68 | 19 | 65 | 62 | 40 | 49

**Figure 1: DSC traces of compound 2h during (a) second cooling and (b) second heating (heating/cooling rate 5 K/min).**
Table 1: Phase transition temperatures [°C] and (enthalpies [kJ/mol])

| 2  | n  | Cr₁   | Cr₂   | Cr₃   | Col     | I     |
|----|----|-------|-------|-------|---------|-------|
| a  | 5  | 51 (10.1) | 79 (4.4) | 191 (15.3) | --      | 2. heating |
| b  | 6  | 46 (8.3)   | 69 (7.4) | 142 (11.2) | --      | 2. heating |
| c  | 7  | 10 (1.7)   | 41 (0.6) | 55 (0.6)   | --      | 2. heating |
| d  | 8  | 4 (15.0)   | 41 (27.7) | 62 (7.2)   | --      | 2. heating |
| e  | 9  | --6 (11.6) | 35 (4.2) | --       | 37 (3.8) | 2. heating |
| f  | 10 | 1 (−2.7)   | 11 (−0.8) | --       | 26 (−5.3) | 2. cooling |
| g  | 11 | 7 (4.1)    | 40 (12.5) | --       | 46 (5.6) | 2. heating |
| h  | 12 | 24 (−7.9)  | --     | --       | 39 (−5.7) | 2. cooling |
| i  | 13 | 29 (7.4)   | --     | --       | 43 (1.0) | 2. heating |
| j  | 14 | 20 (−7.8)  | --     | --       | 40 (−1.1) | 2. cooling |
| k  | 15 | 3 (19.4)   | --     | --       | 36 (10.3) | 2. heating |
| l  | 16 | 0 (−18.6)  | --     | --       | 33 (−9.7) | 2. cooling |
| m  | 17 | 16 (18.5)  | --     | --       | 33 (11.9) | 2. heating |
| n  | 18 | 13 (−18.9) | --     | --       | 28 (−13.4) | 2. cooling |
| o  | 19 | 16 (9.6)   | --     | --       | 41 (2.5) | 2. heating |
| p  | 20 | 16 (−5.8)  | --     | --       | 29 (−1.8) | 2. cooling |
| q  | 21 | 25 (8.0)   | --     | --       | 36 (20.1) | 2. heating |
| r  | 22 | 20 (−10.3) | --     | --       | 32 (−16.2) | 2. cooling |
| s  | 23 | 22 (−5.2)  | --     | --       | 41 (36.2) | 2. heating |
| t  | 24 | 26 (−17.3) | --     | --       | 36 (−17.3) | 2. cooling |

Cr crystalline, Col columnar, I isotropic; • phase was observed, -- phase was not observed; heating/cooling rate 10 K/min for 2a–e,i,j, 5 K/min for 2f–h,k.l.

The crossover from rectangular columnar to hexagonal columnar mesophases with increasing chain lengths has been observed in other columnar systems [32,33] and has been attributed to the enhanced core–core interaction necessary for the formation of the Col phases [34]. According to molecular modelling [35] and comparison with the XRD data each disk within the hexagonal and rectangular columnar pattern is occupied by one tetraphenylene molecule. For better visibility only the modelled tetraphenylene (octakis)acyl core unit is shown in Figure 3, which reveals the saddle shape.

Next, the clearing points of mesogenic compounds 2e–l were plotted against the chain lengths n (Figure 4). An anomalous odd-even effect can be seen, which inverts at n = 11.
Table 2: X-Ray diffraction data for compounds 2e–l.

| 2  | $T$ [$^\circ$C] | $\theta$ [$^\circ$] | $d_{obs}$ [Å] | $hk$ | $d_{calc}$ [Å] | Mesophase parameters |
|----|----------------|---------------------|---------------|------|----------------|----------------------|
| 2e | 20             | 1.71                | 25.9          | (20) | 25.9           | Col$_r$              |
|    | 2.93           | 15.1                | (11)          | 15.1 |                |                      |
|    | 3.33           | 13.3                | (21)          | 13.5 |                |                      |
| 2f | 32             | 1.73                | 25.6          | (20) | 18.4           | Col$_r$              |
|    | 2.32           | 19.0                | (11)          | 19.0 |                |                      |
|    | 3.34           | 13.2                | (31)          | 13.1 |                |                      |
| 2g | 15             | 1.60                | 27.7          | (20) | 27.7           | Col$_r$              |
|    | 2.17           | 20.4                | (11)          | 20.4 |                |                      |
|    | 3.14           | 14.1                | (31)          | 14.1 |                |                      |
| 2h | 20             | 1.51                | 29.3          | (20) | 29.3           | Col$_r$              |
|    | 2.25           | 19.6                | (11)          | 19.6 |                |                      |
| 2i | 25             | 1.47                | 30.1          | (20) | 30.1           | Col$_r$              |
|    | 2.28           | 19.4                | (11)          | 19.4 |                |                      |
| 2j | 30             | 1.46                | 30.3          | (10) | 30.6           | Col$_h$              |
|    | 2.47           | 17.9                | (11)          | 17.7 |                |                      |
| 2k | 20             | 1.40                | 31.6          | (10) | 31.9           | Col$_h$              |
|    | 2.39           | 18.5                | (11)          | 18.4 |                |                      |
| 2l | 20             | 1.35                | 32.8          | (10) | 33.1           | Col$_h$              |
|    | 2.32           | 19.0                | (11)          | 19.1 |                |                      |
|    | 3.50           | 12.6                | (21)          | 12.5 |                |                      |

*a*Diffraction angle $\theta$; observed and calculated diffraction spacings $d_{obs}$ and $d_{calc}$; Miller indices $hk$.

For the previously studied tetraphenylene derivatives with alkoxy, alkanoate and $p$-alkoxybenzoate chains the inversion was observed at $n = 12$–13 [31]. Although in all four cases an anomalous odd-even effect is present, the chain length dependence of the clearing temperatures differs somewhat. For derivatives with alkoxy or alkanoate chains directly attached to the tetraphenylene unit, the oxygen atom is part of the chain and thus odd carbon chains are actually even-numbered. They should thus have an elongated shape which should lead to a higher degree of orientational order and hence a higher clearing temperature than the odd-numbered chains (including oxygen), i.e. those with an even-number of carbon atoms. The data in Figure 4 suggest that for 3,4,5-trialkoxygallic esters 2 this argument does not hold and the orientational order and hence the clearing temperature is determined both by the alkoxy chain lengths as well as the rigid gallic acid moiety. In order to eliminate the influence of the alkyl side chain on the odd-even effect of the tetraphenynes the melting temperatures $T_{m\text{alk}}$ of $n$-alkanes were subtracted from the clearing points $T_{cl}$ of the respective tetraphenynes 2 (Figure 5). An almost regular effect could be seen. Thus it seems that transition temperatures are also governed by the influence of the gallic ester moiety on the dynamic properties of the alkyl tails.

**Conclusion**

In conclusion, only columnar mesophases have been found for gallic ester-substituted tetraphenylenes 2e–l with a minimum chain length of $n = 9$. An anomalous odd-even effect was detected, in which the alternation of the melting transition inverses at $n = 11$. The results agree with previous findings, and
suggest that the anomalous odd-even effect is a more general phenomenon than previously thought. Investigations to extend this concept to other classes of liquid crystals are currently in progress.

### Experimental General

Melting points were measured on a Mettler Toledo DSC822 and are uncorrected. NMR spectra were recorded on a Bruker Avance 300 and Avance 500 spectrometer. FT-IR spectra were recorded on a Bruker Vektor22 spectrometer with MKII Golden Gate Single Reflection Diamant ATR system. Mass spectra were recorded on a Finnigan MAT 95 and a Varian MAT 711 apparatus. 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) provided 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 of a brass block, the temperature of which was controlled by a Lakeshore controller and kept in a 1.5 T magnetic field for alignment.

Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC822, and polarizing optical microscopy (POM) using an Olympus BX50 polarizing microscope combined with a Linkam LTS350 hot stage and a Linkam TP93 central processor. Flash chromatography was performed using Kieselgel 60, 40–63 μm (Fluka). All solvents were dried, and reactions were performed in dried glassware. The used petroleum ether (PE) had a boiling range of 30–75 °C. Octamethoxytetraphenylen e1 was prepared as described in ref. [31].

### General procedure for the preparation of heptakis[(3,4,5-trialkoxybenzoyl)oxy]tetraphenyl-2-yl 3,4,5-trialkoxybenzoates (2)

To a solution of octamethoxytetraphenylen e1 (0.14 g, 0.25 mmol) in CH₂Cl₂ (2 mL) were added BBr₃ (2.2 mL, 2.2 mmol, 1 M solution in CH₂Cl₂) at −50 °C and the mixture was stirred for 1 h at room temp. The solvent was removed in vacuo and the residue was dissolved in degassed MeOH (5 mL) for 1 h and evaporated. The residue was dissolved in CH₂Cl₂ (2 mL), treated with DMAP (4 mg, 0.03 mmol) and pyridine (1 mL) and gallic acid chloride (5 mmol) were added dropwise. After stirring overnight at 30 °C, the mixture was diluted with CH₂Cl₂ (10 mL), hydrolyzed with 2 M HCl and the layers separated. The aqueous layer was extracted with CH₂Cl₂ (2 × 10 mL), the organic layers were washed with sat. NaHCO₃ (10 mL), H₂O (10 mL), dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography on SiO₂ (hexanes/ethyl acetate 20 : 1) to yield colorless waxy solids.

3,6,7,10,11,14,15-Heptakis[(3,4,5-dodecyloxybenzoyl)oxy]tetraphenyl-2-yl 3,4,5-tridodecyloxybenzoate (2h)

270 mg (19%) of a colorless solid. ¹H NMR (500 MHz, CDCl₃): δ = 0.85–0.89 (m, 72H), 1.25–1.49 (m, 432H), 1.70–1.75 (m, 48H), 3.79–3.86 (m, 32H), 3.98 (t, J = 6.5 Hz, 16H), 7.24 (s, 16H), 7.39 (s, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 14.1, 22.7, 26.1, 29.4, 29.6, 29.7, 29.8, 29.8, 30.2, 30.2, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.2, 176.8 ppm. FT-IR (ATR): ν = 2921 (vs), 2852 (s), 1976 (w), 1743 (m), 1585 (m), 1499 (w), 1466 (w), 1430 (m), 1390 (w), 1335 (s), 1291 (w), 1240 (w), 1190 (s), 1114 (s), 947 (w), 802 (w), 748 (w), 623 (s), 454 (w) cm⁻¹. UV/VIS (n-hexane); λmax (lg εmax) = 275 (5.15), 214 (5.60) nm. C₃₆₈H₆₂₄O₄₀ (5688.9) calcd. C 77.69, H 11.06; found: C 77.74, H 10.95.

### Supporting Information

Supporting information includes experimental and spectroscopic data for compounds 2a–f, 2g–l, and X-ray diffraction measurements of derivatives 2f,l.

### Supporting Information File 1

Analytical data of compounds 2a–f, 2g–l.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-5-57-S1.pdf]
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