This article was downloaded by: [Selcuk Universitesi] On: 20 December 2014, At: 03:27 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/gmcl20</u>

Synthesis and Characterization of Triphenylene-Dione Half-Disc Mesogens

Alexander Paraskos ^a , Yutaka Nishiyama ^a & Timothy Swager ^a

^a Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA Published online: 18 Oct 2010.

To cite this article: Alexander Paraskos, Yutaka Nishiyama & Timothy Swager (2004) Synthesis and Characterization of Triphenylene-Dione Half-Disc Mesogens, Molecular Crystals and Liquid Crystals, 411:1, 363-375, DOI: <u>10.1080/15421400490435396</u>

To link to this article: http://dx.doi.org/10.1080/15421400490435396

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or

indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions



SYNTHESIS AND CHARACTERIZATION OF TRIPHENYLENE-DIONE HALF-DISC MESOGENS

Alexander J. Paraskos, Yutaka Nishiyama, and Timothy M. Swager Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Novel half-disc mesogens of general structure 6,7,10,11-tetrakis(alkoxy)triphenylene-1,4-dione were synthesized and their phases characterized by polarized microscopy, differential scanning calorimetry and X-ray diffraction. These compounds were found to form hexagonal columnar mesophases upon heating, despite their half-disc molecular shapes. X-ray diffraction suggests that within the mesophases a dimeric mesogenic subunit exists, driven by dipolar forces, in which the molecules are oriented antiparallel to one another. Such a dimer is approximately disc-shaped, and may explain the formation of columnar phases by these half-disc molecules.

INTRODUCTION

With the discovery that disc-shaped molecules can stack and form columnar mesophases a new paradigm was born for the rational design of novel liquid crystals [1]. This discovery highlights the importance of considering shape anisotropy and structure-property relationships when creating novel mesogens that might potentially display new mesophases.

Since then, it has been shown that many non-discoid molecules are capable of forming columnar mesophases as well. For example, polycatenar mesogens frequently display columnar mesophases arising through the formation of aggregates [2] or dimers [3] of molecules within the columns. The design of metallomesogens in which half-disc subunits are brought together covalently through a central metal atom(s) to form disc-shaped [4], propeller-shaped [5], butterfly-shaped [6] and rod/half-disc shaped [7] mesogenic

We are grateful for the generous financial support from the National Science Foundation and the Japanese Society for the Promotion of Science.

Address correspondence to Timothy M. Swager Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

A. J. Paraskos et al.

units has demonstrated that unfavorably-shaped subunits can be strategically combined to form molecules which are mesogenic. The assembly of mesogenic units through non-covalent forces such as hydrogen-bonding [8], coordination polymers [9], microphase segregation [10] and dipoledipole interactions [11] has also proven effective.

Herein we describe the synthesis and phase behavior of a series of mesogens of general structure 6,7,10,11-tetrakis(alkoxy)triphenylene-1,4-dione. These deep-red coloured organic dyes have been found to display hexagonal columnar mesophases due to a correlated organization of their shapes.

RESULTS AND DISCUSSION

Synthesis

A number of triphenylene-based quinones were synthesized and studied (Scheme 3). The synthesis of compound **18** and has been previously described by our group [12], and a similar synthetic route was followed for the synthesis of compounds 14-17. Williamson ether synthesis of the appropriate alkyl bromide with catechol affords the corresponding 1,2dialkoxybenzene, which is iodinated with periodic acid and iodine yielding 3,4-dialkoxy-1-iodobenzene [13]. Ullman coupling of the 3,4the dialkoxybenzenes is carried out neat with copper (220°C) yielding the corresponding 3,3',4,4'-tetraalkoxybiphenyl cleanly in 70–75% yield after precipitation from CHCl₃/MeOH (Scheme 1). Alternatively, etherification of 5-iodo-2-methoxyphenol, synthesized by the previously reported method [14], with 1-bromo-2-ethylhexane provides 2-(2-ethylhexyloxy)-4-iodo-1-methoxybenzene in good yield after distillation. Biphenyl 7 can then be synthesized via a zinc/palladium (0) coupling in good yields (Scheme 2). Cyclization of the resulting biphenyl compounds with *p*-dimethoxybenzene and iron (III) chloride in DCM yields the parent triphenylenes **8–13**, which are then oxidatively demethylated with cerium ammonium nitrate yielding the desired mesogenic quinones **14–19** (Scheme 3).

Phase Behaviour

The phase behaviour of the mesogens 14-19 is listed in Table 1. Despite their half-disc shapes, compounds 14, 15 and 16, possessing *n*-hexyloxy, *n*-octyloxy and *n*-decyloxy sidechains, respectively, all exhibit enantiotropic Col_h mesophases as identified by polarized microscopy and X-ray diffraction. When viewed by polarized microscopy these compounds exhibit petal-like textures possessing features that are clearly hexagonal in nature (Fig. 1). Compound 17, with *n*-dodecyloxy sidechains, exhibits a relatively



SCHEME 1 Synthesis of 3,3'4,4'-tetrakis(n-alkoxy)biphenyls.

narrow monotropic Col_h mesophase, as does the bis(2-ethylhexyl)dimethyl triphenylene quinone **19**, which represents an unusual example of a columnar phase exhibited by a triphenylene-type compound possessing only two alkoxy sidechains. Quinone **18**, possessing four 2-ethylhexyl sidechains, exhibits a Col_h mesophase at room temperature. In stark contrast to the quinone compounds, none of the parent triphenylenes **8–13** are liquid-crystalline, presumably as a consequence of their half-disc shapes.

XRD Studies

Variable temperature X-ray diffraction studies were performed for the columnar phases exhibited by each of the quinones, with the exception



SCHEME 2 Synthesis of 3,3'-bis(2-ethylhexyloxy)-4,4-dimethoxybiphenyl.



SCHEME 3 Synthesis of mesogenic triphenylene quinones.

of compound 16 (Table 2). The $Col_{\rm H}$ phases of these compounds are all characterized by the observation of sharp (100) peaks in the low angle region. The diffraction patterns of compounds 15 and 17 also exhibit sharp (110) and (200) peaks, confirming the hexagonal nature of the phases. The wide-angle regions of the diffraction patterns all display broad halos at approximately 3.5 A, corresponding to the distance between neighboring mesogens within individual columns. In addition, broad halos at 4.6 A correspond to the distance between liquid-like sidechains, confirming that the phases are indeed liquid crystalline as opposed to crystal or plastic phases. Further analysis of the wide-angle region of compound **19** suggests an antiparallel (dimerized) packing of the molecules within the columns, as evidenced by the appearance of an additional diffuse scattering peak centered at approximately 6.9 Å. (Fig. 2) This behaviour has been observed repeatedly by our group and other groups for mesogens in which packing and dipolar forces combine to cause an antiparallel dimer association of molecules within both columnar [14] and lamellar phases [15]. Such dimerization, most likely driven by dipole-dipole interactions (AM1 calculations on a model compound suggest a molecular dipole of 1.27D) in combination with the half-disc shape may explain the relative stability of the columnar phases of these half-disc mesogens. This would also explain the lack of mesogenicity observed for the parent triphenylenes, as these molecules lack a significant dipole and so most likely would not possess a driving force to organize in this fashion.

SUMMARY

A variety of triphenylene quinones were prepared and shown to exhibit Col_h mesophases. Their ability to form columnar phases despite their half-disc shape may be explained by the formation of an antiparallel dimers





Transition temperatures (°C) and enthalpies (in parentheses, kJ/mol) were determined by DSC (10°C/min) and are given above and below the arrows.

of molecules within the liquid crystal phases, which have been observed by X-ray diffraction studies. Such a correlated organization of molecules, driven by dipole-dipole interactions, results in the formation of mesogenic units that are roughly disc-shaped. Further supporting this idea is the fact

A. J. Paraskos et al.



FIGURE 1 Polarized microscopy of the Col_h phase of 15 at 111°C (top) and 109°C (bottom) (both 100 × magnification). (See COLOR PLATE XI)

that the parent triphenylene compounds, whose dipoles are apparently not significant enough to drive an antiparallel association of molecules, are not liquid crystalline.

EXPERIMENTAL SECTION

General

Dichloromethane was dried by passing through activated alumina columns. Anhydrous methanol was purchased from Aldrich (sure-seal) and stored over activated molecular sieves before use. All other chemicals were

369/	[1411]

Compd	Mesophase	Lattice constant (Å)	Spacing obsd	Miller indices	Å (calcd)	Halos obsd
14	Col _b at 75°C	19.1	16.5	100		3.5
				110	9.5	4.5
				200	8.3	
15	Col _h at 92°C	20.4	17.7	100		3.5
			10.3	110	(10.2)	4.6
			8.9	200	(8.8)	
17	Col_{h} at 76°C	24.4	21.1	100		3.7
			12.2	110	(12.2)	4.6
			10.6	200	(10.6)	
18	Col_h at 90°C	20.2	17.5	100		3.7
				110	(10.1)	4.6
				200	(8.8)	
19	Col _h at 100°C	17.0	14.7	100		3.5
				110	(8.5)	4.6
				200	(7.4)	6.9

TABLE 2 XRD for Compounds 14-15 and 17-19

of reagent grade and were used without further purification. 1,2-Dihexyloxy-, 1,2-dioctyloxy, 1,2-didecyloxy, 1,2-didecyloxy and 1,2-di(2-ethylhexyloxy) benzenes were prepared by the alkylation of catechol with alkyl bromide. Air and water sensitive reactions employed standard Schlenk techniques under argon atmosphere. NMR spectra were obtained on



FIGURE 2 Proposed antiparallel stacking of mesogenic quinones in the columnar phase.

Varian Mercury-300, Bruker DPX-400 or Varian Inova-500 spectrometers. All chemical shifts are referenced to residual $CHCl_3$ (7.27 ppm for ¹H, 77.0 ppm for ¹³C). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), and m (multiplet). High resolution mass spectra were obtained at the MIT Department of Chemistry Instrumentation facility (DCIF) on a Finnigan MAT 8200 or on а Bruker Daltonics Apex II 3T FT-ICR MS. Infrared spectra were recorded on a Nicolet Impact 410 in KBr pellets. DSC investigations were carried out on a Perkin-Elmer DSC-7. Optical microscopy was carried out on a Leica polarizing microscope in combination with a Linkam LTS350 hotstage. X-ray diffraction studies were carried out on samples in capillary tubes with an INEL diffractometer with a 2 kW CU K_{α} X-ray source fitted with an INEL CPS-120 position-sensitive detector. The detectors were calibrated using a silver behenate standard produced by Eastman Kodak.

2-(2-ethylhexyloxy)-4-iodo-1-methoxybenzene (6)

5-Iodo-2-methoxyphenol (30 g, 120 mmol) and K₂CO₂ (33.2 g. 240 mmol) were successively added to ethanol (150 mL) and stirred at rt. for 0.5 h, after which 1-bromo-2-ethylhexane (23.2 g, 120 mmol) was added to the solution and vigorously stirred at 85° C for 96 h. Additional K₂CO₃ (8.3 g, 60 mmol) was added to the solution after stirring for 24, 48 and 72 h. Upon cooling the reaction mixture was diluted with diethyl ether (100 mL), filtered and the remaining solids were washed with diethyl ether (50 ml). The solvent was removed under reduced pressure; the residual yellow oil was dissolved in hexane (200 mL) and washed with 1 M NaOH solution $(100 \,\mathrm{mL} \times 2)$ and H₂O $(150 \,\mathrm{ml})$, respectively. After drying over MgSO₄, the organic layer was concentrated under reduced pressure and the residue was distilled to afford **6** as a colorless oil (37.0 g, 85%). ¹H NMR (CDCl₃, δ): 0.91 (t, J = 6.3 Hz, 3H), 0.94 (t, J = 6.3 Hz, 3H), (m, J = 6.3 Hz, 1H), 1.80 1.58–1.30 (m, 8H), 3.83 (s, 3H), 3.84 (d, J = 6.3 Hz, 2H), 6.62 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 2.1 Hz, 1H), 7.21(dd, J = 2.1, 8.7 Hz, 1H). ¹³C NMR (CDCl₃, δ): 11.26, 14.40, 23.31, 24.00, 29.21, 30.60, 39.34, 56.35, 72.17, 82.64, 114.03, 122.10, 129.65, 149.75, 149.99.

3,3'-Di(2-ethylhexyloxy)-4,4'-dimethoxybiphenyl (7)

10% Pd-C (15.7 g) and Zn dust (15.7 g, 240 mmol) were added to a mixture of acetone/H₂O (1/1 800 mL), and the resulting suspension was stirred at room temperature for 1 h after which 2-(2-ethylhexyloxy)-4-iodo-1-methoxybenzene was added dropwise and stirred at for 48 h. Hexane (150 ml) was added to the resulting solution and the solution was filtered through Celit pad. The organic layer was separated, then aqueous layer was extracted with diethyl ether (100 mL). The combined organic layers were washed with saturated brine (100 mL × 2), dried over MgSO₄,

and then concentrated under reduced pressure leaving a light yellow oil. Purification by reduced distillation afforded **7** as a clear oil (16.2 g, 86%). ¹H NMR (CDCl₃, δ): 0.92 (t, J = 7.5 Hz, 6H), 0.96 (t, J = 7.5 Hz, 6H), 1.27–1.51 (m, 16H), 1.85 (m, J = 6.0 Hz, 2H), 3.90 (s, 6H), 3.97 (d, J = 6.0 Hz, 4H), 6.94 (d, J = 9.0 Hz, 2H), 7.08 (s, 2H), 7.09 (d, J = 9.0 Hz, Hz, 2H). ¹³C (CDCl₃, δ): 11.23, 14.32, 23.29, 23.98, 29.22, 30.64, 39.43, 56.53, 72.28, 112.61, 112.73, 119.28, 134.55, 149.14, 149.34.

1,4-Dimethoxy-6,7,10,11-tetrakis(hexyloxy)triphenylene (8)

To a suspension solution of $FeCl_3$ (1.36 g, 8 mmol) in CHCl₃ (50 mL) was added tetra(hexyloxy)biphenyl (1 mmol) dropwise added to at 0°C. 1,4-Dimethoxybenzene (0.56 g, 4 mmol) was then added and stirred at rt. for 5 h. The reaction mixture was quenched with anhydrous MeOH (30 mL) and then stirred at r.t for 0.5 h. The solvent was removed under reduced pressure and the residue solid was dissolved in diethyl ether (100 mL) and H_{2O} (70 mL). After separating of the organic layer, aqueous layer was extracted with diethyl ether (50 mL \times 2). The combined organic layers were washed with saturated brine $(100 \text{ mL} \times 2)$, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/CH₂Cl₂ 2:1 eluent) to afford a light brown solid. The solid was further purified by recrystallization from MeOH/CHCl₃ yielding **8** as white plates.¹H NMR (CDCl₃, δ): 0.89–0.93 (m, 12 H), 1.32-1.43 (m, 16H), 1.32-1.51 (m, 8H), 1.82-1.99 (m, 8H), 3.91 (s, 6H), 4.12 (t, J = 6.6 Hz, 4H), 4.17 (t, J = 6.6 Hz, 4H), 7.00 (s, 2H), 7.73 (s, 2H), 9.06 (s, 2H). ¹³C NMR (CDCl₃, δ): 14.39, 22.97, 26.12, 26.15, 29.53, 29.63, 31.98, 57.43, 69.17, 69.67, 106.60, 110.50, 112.97, 122.46, 123.22, 125.48, 147.68, 148.71, 152.55. HRMS-ESI (m/z): $(M+H)^+$ calcd for $C_{44}H_{64}O_6$ 689.4776, found 689.4760.

1,4-Dimethoxy-6,7,10,11-tetrakis(octyloxy)triphenylene (9)

Preparation same as for **8**. ¹H NMR (CDCl₃, δ): 0.89–0.93 (m, 12H), 1.32–1.42 (32H), 1.56–1.59 (m, 8H), 1.94–1.96 (m, 8H), 3.99 (s, 6H), 4.21–4.25 (m, 8H), 7.09 (s, 2H), 7.82 (s, 2H), 9.16 (s, 2H). ¹³C NMR (CDCl₃, δ): 14.10, 14.12, 22.68, 22.69, 26.13, 29.07, 29.15, 29.31, 29.44, 31.82, 68.72, 69.00, 103.83, 109.37, 122.17, 126.60, 128.80, 137.67, 150.58, 151.05, 189.48.

1,4-Dimethoxy-6,7,10,11-tetrakis(decyloxy)triphenylene (10)

Preparation same as for **8**. ¹H NMR (CDCl₃, δ): 0.87–0.91 (m, 12H), 1.29–1.44 (m, 48), 1.45–1.64 (m, 8H), 1.85–2.01 (m, 8H), 4.00 (s, 6H), 4.18–4.27 (m, 8H), 7.10 (s, 2H), 7.81 (s, 2H), 9.15, (s, 2H). (¹³C NMR (CDCl_3, δ) : 14.34, 22.92, 26.41, 29.51, 29.60, 29.77, 29.85, 29.92, 32.15, 57.34, 57.51, 69.20, 69.70, 106.66, 110.47, 113.05, 122.56, 123.31, 125.58, 147.82, 148.86, 152.70. HRMS-EI (m/z): (M+H))⁺ calcd for C₆₀H₉₆O₆ 912.7207, found 912.7207.

1,4-Dimethoxy-6,7,10,11-tetrakis(dodecyloxy)triphenylene (11)

Preparation same as for **8**. ¹H NMR (CDCl₃, δ): 0.89–0.93 (m, 12H), 1.28–1.56 (m, 80H), 1.94–1.96 (m, 8H), 4.00 (s, 6H), 4.21 (t, J = 6.6 Hz, 4H), 4.25 (t, J = 6.6 Hz, 4H), 7.10 (s, 2H), 7.81 (s, 2H), 9.15 (s, 2H). ¹³C NMR (CDCl₃, δ): 14.45, 23.01, 26.50, 29.58, 29.69, 29.82, 29.85, 29.98, 30.04, 32.23, 57.42, 69.19, 69.69, 106.62, 110.49, 113.00, 122.47, 123.23, 125.49, 147.68, 148.73, 152.56. HRMS-ESI (m/z): (M+Na)⁺ calcd for C₆₈H₁₁₂O₆ 1047.8351, found 1047.8315.

1,4-Dimethoxy-6,7,10,11-tetrakis(2-ethylhexyloxy)triphenylene (12)

Synthesis and characterization previously described. [11]

1,4,6,10-Tetramethoxy-7,11-di(2-ethylhexyloxy)triphenylene (13)

¹H NMR (CDCl₃, δ): 0.94 (t, J = 7.2 Hz, 6H), 1.03 (t, J = 7.2 Hz, 6H), 1.37–1.66 (m, 16H), 1.98 (m, J = 6.0 Hz, 2H), 4.02 (s, 6H), 4.05 (s, 6H), 4.17 (d, J = 6.0 Hz, 4H), 7.11 (s, 2H), 9.19 (s, 2H), 7.83 (s, 2H). ¹³C NMR (CDCl₃, δ): 11.49, 14.44, 23.41, 24.13, 29.32, 30.87, 39.41, 56.17, 57.40, 72.23, 105.88, 110.43, 111.49, 122.39, 123.06, 125.45, 148.19, 148.60, 152.53. HRMS-ESI (m/z): (M+H)⁺ calcd for C₃₈H₅₂O₆ 605.3837, found 605.3822.

6,7,10,11-Tetra(hexyloxy)triphenylene-1,4-dione (14)

To a stirred THF (60 mL) solution of **8** (1.69 g, 2.45 mmol) an H₂O solution (15 mL) of cerium (IV) ammonium nitrate (2.82 g, 5.13 mmol) was added dropwise and stirred at room temperature for 2 h. The resulting solution was poured into diethyl ether (500 mL) and washed with saturated NaHCO₃ solution (100 ml × 2) followed by water (100 mL × 3), then dried over MgSO₄. The solvent was removed under the reduced pressure, and the crude product was subsequently purified by column chromatography on silica gel (1:1 hexanes/CH₂Cl₂ eluent) followed by precipitation from CH₂Cl₂/MeOH yielding **14** (11.21 g, 1.83 mmol, 75%) as a deep red solid. ¹H NMR (CDCl₃, δ): 0.89–0.93 (m, 12H), 1.38–1.43 (m, 16H), 1.49–1.60 (m, 8H), 1.95 (m, 8H), 4.22–4.26 (m, 8H), 6.84 (s, 2H), 7.72 (s, 2H), 8.93 (s, 2H). ¹³C NMR (CDCl₃):

373/[1415]

14.37, 22.95, 26.10, 29.33, 29.40, 31.93, 68.99, 69.28, 104.07, 109.58, 122.38, 126.87, 129.00, 137.87, 150.73, 151.21, 189.59. IR (KBr): 2954, 2928, 2856, 1647, 1614, 1531, 1510, 1461, 1438, 1382, 1265, 1160, 1086. HRMS-ESI (m/z): (M+H)⁺ calcd for C₄₂H₅₈O₆ 659.4306, found 659.4331.

6,7,10,11-Tetra(octyloxy)triphenylene-1,4-dione (15)

Preparation same as for **14**. ¹H NMR (CDCl₃, δ): 0.89–0.93 (m, 12H), 1.32–1.43 (m, 32H), 1.49–1.62 (8H), 1.95–1.98(8H), 4.22– 4.25 (8H), 6.82 (s, 2H), 7.68 (s, 2H), 8.91 (s, 2H). ¹³C NMR (CDCl₃, δ): 14.11, 14.12, 22.68, 22.69, 26.13, 29.07, 29.15, 29.32, 29.45, 31.83, 31.84, 68.71, 68.99, 103.81, 109.35, 122.17, 126.60, 128.80, 137.67, 150.57, 151.04, 189.48. IR (KBr): 2953, 2923, 2851, 1653, 1613, 1528, 1510, 1463, 1382, 1266, 1186, 1158, 1083, 872, 823.

6,7,10,11-Tetra(decyloxy)triphenylene-1,4-dione (16)

Preparation same as for **14**. ¹H NMR (CDCl₃, δ): 0.89–0.93 (m, 12H), 1.32–1.43 (m, 48H), 1.49–1.62 (8H), 1.95–1.98(8H), 4.22–4.25 (8H), 6.82 (s, 2H), 7.68 (s, 2H), 8.91 (s, 2H). ¹³C NMR (CDCl₃, δ): 14.33, 14.34, 22.92, 26.36, 26.37, 29.31, 29.40, 29.60, 29.71, 29.73, 29.77, 29.83, 29.89, 32.15, 32.16, 69.01, 69.31, 104.22, 109.73, 122.46, 126.93, 129.09, 137.94, 150.88, 151.35, 189.72. IR (KBr): 2953, 2971, 2850, 1645, 1613, 1509, 1465, 1437, 1383, 1264, 1158, 1082, 863, 824. HRMS-EI (m/z): (M+H)⁺ calcd for C₅₈H₉₀O₆ 882.6737, found 882.6738.

6,7,10,11-Tetra(dodecyloxy)triphenylene-1,4-dione (17)

Preparation same as for **14**. ¹H NMR (CDCl₃, δ): 0.90 (t, J = 6.6 Hz, 12H), 1.28–1.61 (m, 80H), 1.98 (m, 8H), 4.24 (t, J = 6.6 Hz, 4H), 4.28 (t, J = 6.6 Hz, 4H), 6.87 (s, 2H), 7.76 (s, 2H), 8.96 (s, 2H). ¹³C NMR (CDCl₃, δ): 14.46, 23.01, 26.46, 29.37, 29.46, 29.69, 29.79, 29.81, 29.99, 30.04, 32.23, 69.01, 69.31, 104.12, 109.62, 122.38, 126.87, 129.01, 137.88, 150.75, 151.22, 189.58. IR (KBr): 2953, 2920, 2849, 1653, 1612, 1508, 1466, 1438, 1382, 1266, 1164, 1083. HRMS-ESI (m/z): (M+H)⁺ calcd for C₆₆H₁₀₆O₆ 995.8062, found 995.8104.

6,7,10,11-Tetra(2-ethylhexyl)triphenylene-1,4-dione (18)

Synthesis and characterization previously described. [12]

6,10-Dimethoxy-7,11-bis(2-ethylhexaloxy)triphenylene-1,4dione (19)

Preparation same as for **14**. ¹H NMR (CDCl₃, δ): 0.92 (t, J = 7.2 Hz, 6H), 1.02 (t, J = 7.2 Hz, 6H), 1.25–1.66 (m, 16H), 1.98 (m, J = 6.0 Hz, 2H), 4.07

(s, 6H), 4.18 (d, J = 6.0 Hz, 4H), 6.87 (s, 2H), 7.75 (s, 2H), 8.97 (s, 2H). ¹³C NMR (CDCl₃, δ):11.54, 14.41, 23.36, 24.12, 29.32, 30.90, 39.27, 56.14, 71.89, 103.57, 108.59, 122.23, 126.68, 129.01, 137.80, 151.08, 151.21, 189.48. IR (KBr): 2958, 2930, 2872, 2861, 1638, 1615, 1522, 1508, 1463, 1421, 1382, 1263, 1151, 1081, 868. HRMS-ESI (m/z): (M + H)⁺ calcd for C₃₆H₄₆O₆ 575.3367, found 575.3388.

REFERENCES

- Chandrasekhar, S., Sadashiva, B. K., & Suresh, K. A. (1977). *Pramana*, 9, 471; Cammidge, A. N. & Bushby, R. J. (1998). In: *Handbook of Liquid Crystals*, Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., & Vill, V. (Eds.), Wiley-VCH: Weinheim, Vol. 2B, 693–720.
- [2] Nguyen, H., Destrade, C., & Malthête, J. (1997). Adv. Mater., 9, 375–388 and references therein.
- Kishikawa, K., Harris, M. C., & Swager, T. M. (1999). Chem. Mater., 11, 867–871;
 Levitsky, I. A., Kishikawa, K., Eichhorn, S. H., & Swager, T. M. (2000). J. Am. Chem. Soc., 122, 2474–2479.
- [4] Lai. C. K., Serrette, A. G., & Swager, T. M. (1992). J. Am. Chem. Soc., 114, 7948–7949;
 Zheng, H., Lai, C. K., & Swager, T. M. (1994). Chem. Mater., 6, 101–103; Serrette, A. G.,
 Lai, C. K., & Swager, T. M. (1994). Chem. Mater., 6, 2252–2268; Zheng, H., Lai, C. K., &
 Swager, T. M. (1995). Chem. Mater., 7, 2067–2077; Zheng, H., Xu, B., & Swager, T. M.
 (1996). Chem. Mat., 8, 907–911; Trzaska, S. T. & Swager, T. M. (1998). Chem. Mater., 10, 438–443; Trzaska, S. T., Zheng, H., & Swager, T. M. (1999). Chem. Mater., 11, 130–134.
- [5] Zheng, H. & Swager, T. M. (1994). J. Am. Chem. Soc., 116, 761–762. Zheng, H. & Swager, T. M. (1995). Mol. Cryst. Liq. Cryst., 260, 301–306; Trzaska, S. T., Hsu, H., & Swager, T. M. (1999). J. Am. Chem. Soc., 121, 4518–4519.
- [6] Hegmann, T., Neumann, B., Kain, J., Diele, S., & Tschierske, C. (2000). J. Mater. Chem., 10, 2244–2248.
- [7] Hegmann, T., Peidis, F., Diele, S., & Tschierske, C. (2000). Liq. Cryst., 27, 1261–1265.
- [8] Kato, T., Mizoshita, N., & Kanie, K. (2001). Macromol. Rapid Commun., 22, 797–814. Kato, T. (1998). In: Handbook of Liquid Crystals, Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., & Vill, V. (Eds.), Wiley-VCH: Weinheim, Vol. 2B, 969–979.
- [9] Serrette, A. G. & Swager, T. M. (1993). J. Am. Chem. Soc., 115, 8879–8880; Serrette, A. & Swager, T. M. (1994). Angew. Chem. Int. Ed. Engl., 33, 2342–2345.
- [10] Plehnert, R., Schröter, J. A., & Tschierske, C. (1998). J. Mater. Chem., 8, 2611–2626;
 Tschierske, C. (1998). J. Mater. Chem., 8, 1485–1508; Pegenau, A., Hegmann, T.,
 Tschierske, C., & Diele, S. (1999). Chem. Eur. J., 5, 1643–1660; Tschierske, C. (2001).
 J. Mater. Chem., 11, 2647–2671.
- [11] Omenat, A., Barberá, J., Serrano, J. L., Houbrechts, S., & Persoons, A. (1999). Adv. Mater., 11, 1292–1295; Kishikawa, K., Furusawa, S., Yamaki, T., Kohmoto, S., Tamamoto, M., & Yamaguchi, K. (2002). J. Am. Chem. Soc., 8, 1597–1605; Paraskos, A. J. & Swager, T. M. Chem. Mater., submitted; Eichhorn, S. H., Paraskos, A. J., & Swager, T. M. J. Am. Chem. Soc., submitted.
- [12] Rose, A., Lugmair, C. G., & Swager, T. M. (2001). J. Am. Chem. Soc., 123, 11298–11299.
- [13] Weck, M., Mohr, B., Maughon, B. R., & Grubbs, R. H. (1997). *Macromolecules*, 30, 6430–6437; Bacher, A., Erdelen, C. H., Paulus, W., Ringsdorf, H., Schmidt, H. W., & Schuhmacher, P. (1999). *Macromolecules*, 32, 4551.

- [14] Levitsky, I. A., Kishikawa, K., Eichhorn, S. H., & Swager, T. M. (2000). J. Am. Chem. Soc., 11, 2474–2479; Trzaska, S. T. & Swager, T. M. (1998). Chem. Mater., 10, 438–443; Zheng, H., Xu, B., & Swager, T. M. (1996). Chem. Mater., 8, 907–911; Zheng, H., Lai, C. K., & Swager, T. M. (1994). Chem. Mater., 6, 101–103.
- [15] Kishikawa, K., Furusawa, S., Yamaki, T., Kohmoto, S., Tamamoto, M., & Yamaguchi, K. (2002). J. Am. Chem. Soc., 8, 1597–1605; Paraskos, A. J. & Swager, T. M. (2002). Chem. Mater., 14, 4543–4549; Eichhorn, S. H., Paraskos, A. J., & Swager, T. M. (2002). J. Am. Chem. Soc., 124, 12742–12751.