Crown ethers with lateral *ortho*-terphenyl units: effect of ester groups and sodium salts on the mesomorphic properties

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Unsymmetrical crown ether derivatives 7 and 12 with one lateral *o*-terphenyl unit bearing different ester substituents were synthesized starting from methoxymethyl (MOM) protected bromobenzenes 3 and 8 by conversion into the respective borolanes 4 and 9, twofold Suzuki coupling with dibromobenzo[15]crown-5, acidic deprotection and finally esterification either with various alkanoic chlorides or gallic acids. Reaction with NaI provided the complexes [NaI \cdot (7a–g)] and [NaI \cdot (12a–d)], respectively. Uncomplexed crown ethers as well as their complexes [NaI \cdot 7a–c] and [NaI \cdot (12a–d)] are non-mesogenic. In the case of [NaI \cdot (7d–g)], however, the complexation induced a mesophase formation. As exemplarily shown for [NaI \cdot 7d], different textures were observed upon cooling, a fan-shaped texture, which is typical for a columnar hexagonal mesophase, and a striped fan-shaped texture, indicating a second mesophase Col_x at low-temperature. From the SAXS diffraction pattern this mesophase was assigned to be columnar rectangular. For [NaI \cdot 7g] a different diffraction pattern was found, from which the low-temperature mesophase might be attributed to a soft crystal or a highly ordered columnar mesophase with orthorhombic symmetry.

1.0 Introduction

The combination of crown ethers or azacrowns with mesogenic groups in one molecular entity leads to unprecedented properties of these novel materials. Prominent examples with respect to discotic liquid crystals are induction or stabilization of mesophases by selective cation complexation^{1,2} as described first by Percec, ^{2k} elastic anisotropy,³ membranes containing ion-selective transport channels,⁴ amphiphilic metallomesogens with high charge carrier mobilities, which can be used as high performance organic field effect transistors⁵ and conducting wires,⁶ induction of tubular mesophases,⁷ organic gelators^{6b,e,8} and helical fibers for self-assembly at gel-graphite interfaces.^{9–11} Recently we reported on the mesomorphic properties of unsymmetrical benzo[15]crown-5 ethers **1** with only one *o*-terphenyl unit bearing alkoxy side chains, which stabilize the mesophases (Scheme 1).¹²

Uncomplexed derivatives 1 with chain lengths of at least C_{12} formed smectic mesophases, while complexation with alkali metal salts induced a transformation to columnar mesophases.¹² Regarding wedge-shaped benzo[15]crown-5 ether derivatives 1, we were particularly interested in whether the change of polarity together with geometric restraints by replacement of the four peripheral alkoxy chains with four various ester moieties would exert any influence on the mesophase. Ester groups not only change the polarity of the side chains as compared to ether side chains, but also



decrease the electron density to some extent in the aromatic ring, which is directly attached to the crown ether moiety. Furthermore, the influence of sodium iodide on the self-organisation is investigated. NaI fits perfectly into the [15]-crown-5 ether (\emptyset 1.7–2.2 Å) due to its cationic radius of 0.9 Å. Comparison of the mesomorphic properties of mesogens with different side chains but the same core and the same alkali salt allows a more detailed understanding of the structure-property relationships in columnar liquid crystals.

2.0 Experimental

Melting points were measured on a Mettler Toledo DSC822 and are uncorrected. NMR spectra were recorded on an Avance 300 and Avance 500 spectrometer, Bruker. FTIR spectra were recorded on a Vektor22 spectrometer, Bruker, with MKII Golden Gate Single Reflection Diamant ATR system. Mass spectra were recorded on a Finnigan MAT 95 and a Varian MAT 711 apparatus. Elemental analysis were performed on a Carlo Erba Strumentazione Elemental Analyzer Model 1106. X-Ray powder experiments were performed on a Nanostar, Bruker;

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software: SAXS 4.1.26. The samples were kept in Hilgenbergglass capillaries of 0.7 mm outside diameter in a temperaturecontrolled heating stage (± 1 °C). A monochromatic Cu–K_{$\alpha 1$} beam ($\lambda = 1.5405$ Å) was obtained using a ceramic tube generator (1500 W) with cross-coupled Göbel-mirrors as the monochromator. The diffraction patterns were recorded on a real-time 2D-detector (HI-STAR, Bruker). The calibration of the patterns occurred with the powder pattern of Ag-Behenate.

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.

2.1 Materials synthesis

Synthesis of 4-bromo-1,2-bis(methoxymethoxy)benzene (3). To a solution of 2 (4.50 g, 23.8 mmol) and dimethoxymethane (90 mL, 77.4 g, 1.0 mol) in CHCl₃ (150 mL) at 0 °C P₄O₁₀ (67 g, 0.47 mol) was added portionwise and the reaction mixture stirred for 30 min (tlc control). The reaction mixture was filtered and the filtrate washed successively with an aqueous Na₂CO₃ solution $(3 \times 100 \text{ mL})$ and HCl (1 N, 2 × 100 mL), dried (MgSO₄) and concentrated. The residue was chromatographed on SiO₂ with hexanes–EtOAc (9:1, $R_f = 0.26$) to give **3** as a colorless oil, 4.66 g; yield 71%. ¹H NMR (CDCl₃, 500 MHz): δ 3.51, 3.52 (2s, 6 H, CH₃), 5.20, 5.22 (2s, 4 H, ArOCH₂OCH₃), 7.03 (d, J_{5,6} = 8.7 Hz, 1 H, 5-H), 7.08 (dd, $J_{6,5} = 8.7$, $J_{6,2} = 2.2$ Hz, 1 H, 6-H), 7.31 (d, $J_{2,6} = 2.2 \text{ Hz}, 1 \text{ H}, 2 \text{-H}$). ¹³C NMR (CDCl₃, 125 MHz): δ 53.1 (CH₃), 95.4 (OCH₂OCH₃), 114.3 (C-1), 118.0, 119.9, 125.1 (C-2, C-6, C-5), 146.4, 148.0 (C-4, C-3). FT-IR (ATR): v = 2955, 2901, 2827 (w), 1587 (w), 1490, 1386, 1246, 1150, 1072 (m) cm⁻¹. Anal. calcd for C₁₀H₁₃BrO₄: C, 43.34; H, 4.73. Found: C, 43.06; H, 4.71%.

Synthesis of borolanes 4 and 9. Under an inert gas atmosphere n-BuLi (2.00 mL, 3.20 mmol, 1.6 M in hexane) was added dropwise to a solution of 3 or 8 (2.00 mmol) in abs. THF (100 mL) and the reaction mixture stirred at -78 °C for 10 min. After addition of B(OMe)₃ (0.39 mL, 0.36 g, 3.50 mmol) and stirring for 30 min, the reaction mixture was warmed to r.t. within 2 h. Then pinacol (0.40 g, 3.40 mmol) in THF (ca. 2 mL) was added and the reaction mixture stirred for 1 h. After dropwise addition of conc. HOAc (0.20 mL, 0.21 g, 3.50 mmol), the reaction mixture was stirred for a further 18 h. The solvent was removed under vacuum, the residue taken up in CH₂Cl₂, washed with water, dried (MgSO₄) and concentrated. Chromatography on SiO₂ with hexanes-EtOAc (8:1, $R_f = 0.18$) gave 4 as a colorless solid, 0.47 g; yield, 68%. Mp 50 °C. ¹H NMR (CDCl₃, 500 MHz): δ 1.32 [s, 12 H, OC(CH₃)₂C(CH₃)₂O], 3.50, 3.54 (2s, 6 H, CH₃), 5.26, 5.28 (2s, 4 H, OC H_2 OCH₃), 7.15 (d, $J_{5.6} = 8.0$ Hz, 1 H, 5-H), 7.44 (dd, $J_{6.5} =$ 8.0, $J_{6,2} = 1.1$ Hz, 1 H, 6-H), 7.54 (d, $J_{2,6} = 1.1$ Hz, 1 H, 2-H). ¹³C NMR (CDCl₃, 125 MHz): δ 24.9 [OC(CH₃)₂C(CH₃)₂O], 56.2, 56.3 (CH₃), 83.7 [OC(CH₃)₂C(CH₃)₂O], 95.1, 95.5 (OCH₂OCH₃), 115.7, 122.8 (C-5, C-6), 129.9 (C-2), 146.5, 150.2 (C-3, C-4). FT-IR (ATR): v = 2973 (w), 1601 (w), 1424, 1382, 1351, 1249, 1143, 1126, 1070 (m) cm⁻¹. Anal. calcd for C₁₆H₂₅BO₆: C, 59.28; H, 7.77. Found: C, 59.24; H, 7.74%. Chromatography on SiO₂ with hexanes-Et₂O (20:1) gave 9 as a colorless oil, 5.77 g; yield: 61%. $R_f = 0.20$. ¹H NMR (CDCl₃, 300 MHz): δ 1.33 [s, 12 H,

OC(CH₃)₂C(CH₃)₂O], 3.47 (s, 3 H, CH₃), 5.20 (s, 2 H, OCH₂OCH₃), 7.01–7.04 (m, 2 H, 3-H, 5-H), 7.74–7.77 (m, 2 H, 2-H, 6-H). ¹³C NMR (CDCl₃, 125 MHz): δ 24.9 [OC(CH₃)₂C (CH₃)₂O], 56.0 (CH₃), 83.6 [OC(CH₃)₂C(CH₃)₂O], 94.1 (OCH₂OCH₃), 115.4, 136.5 (C-2, C-3, C-5, C-6), 159.8 (C-4). FT-IR (ATR): ν = 2976 (s), 1604 (w), 1357, 1316, 1272, 1233, 1139, 1077, 993, 920, 859, 835 (s) cm⁻¹. Anal. calcd for C₁₄H₂₁BO₄: C, 63.66; H, 8.01. Found: C, 63.45; H, 8.00%.

Suzuki coupling of borolanes with 4,5-dibromobenzo[15]crown-5 to crown ethers 6a and 10a. To a solution of 5 (0.04 g, 0.10 mmol) in degassed dimethoxyethane-water (10 mL:1 mL) the respective 4 or 9 (0.23 mmol), K₂CO₃ (0.16 g, 1.15 mmol), KF (0.07 g, 1.15 mmol) and Pd(PPh₃)₄ (0.02 g, 0.02 mmol) were successively added, and the reaction mixture stirred at 95 °C for 48 h. The reaction mixture was cooled to r.t. and concentrated. The residue was taken up in CH₂Cl₂ (100 mL), washed with water (3 \times 40 mL), dried (MgSO₄), concentrated and purified by chromatography on SiO₂ with hexanes–EtOAc (1:5, $R_f = 0.14$) (for **6a**) or CH_2Cl_2 -EtOAc (4:1, $R_f = 0.20$) (for 10a). Product 6a was precipitated from CH2Cl2-ethanol at +4 °C as a colorless solid, 1.33 g; yield, 40%. Mp 95.4 °C. ¹H NMR (CDCl₃, 500 MHz): δ 3.35, 3.50 (2 s, 12 H, CH₃), 3.78 [s, 8 H, CH₂O(CH₂-CH2O)2CH2], 3.93 (s, 4 H, ArOCH2CH2O), 4.19-4.20 (m, 4 H, ArOCH₂CH₂O), 4.95, 5.20 (2s, 8 H, OCH₂OCH₃), 6.83-6.86 (m, 4 H, 2'-H, 5'-H), 6.91 (s, 2 H, 3-H, 6-H), 7.05–7.06 (m, 2H, 6'-H). ¹³C NMR (CDCl₃, 125 MHz): δ 55.9, 56.2 (CH₃), 69.5, 69.7 [CH₂O(CH₂CH₂O)₂CH₂], 70.7, 71.2 (ArOCH₂CH₂O), 95.4, 95.5 (OCH₂OCH₃), 116.3, 116.4 (2'-C, C-3, C-6), 119.1 (C-5'), 123.5 (C-6'), 133.1 (C-5, C-4), 136.0 (C-1'), 145.8, 146.8 (C-3', C-4'), 148.3 (C-1, C-2). FT-IR (ATR): v = 2869 (ms), 1604 (w), 1495, 1453, 1354, 1244, 1196, 1153, 1132, 1070 (m) cm⁻¹. MS (EI): m/z (%) = 663(1), 662(6), 661(23), 660(65) [M⁺], 584(4), 508(3), 376(8), 45 (100) [CH₂OCH₃]. HRMS (EI): m/z (%) calcd for C₃₄H₄₄O₁₃: 660.2782. Found: 660.2782. Product 10a was precipitated from CH₂Cl₂-ethanol at +4 °C as a colorless solid, 1.91 g; yield, 46%. Mp 91.6 °C. ¹H NMR (CDCl₃, 500 MHz): δ 3.47 (s, 6 H, CH₃), 3.78 [s, 8 H, CH₂O(CH₂CH₂O)₂CH₂], 3.92-3.94 (m, 4 H, ArOCH₂CH₂O), 4.18–4.20 (m, 4 H, ArOCH₂CH₂O), 5.15 (s, 4 H, OCH₂OCH₃), 6.87–6.88 (m, 6 H, 6-H, 3-H, 2'-H, 6'-H), 7.02-7.04 (m, 4 H, 3'-H, 5'-H). ¹³C NMR (CDCl₃, 125 MHz): § 56.0 (CH₃), 69.4, 69.7 [CH₂O(CH₂CH₂O)₂CH₂], 70.7, 71.2 (ArOCH₂CH₂O), 94.6 (OCH₂OCH₃), 115.7 (C-6', C-2'), 116.6 (C-6, C-3), 130.9 (C-5', C-3'), 133.1, 135.2 (C-5, C-1'), 148.2 (C-1, C-2), 155.8 (C-4'). FT-IR (ATR): v = 2931, 2864 (m), 1603, 1494, 1442, 1355 (s), 1230, 1195, 1149, 1074, 1056 (s), 986, 919, 831 (s) cm⁻¹. Anal. calcd for C₃₀H₃₆O₉: C, 66.65; H, 6.71. Found: C, 66.69; H, 6.75%. Single crystals of the sodium complex $[NaI \cdot 10]$ were crystallized from CH₂Cl₂-MeOH/THF.

Crystal structure determination of complex [NaI 10a]. Crystal data. C₃₀H₃₆INaO₉, M = 690.50, monoclinic, a = 20.0711(14), b = 8.4281(6), c = 21.3869(14) Å, V = 3551.2(4) Å³, T = 293 K, space group P2(1)/n, Z = 4, 7318 reflections measured, 3093 unique, which were used in all calculations. The final $wR(F_2)$ was 0.1769 (all data).

Deprotection and alkylation with alkanoic chlorides to crown ethers 7. To a solution of 6a (0.97 g, 1.46 mmol) in methanol–CH₂Cl₂ (10 mL:10 mL) conc. HCl (3 mL) was added and the

reaction mixture stirred at r.t. for 4 h. The solvent was removed under vacuum and 4,5-bis(3',4'-dihydroxyphenyl)benzo[15]crown-5 (6b) precipitated from CH_2Cl_2 -acetone at +4 °C as a colorless solid, 0.71 g; yield, quant. The product was used in the next step without further purification. Mp 217 °C. ¹H NMR (d₆-DMSO, 500 MHz): & 3.63-3.66 [m, 8 H, CH₂O(CH₂CH₂O)₂-CH2], 3.78-3.80 (m, 4 H, ArOCH2CH2O), 4.10-4.11 (m, 4 H, ArOC H_2 CH₂O), 6.35 (dd, $J_{6',5'} = 8.2$, $J_{6',2'} = 2.1$ Hz, 2 H, 6'-H), $6.52 (d, J_{2',6'} = 2.1 \text{ Hz}, 2 \text{ H}, 2'-\text{H}), 6.57 (d, J_{5',6'} = 8.2 \text{ Hz}, 2 \text{ H}, 5'-\text{H}),$ 6.80 (s, 2 H, 3-H, 6-H), 8.74 (br s, 4 H, OH). ¹³C NMR (d₆-DMSO, 125 MHz): & 68.7, 68.9, 69.9, 70.4 [CH₂O(CH₂CH₂O)₂-CH₂, ArOCH₂CH₂O], 115.1, 115.9, 117.0, 120.5 (C-2', C-5', C-6', C-3, C-6), 132.6, 132.7 (C-4, C-5, C-1'), 143.7, 144.5, 147.2 (C-1, C-2, C-3', C-4'). MS (EI): *m*/*z* (%) = 486 (5), 485 (28), 484 (100) [M⁺], 352 (23), 326 (5), 45 (4). HRMS (EI): m/z (%) calcd for C₂₆H₂₈O₉: 484.1733. Found: 484.1738.

To a solution of **6b** (0.07 g, 0.15 mmol) in THF (3 mL) at 0 °C DMAP (8.55 mg, 0.07 mmol), Et₃N (0.30 mL, 0.22 g, 2.13 mmol) and the appropriate alkanoic chloride (0.88 mmol) in THF (2 mL) were successively added. The reaction mixture was allowed to warm to r.t. and stirred for a further 18 h. The yellow suspension was then concentrated, the residue taken up in CH_2Cl_2 (20 mL), washed with water (3 × 10 mL), dried (MgSO₄) and concentrated. The crude products **7** were purified by chromatography on SiO₂ with hexanes–EtOAc and obtained as colorless oil (**7a,b**) or colorless solid (**7c–g**).

Deprotection and alkylation with gallic acids 11 to crown ethers 12. A solution of **10a** (1.06 g, 1.95 mmol) in methanol–CH₂Cl₂ (20 mL:10 mL) and conc. HCl (4 mL) was stirred at r.t. for 1 h. After removal of the solvent under vacuum, 4,5-bis(4'-hydroxy-phe-nyl)benzo[15]crown-5 (**10b**) was obtained as a colorless precipitate, 0.82 g; yield, quant. The product was used in the next step without further purification. Mp 213.9 °C. ¹H NMR (d₆-DMSO, 500 MHz): δ 3.62–3.66 [s, 8 H, CH₂O(CH₂CH₂O)₂CH₂], 3.78–3.80 (m, 4 H, ArOCH₂CH₂O), 4.11–4.13 (m, 4 H, ArOCH₂CH₂O), 6.60–6.62 (m, 4 H, 3'-H, 5'-H), 6.86–6.90 (m, 6 H, 6-H, 3-H, 2'-H, 6'-H), 9.30 (bs, 2 H, OH). ¹³C NMR (d₆-DMSO, 125 MHz): δ 68.7, 68.9, 70.0, 70.4 [CH₂O(CH₂CH₂O)₂CH₂, ArOCH₂CH₂O], 114.7 (C-3', C-5'), 115.9 (C-3, C-6), 130.6 (C-2', C-6'), 131.9, 132.5 (C-4, C-5, C-1'), 147.4 (C-1, C-2), 155.7 (C-4'). Anal. calcd for C₂₆H₂₈O₇: C, 69.01; H, 6.24. Found: C, 68.84; H, 6.21%.

A solution of **10b** (0.11 g, 0.25 mmol) in THF–DMSO (15 mL:1 mL) was added dropwise to a solution of the respective **11a–d** (0.80 mmol), DCC (0.22 g, 1.05 mmol) and DMAP (0.02 g, 0.15 mmol) in CH₂Cl₂ (10 mL) at 0 °C. The reaction mixture was warmed to r.t. and stirred for 18 h. The precipitate was filtered off. The filtrate was concentrated and the residue taken up in CH₂Cl₂ (30 mL), washed with HCl (1 N, 2×10 mL) and water (1×10 mL), dried (MgSO₄) and concentrated. The residue was chromatographed on SiO₂ with hexanes–EtOAc and the products **12** precipitated from CH₂Cl₂–ethanol at +4 °C and obtained as colorless solids.

Complexation of 7 and 12 with Nal. A solution of NaI (0.02 mmol) in acetone (1 mL) was added to a solution of the appropriate 7 or **12** (0.02 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was allowed to stay at r.t. for 16 h. The solvent was then evaporated under a weak nitrogen flow, the residue taken up in CH_2Cl_2 (2 mL) and unsolved NaI filtered off through cellulose. The filtrate was

concentrated and the remaining solid freeze-dried under high vacuum. Even upon prolonged standing at r.t. complexes showed no sign of hygroscopic properties and NMR and DSC data were reproducible. The complexes were obtained as light yellow solids. [NaI·7d]: 29.7 mg. DSC, Cr 94.9 °C [53.0 kJ mol⁻¹] Col_r 121.8 °C [1.3 kJ mol⁻¹] I (1. heating curve). ¹H NMR (CDCl₃, 500 MHz): δ 0.87-0.90 (m, 12 H, CH₃), 1.27-1.39 [m, 56 H, OCOCH₂CH₂-(CH₂)₇CH₃], 1.67–1.77 [m, 8 H, OCOCH₂CH₂(CH₂)₇CH₃], 2.49-2.52 [m, 8 H, OCOCH₂(CH₂)₈CH₃], 3.77-3.79 [m, 4 H, CH₂O(CH₂CH₂O)₂CH₂], 3.90–3.91 [m, 4 H, CH₂O(CH₂CH₂O)₂-CH2], 4.08-4.10 (m, 4 H, ArOCH2CH2O), 4.29-4.31 (m, 4 H, ArOC H_2 CH₂O), 6.87 (dd, $J_{6',5'} = 8.3$, $J_{6',2'} = 2.2$ Hz, 2 H, 6'-H), 6.93 (s, 2 H, 3-H, 6-H), 6.98 (d, *J*_{2',6'} = 2.2 Hz, 2 H, 2'-H), 7.01 (d, $J_{5',6'} = 8.3$ Hz, 2 H, 5'-H). ¹³C NMR (CDCl₃, 125 MHz): δ 14.1 (CH₃), 22.7, 24.90, 24.94, 29.17, 29.19, 29.3, 29.4, 29.50, 29.53, 29.60, 29.63, 31.9 [OCOCH₂(CH₂)₇CH₃], 34.05, 34.11 [OCOCH₂(CH₂)₇CH₃], 67.4, 67.8 (ArOCH₂CH₂O), 69.19, 69.22 [CH₂O(CH₂CH₂O)₂], 114.7 (C-3, C-6), 123.1 (C-5'), 124.6 (C-2'), 128.0 (C-6'), 132.7 (C-4, C-5), 138.7 (C-1'), 141.1, 141.9 (C-3', C-4'), 146.2 (C-4, C-5), 170.9, 171.0 (*C*=O). FT-IR (ATR): v = 2921, 2852 (s), 1765 (s), 1493, 1458 (s), 1245, 1102, 1053 (s) cm⁻¹. MS (MALDI-TOF): $m/z = 1179.8 [M^+ + Na]$, calcd for $C_{70}H_{108}NaO_{13}^+$ 1179.8. [NaI · 7e]: 10.1 mg. DSC, Cr₁ 40.9 °C [1.9 kJ mol⁻¹] Cr₂ 97.3 °C [49.9 kJ mol⁻¹] Col 131.8 °C [0.8 kJ mol⁻¹] I. ¹H NMR (CDCl₃, 500 MHz): δ 0.87-0.90 (m, 12 H, CH₃), 1.27-1.39 [m, 64 H, OCOCH₂CH₂(CH₂)₈CH₃], 1.69–1.73 [m, 8 H, OCOCH₂CH₂-(CH₂)₈CH₃], 2.48–2.51 [m, 8 H, OCOCH₂(CH₂)₉CH₃], 3.78–3.79 [m, 4 H, CH₂O(CH₂CH₂O)₂CH₂], 3.89–3.91 [m, 4 H, CH₂O(CH₂CH₂O)₂CH₂], 4.07–4.09 (m, 4 H, ArOCH₂CH₂O), 4.28–4.30 (m, 4 H, ArOC H_2 CH₂O), 6.86 (dd, $J_{6',5'} = 8.3$, $J_{6',2'} = 2.0$ Hz, 2 H, 6'-H), 6.92 (s, 2 H, 3-H, 6-H), 6.98 (d, J_{2',6'} = 2.0 Hz, 2 H, 2'-H), 7.00 (d, $J_{5',6'} = 8.3$ Hz, 2 H, 5'-H). ¹³C NMR (CDCl₃, 125 MHz): b 14.1 (CH₃), 22.7, 24.9, 25.0, 29.17, 29.19, 29.21, 29.3, 29.4, 29.51, 29.53, 29.6, 29.65, 29.69, 31.9 [OCOCH₂(CH₂)₉CH₃], 34.0, 34.1 [OCOCH₂(CH₂)₉CH₃], 67.5, 68.0 (ArOCH₂CH₂O), 69.3 [CH₂O(CH₂CH₂O)₂], 114.8 (C-3, C-6), 123.1 (C-5'), 124.7 (C-2'), 128.0 (C-6'), 132.7 (C-4, C-5), 138.7 (C-1'), 141.1, 141.9 (C-3', C-4'), 146.4 (C-4, C-5), 170.9, 171.0 (C=O). FT-IR (ATR): v = 2917, 2849 (m), 2360, 2341 (s), 1770 (s), 1558, 1541, 1506, 1496 (m), 1245, 1100 (s), 719 (s) cm⁻¹. MS (MALDI-TOF): m/z (%) = 1235.7 [M⁺ + Na], calcd for C₇₄H₁₁₆NaO₁₃⁺ 1235.8. [NaI·7f]: 23.8 mg. DSC, Cr 58.6 °C [6.7 kJ mol⁻¹] LC₂ 103.0 °C [10.7 kJ mol⁻¹] LC₁ 136.7 °C [0.9 kJ mol⁻¹] I. ¹H NMR (CDCl₃, 500 MHz): δ 0.87-0.90 (m, 12 H, CH₃), 1.27-1.39 [m, 72 H, OCOCH₂CH₂(CH₂)₉CH₃], 1.64–1.73 [m, 8 H, OCOCH₂CH₂-(CH₂)₉CH₃], 2.49–2.52 [m, 8 H, OCOCH₂(CH₂)₁₀CH₃], 3.78–3.79 [m, 4 H, CH₂O(CH₂CH₂O)₂CH₂], 3.91–3.92 [m, 4 H, CH₂O(CH₂CH₂O)₂CH₂], 4.09–4.11 (m, 4 H, ArOCH₂CH₂O), 4.29–4.31 (m, 4 H, ArOC H_2 CH₂O), 6.86 (dd, $J_{6',5'} = 8.3, J_{6',2'} = 2.0$ Hz, 2 H, 6'-H), 6.92 (s, 2 H, 3-H, 6-H), 6.98 (d, J_{2',6'} = 2.0 Hz, 2 H, 2'-H), 7.00 (d, $J_{5',6'} = 8.3$ Hz, 2 H, 5'-H). ¹³C NMR (CDCl₃, 125 MHz): δ 14.1 (CH₃), 22.7, 24.91, 24.94, 29.18, 29.20, 29.34, 29.4, 29.52, 29.54, 29.6, 29.66, 29.69, 29.71, 31.9 [OCOCH₂(CH₂)₁₀CH₃], 34.0, 34.1 [OCOCH₂(CH₂)₁₀CH₃], 67.3, 67.8 (ArOCH₂CH₂O), 69.17, 69.20 [CH₂O(CH₂CH₂O)₂], 114.6 (C-3, C-6), 123.1 (C-5'), 124.6 (C-2'), 128.0 (C-6'), 132.7 (C-4, C-5), 138.6 (C-1'), 141.1, 141.9 (C-3', C-4'), 146.2 (C-4, C-5), 170.9, 171.0 (C=O). FT-IR (ATR): v = 2918, 2850 (m), 1765 (s), 1492, 1465, 1363 (m), 1246, 1111 (s) cm^{-1} . MS (MALDI-TOF): m/z (%) = 1291.9 [M⁺ + Na], calcd for

 $C_{78}H_{124}NaO_{13}^{+}$ 1291.9. [NaI·7g]: 21 mg. DSC, Cr_1 41.1 °C [22.5 kJ mol-1] Cr2 90.6 °C [32.7 kJ mol-1] Col 117.1 °C (POM) I. 1H NMR (CDCl₃, 500 MHz): δ 0.87-0.90 (m, 12 H, CH₃), 1.30-1.39 [m, 80 H, OCOCH₂CH₂(CH₂)₁₀CH₃], 1.66-1.73 [m, 8 H, OCOCH₂CH₂(CH₂)₁₀CH₃], 2.48-2.51 [m, 8 H, OCOCH₂-(CH₂)₁₁CH₃], 3.77–3.79 [m, 4 H, CH₂O(CH₂CH₂O)₂CH₂], 3.88-3.90 [m, 4 H, CH₂O(CH₂CH₂O)₂CH₂], 4.06-4.08 (m, 4 H, ArOCH₂CH₂O), 4.27-4.29 (m, 4 H, ArOCH₂CH₂O), 6.87 (dd, $J_{6',5'} = 8.3, J_{6',2'} = 2.0$ Hz, 2 H, 6'-H), 6.92 (s, 2 H, 3-H, 6-H), 6.98 (d, $J_{2',6'} = 2.0$ Hz, 2 H, 2'-H), 7.00 (d, $J_{5',6'} = 8.3$ Hz, 2 H, 5'-H). ¹³C NMR (CDCl₃, 125 MHz): δ 14.1 (CH₃), 22.7, 24.9, 25.0, 29.20, 29.21, 29.35, 29.38, 29.5, 29.6, 29.69, 29.71, 29.74, 31.9 [OCOCH₂(CH₂)₁₁CH₃], 34.07, 34.13 [OCOCH₂(CH₂)₁₁CH₃], 67.7, 68.1 (ArOCH2CH2O), 69.4, 69.5 [CH2O(CH2CH2O)2], 114.9 (C-3, C-6), 123.1 (C-5'), 124.7 (C-2'), 128.0 (C-6'), 132.7 (C-4, C-5), 138.8 (C-1'), 141.1, 141.9 (C-3', C-4'), 146.6 (C-4, C-5), 170.9, 171.0 (C=O). FT-IR (ATR): v = 2918, 2850 (m), 2360 (s), 1764 (s), 1495, 1457, 1362 (m), 1246, 1185, 1108, 1056 (s), 943 (m) cm⁻¹. MS (MALDI-TOF): m/z (%) = 1347.9 [M⁺ + Na], calcd for C₈₂H₁₃₂NaO₁₃⁺ 1347.9.

3.0 Results and discussion

3.1 Synthesis of benzo[15]crown-5 ether derivatives 7 and 12 and their NaI complexes

The synthetic strategy to crown ethers 7 with alkyl ester groups is shown in Scheme 2. In order to avoid tedious chromatographic purification steps of intermediates with long side chains, we envisaged introducing first protecting groups which can be carried throughout the synthesis and can be replaced by alkyl carboxylates in the last step. For our purposes we chose the methoxymethyl (MOM) group because the final deprotection should not interfere with the crown ether moiety. Following a procedure by Fujita and coworkers¹³ 4-bromocatechol **2** was treated with dimethoxymethane in CH₂Cl₂ in the presence of P₄O₁₀ to give the bis-MOM-protected bromide **3** in 71% yield. In a one-pot procedure^{12,14} compound **3** was converted into the borolane **4**, which was isolated in 68% yield. Twofold Suzuki cross-coupling of **4** with dibromide **5**^{6e,12,15} in the presence of Pd(PPh₃)₄, K₂CO₃ and KF^{12,14a} followed by deprotection of **6a** under acidic conditions according to the method by Fletcher and Yardley¹⁶ and final esterification with acid chlorides in the presence







A similar strategy was used for the synthesis of gallic ester derivatives 12 (Scheme 3). Under the conditions described above, 1-bromo-4-methoxymethoxybenzene 818 was converted into the borolane 9 in 61% yield. Suzuki coupling with dibromide 5 gave the MOM-protected crown ether 10a in 46% yield. Subsequent acidic deprotection and esterification with gallic acid derivatives 11 in the presence of DCC and DMAP employing the conditions by Hess and Sheehan¹⁹ yielded the diesters 12 in 63-73%. Their complexation to $[NaI \cdot (12a-d)]$ proceeded smoothly. It should be noted that complexation of 7 and 12 could be monitored by NMR spectroscopy. For example, the ¹H NMR spectrum of 7d revealed downfield shifts upon complexation from $\delta = 4.18-4.20$ to 4.29-4.31 ppm for ArOCH₂CH₂O, from $\delta = 3.93-3.94$ to 4.08-4.10 ppm for ArOCH₂CH₂O, and from $\delta = 6.90$ to 6.93 ppm for 3-H and 6-H, whereas the ¹³C NMR spectrum revealed upfield shifts for C3, C6 from $\delta = 116.1$ to 114.7 and for C1, C2 from $\delta = 148.6$ to 146.2 ppm. In the case of series 12, similar shifts were found. Most characteristic is the upfield shift for C3, C6 from $\delta = 116.5$ to 115.4 ppm upon complexation (e.g. 12b).

It should be noted that upscaling is easily possible and purification of the crude tetra- and diesters 7 and 12 can be conveniently achieved by simple recrystallization from CH_2Cl_2 -ethanol. Structure and purity of all compounds were determined by conventional spectroscopic methods, mass spectrometry and elemental analysis.

3.2 Thermotropic properties

The thermotropic properties of molecules 7 and 12 and their sodium salts were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

3.2.1 Mesomorphic behavior of gallic ester derivatives 12a– d and their NaI complexes. Neither the uncomplexed derivatives 12a–d nor the corresponding complexes with sodium iodide [NaI·(12a–d)] revealed any liquid crystalline properties. Taking similar observations by Donnio and coworkers²⁰ into account, the absence of mesomorphism is not completely unexpected. Two trisalkyloxygallic acid building blocks assemble a large number of non-polar aliphatic chains to the *o*-terphenyl unit and thus, the polar crown ether unit seems to play a minor role as compared to the volume of the aliphatic chains. Consequently, the tendency

 $\label{eq:table_$

Compd	Phase transition temperature/°C, enthalpies/kJ mol ⁻¹					
	Col _r		Col_h			
NaI·7d	•	90^a	•	116.4 (1.0)	•	
NaI∙7e	•	100^{a}	•	129.4 (0.9)	•	
NaI∙7f	•	b	•	120.2 (0.8)	•	
NaI∙ 7g	• ^c	b	•	135.5 (0.9)	•	

^{*a*} The transition $\text{Col}_r \rightarrow \text{Col}_h$ was determined by X-ray measurement. ^{*b*} The transition $\text{Col}_r \rightarrow \text{Col}_h$ could not be determined neither by POM nor DSC. ^{*c*} Columnar soft crystal. Heating rate 10 K min⁻¹. Col_r = rectangular columnar, Col_h = hexagonal columnar, I = isotropic. for nanosegregation for compounds **12** and their sodium salts is dramatically reduced compared with the ether derivatives **1** (c.p. Scheme 1), resulting in a complete destabilization of mesophases.

3.2.2 Mesomorphic behavior of alkyl ester derivatives 7a-g and their NaI complexes. None of the uncomplexed alkyl esters 7a-g was found to be mesomorphic, and complexes $[NaI \cdot (7a-c)]$ with shorter alkyl chains (n = 6-8) melted directly into an isotropic liquid. In contrast, the corresponding complexes $[NaI \cdot (7d-g)]$ with longer alkyl chain lengths (n = 9-12) displayed mesomorphism. These findings for 7 and 12 indicate that



Fig. 1 DSC curves of [NaI·7d]. Heating/cooling rate 10 K min⁻¹.



Fig. 2 Textures of complex [NaI·7d] as seen between crossed polarizers upon cooling from the isotropic state (cooling rate 1 K min⁻¹). (a) Fanshaped texture of the Col_h phase at 113 °C and (b) striped fan-shaped texture of the second Col_x phase at 78 °C (magnification $200 \times$).

mesomorphism in the series of ester derivatives depends on a sensitive balance of core size and volume fraction of aliphatic chains. Upon heating the DSC curves of complexes [NaI \cdot (7d,e)] with decyl and undecyl chains showed a large endothermal melting transition from a crystalline to a liquid crystalline state at 87 °C and 89 °C and a small clearing transition at 122 °C and 131 °C, respectively. All other consecutive heating (Table 1) and cooling cycles exhibited only the clearing transition.

Complexes [NaI·(**7f**,**g**)] with longer dodecyl and tridecyl chains revealed a more complex thermotropic behaviour upon first heating with several melting and recrystallization transitions before they cleared from the high temperature mesophase to the isotropic liquid. However, all further heating and cooling curves showed again only a transition from the mesophase to the isotropic liquid (Table 1). No recrystallization could be observed even after prolonged annealing below the initial melting temperature. Typical DSC heating and cooling cycles of [NaI·**7d**] are shown in Fig. 1.

Decomposition of the salts did not occur upon heating up to 250 °C as proved by TGA measurements for [NaI \cdot 7g], thus indicating the thermal stability in this temperature range.

In contrast to DSC studies, POM studies of complexes $[NaI \cdot (7d-g)]$ confirmed the presence of two different mesophases. This is exemplarily shown for $[NaI \cdot 7d]$ (Fig. 2).

Upon slow cooling from the isotropic liquid fan-shaped textures were observed at 113 °C (Fig. 2a) which are frequently found for columnar hexagonal (Col_h) mesophases.²¹ Upon further cooling to 78 °C striped fan-shaped textures appeared (Fig. 2b). Although complex [NaI·7d] was highly viscous at this temperature, shearing

was still possible. These slight texture alterations indicate the existence of a second mesophase Col_X at low-temperatures. The increase in birefringence, viscosity and the additional fine structure in the texture points to the formation of a mesophase of higher order. Typically mesogens aggregating in columnar phases exhibit phase sequences from Col_h to Col_r upon cooling.

3.2.3 Comparison of ester derivatives 7, 12 with ethers 1 and the corresponding NaI complexes. For classical disc-shaped hexakisalkyloxytriphenylenes or cone-shaped hexakisalkyloxytribenzocyclononatrienes the replacement of the ether side chains with ester groups resulted in a significant increase of the clearing points, while the melting points remained constant. As a consequence, the mesophase stability was dramatically improved.²² In contrast, wedge-shaped crown ether derivatives 1, 7, and 12 behaved differently. They showed similar melting points in the range 27-64 °C with the alkyl chain length having a stronger influence than the connecting ether or ester moiety. As mentioned above, ethers 1 are mesomorphic (SmA) with a minimum chain length of C12, whereas both esters 7 and 12 do not show any mesophase. Regarding the NaI complexes, mixed results were obtained. Complexes [NaI · 1] with a minimum chain length of C12 displayed columnar phases with melting points around 28-55 °C and clearing temperatures at 157-185 °C, thus, complexation considerably increased the mesophase stability. Complexation of 7 to [NaI·7] shifted the melting points from 34-63 °C to 72-118 °C for non-mesomorphic esters 7a-c (chain lengths \leq C9) and to 95–103 °C for mesogens 7d–g (chain lengths



Fig. 3 X-Ray diffraction pattern and the corresponding small-angle X-ray scattering (SAXS) profiles of an oriented sample of [NaI \cdot 7d] (obtained by prolonged annealing) in the Col_h phase at 95 °C (a), (b) and in the Col_r phase at 75 °C (c), (d). Columns are oriented parallel to the X-ray beam.

>C9), respectively. Clearing temperatures of $[NaI \cdot 7d-g]$ are in the range 117–136 °C. Overall, mesophase stabilities were much lower for ester complexes $[NaI \cdot 7]$ than for ether complexes $[NaI \cdot 1]$. In the case of gallic esters 12, the complexation shifted the melting points from 27–45 °C to much higher temperatures of 131–206 °C and no mesophase could be observed.

3.3 X-Ray diffraction

In order to confirm the preliminary assignment of the mesophases based on POM studies, X-ray diffraction experiments were carried out.



Fig. 4 Wide-angle X-ray scattering (WAXS) profile of [NaI·7d] in the columnar hexagonal mesophase.

Oriented samples were obtained by extrusion from the columnar mesophase or prolonged annealing. A diffraction pattern at small angles of a homeotropic oriented sample of $[NaI \cdot 7d]$ in the Col_h phase is shown in Fig. 3a and the corresponding small-angle X-ray scattering (SAXS) profile in Fig. 3b. Since the columns are parallel aligned with the X-ray beam the diffraction pattern reflects the hexagonal symmetry of the 2D organisation of columns, which is confirmed by the ratio $1:\sqrt{3}:2$ for the reciprocal Bragg distances of the three reflections in Fig. 3b. The reflections are consequently indexed with hk = 10, 11 and 20 and the mesophase symmetry can be assigned to the p6mm plane group. Upon cooling the 10 reflection splits into two reflections (Fig. 3c) as recently observed also for hexacetenar metallomesogens.²³ The indexation of the large number of new small angle reflections clearly verify the rectangular symmetry (p2gg) of the columnar phase (Fig. 3d). Temperature-dependent X-ray measurements during heating and cooling cycles confirmed the enantiotropic nature of the mesophases.

The wide-angle X-ray scattering (WAXS) profile of the Col_h phase of [NaI·7d] (Fig. 4) reveals only a broad halo at 4.6 Å due to the average separation of the liquid alkyl chains and the mesogens along the column.

The higher homologues $[NaI \cdot (7e-g)]$ gave similar results as depicted in Fig. 5a and b for the columnar rectangular mesophases.

In the columnar rectangular phase of $[NaI \cdot 7e]$ two reflections at (i) *ca.* 4.2 Å, and (ii) 4.5 Å appear at the meridian of the



Fig. 5 Small-angle (a) and wide-angle X-ray scattering profiles (b) of complexes $[NaI \cdot (7d-g)]$ in the Col_r mesophase at 70 °C (7g), 75 °C (7d), 80 °C (7f), and 95 °C (7e), and X-ray diffraction pattern of an oriented sample $[NaI \cdot 7e]$ in its columnar rectangular mesophase (c).

diffraction pattern of an oriented sample (Fig. 5c), pointing to additional intracolumnar periodicity.

The data of X-ray diffraction experiments,²⁴ summarized in Table 2, reveal that for both columnar rectangular and columnar hexagonal phases increasing chain lengths led to increasing lattice parameters. With the exception of [NaI·7g], the lattice parameter b of the Col_r phase corresponds to the lattice parameter a of the Col_r phase. That means the relative positions of columns are changing with decreasing temperature.

This can be attributed to the tilt of mesogens versus the columnar axes and thus the formation of an elliptical cross section of the columnar cores as exemplified in Fig. 6.

Another feature of the columnar rectangular mesophase is the change of symmetry of the unit cell with increasing chain length from p2gg for complexes $[NaI \cdot (7d-f)]$ to an orthorhombic structure for derivative $[NaI \cdot 7g]$. A change of symmetry was reported

Table 2 dSpacings and lattice parameters for both low and hightemperature mesophases of sodium complexes [NaI·(7d-g)]

Compd	Mesophase	Lattice spacing/Å	d spacing/Å obsd (calcd)	Miller indices
NaI∙7d	Col _r (p2gg) at 75 °C	a = 68.2	40.7 (40.7)	11
		b = 50.8	34.1 (34.1)	20
			28.4 (28.3)	21
			23.7(23.8) 20.3(20.4)	12
			20.3(20.4) 17.0(17.0)	40
	Col. (p6mm) at 95 °C	a - 46.9	40.6 (40.6)	40
	con _h (ponni) at 55° c	u = 40.9	23 6 (23 5)	11
			20.3 (20.3)	20
NaI∙7e	Col _r (p2gg) at 95 °C	a = 70.3	40.9 (40.9)	11
		b = 50.3	35.1 (35.1)	20
			24.1 (23.7)	12
			21.1 (21.2)	31
			20.4 (20.5)	22
			17.7 (17.6)	40
	Col _h at 90 °C	a = 47.3	41.0 (41.0)	10
			23.8 (23.7)	11
NT T F C		72.4	20.7 (20.5)	20
Nal·7f	$\operatorname{Col}_{r}(p2gg)$ at 80 °C	a = 72.4	42.9 (42.9)	11
		b = 53.2	36.2 (36.2)	20
			25.2(25.0)	12
			22.0(22.0)	22
			181(181)	40
	Col ₂ (p6mm) at 100 °C	a = 49.2	42.6 (42.6)	10
			24.6 (24.6)	11
			21.4 (21.3)	20
NaI∙ 7g	Cr_{col}^{a} at 70 °C	a = 74.5	47.2 (47.2)	110^{b}
		b = 61.1	37.2 (37.2)	200
			23.5 (23.6)	220
			18.6 (18.6)	400
			9.0 (9.0)	001
			7.0 (6.9)	351
			5.8 (5.9)	880
			5.5 (5.6)	6/1
			3.3(3.3)	002
			4.0(4.3)	442
			4.2(4.2)	352
			42(42)	532
	Col _b (p6mm) at 120 °C	a = 49.6	42.9 (42.9)	10
	(Polini) at 120 C		24.6 (24.8)	11
			21.4 (21.5)	20

^a Columnar soft crystal. ^b hkl values in the case of soft crystal phase.



Fig. 6 Schematic illustration of the change of column orientation from Col_{h} to Col_{r} with decreasing temperature; a(hex) = b(rec).

by Hendrikx and Levelut for truxene derivatives.²⁵ Alternatively, the Col_{r} to Col_{h} transition with increasing temperature might also be explained by conformational changes, *i.e.*, with increasing temperature the alkyl chains are more flexible and thus require more space, which can be accommodated better in a columnar hexagonal unit cell than in a columnar rectangular unit cell.²⁶

Upon cooling from the Col_h mesophase complexes [NaI \cdot (7d–f)] formed a disordered Col_r mesophase. In the case of [NaI \cdot 7g], a different diffraction pattern was observed (Fig. 7). Along the meridian two layer lines of reflections with two relatively sharp reflections at the meridian at 4.55 and 8.99 Å are visible. The latter two signals can be indexed as 001 and as 002 reflections. The other



Fig. 7 2D X-ray diffraction pattern of an oriented sample of $[NaI \cdot 7g]$ at 70 °C (a) and a schematic illustration (b). Empty ellipsoids symbolize weak reflections, grey ellipsoids strong reflections.

reflections which are not located at the meridian result from layers with mixed indices hkl, indicating a 3-dimensional order in this columnar mesophase, which was recently also observed in different non-conventional mesogenic materials.²⁷ Thus, the low-temperature mesophase of [NaI·7g] possess a base-centred orthorhombic structure and may be attributed to a soft crystal or a highly ordered columnar liquid crystal. From the comparison of WAXS profiles of [NaI·7g] (Fig. 5b) with the corresponding shorter homologues [NaI·(7d–f)] it is obvious that the reflections at 4.55 and 8.99 Å are much more pronounced for 7g than for the other complexes [NaI·(7d–f)]. In this case, a soft crystal might also be proposed.²⁸

3.4 Arrangement of the molecules in the column: packing study

In order to explain the self-assembly of *o*-terphenyl crown ethers such as **1** into columnar mesophases, we recently used X-ray crystal structure analyses of non-mesogenic short-chain analogues as a tool.¹² The obtained data allowed us to calculate the molecular dimensions. Unfortunately, it was impossible to grow suitable single crystals from complexed [NaI·1]. However, MOM ether complex [NaI·10a] gave single crystals which were analyzed by X-ray crystallography (Fig. 8). In the solid state structure of [NaI·10a] the Na⁺ cation is positioned in the middle of the crown with the iodide anion residing close to the Na⁺ (Na–I distance 2.98 Å), thus allowing sixfold coordination of Na⁺. Although complex [NaI·10a] is not mesogenic, its structural data of the core unit were taken as input parameters for simple molecular modeling of complexes [NaI·(7d–g)].

Based on the studies of Percec^{1c} we propose that nanosegregation and steric constraints should lead to the formation of supramolecular assemblies, in which the polar crown ether moieties are located in the centre of the column, whereas the hydrophobic aliphatic chains point outwards. Due to the twisting of the *o*-terphenyl unit π - π interactions contribute only to a minor extent to the overall intracolumnar stability. The number of molecules per unit cell Z for the columnar hexagonal mesophases of [NaI · (7d-g)] was obtained by eqn (1).²⁹

$$Z = \frac{N_{\rm A}Ah\rho}{M_{\rm w}} \tag{1}$$

where $M_{\rm w}$ = molecular weight, $N_{\rm A}$ = Avogadro's constant, $A = a^2 \cdot \sin 60^\circ$ = cross section of the hexagonal unit cell, h = height of the columnar unit, ρ = density (with ρ = 1 g cm⁻³ as a typical value for organic material); A and h were obtained by SAXS and WAXS experiments.

As discussed above, no sharp WAXS reflections were obtained for the Col_h mesophase due to its disorder. The reflections, which



Fig. 8 Structure of complex [NaI · 10a] in the solid state.



Fig. 9 Simple molecular modeling (Chem3D) of a columnar unit consisting of four $[NaI \cdot 7g]$ molecules.

were caused by core-core and alkyl-alkyl interactions, overlapped resulting in a broad halo at 4.6 Å. Thus the height of the a columnar slice in the Col_h phase was estimated to be h = 4.6 Å. Eqn (1), applied to complex $[NaI \cdot 7g]$ with the lattice parameter a = 49.6 Å yielded Z = 3.9. For the other mesogens [NaI \cdot 7d,e,f] in the hexagonal columnar phases Z values of 4.0, 3.9, and 4.1, det columnarrespectively, were obtained. These results point to a tetramer forming a slice of column. From these results the volume fraction of the core of a columnar slice can be calculated by $V_{core} = V_{unit}$ $_{cell}-Z\!\cdot\!V_{chains}\!^{23}$ Assuming a circular cross section of the column core in the uniaxial hexagonal mesophase, the radius of the core from an ester oxygen to the centre can be estimated by $r_{core} = \sqrt{(V_{core}/(\pi h))}$. The values obtained for the hexagonal phases range from 15.9-16.8 Å and are in excellent agreement with the measured radius of a molecular model (Fig. 9) which amounts to approximately 17 Å.

4.0 Conclusion

Novel ester-substituted [15]crown-5 ethers 7 and 12 with an o-terphenyl unit have been prepared and their mesomorphic behavior studied. Neither the alkanoic esters 7 nor the gallic esters 12 and their sodium complexes [NaI · 12] displayed any liquid crystalline properties. In contrast, complexation of alkanoic esters 7d-g with NaI resulted in the formation of mesophases. The complexes $[NaI \cdot (7d-g)]$ with a minimum alkyl chain length of C10 formed columnar rectangular mesophases at lower temperatures and columnar hexagonal mesophases at higher temperatures. Due to the increased rotational freedom of the molecules around the columnar axis at higher temperature the hexagonal symmetry is preferred for optimum space filling.³⁰ For $[NaI \cdot 7g]$ a low-temperature mesophase was observed, which might be attributed to a soft crystal or highly orderd columnar mesophase with orthorhombic symmetry. The striking difference between the two series of NaI complexes has still not been fully understood and future work is necessary to study the influence of alkali salts on mesomorphic properties.

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