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Ten isomeric five-ring bent-core mesogens: The influence of the direction of the carboxyl connecting groups on the mesophase behaviour

The experimental procedure to prepare compound **IVi/12** via **IIIb/12-PG and IIIb/12** is given. Furthermore, analytical data of the intermediates **IIId/12, IIIe/12** and of the final compounds **IVb/12**, **IVd–j/12** are summarized.

4-(4-n-Dodecyloxybenzoyloxy)phenyl 3-benzyloxybenzoate **IIIb/12-PG**

To a solution of 4-hydroxyphenyl 4-n-dodecyloxybenzoate **IIa** (3.98 g,10 mmol) and 3-benzyloxybenzoic acid **Id** (2.28g; 10 mmol) in 30 ml dichloromethane N,N´-dicyclohexylcarbodiimid (DCC) (2.45g; 12 mmol) and a catalytic amount of 4-dimethylaminopyridine (DMAP) were added. The mixture was stirred at room temperature for about 24 hours. The precipitate was filtered off. After evaporating the solvents the crude material was recrystallized several times from ethanol. Yield: 4.56 g, 75.1 %; melting behaviour (°C): Cr 111 (N 54) I.; Elemental analysis: Mm 608.77 ($C_{39}H_{44}O_6$), calculated (%): C 76.95, H 7.29; found C 76.80, H 7.33.

^{1}H-NMR (400 MHz), $CDCl_3$**:** 8.12 (d, ^{3}J = 8.7, 2H, ArH); 7.82-7.79 (m, 11H, ArH); 6.96 (d, ^{3}J = 8.8, 2H, ArH); 5.14 (s, 2H, OCH_2Ar); 4.05-4.02 (m, 2H, OCH_2); 1.83-1.79 (m, 2H, CH_2); 1.53-1.26 (m, 18H, CH_2); 0.88-0.86 (d, ^{3}J = 6.7, 3H, CH_3).

4-(4-n-Dodecyloxybenzoyloxy)phenyl 3-hydroxybenzoate **IIIb/12**

Compound **IIIb/12-PG** (4.25 g; 7 mmol) was dissolved in ethyl acetate (100 ml) and 5% Pd/C catalyst (0.5 g) was added. The mixture was treated at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. The catalyst was filtered off and the solvent evaporated. The residue was recrystallized from ethanol. Yield: 3.11 g, 86.0 %; melting behaviour (°C): Cr 143 (N 131) I. Elemental analysis: Mm 518.65 ($C_{32}H_{38}O_6$), calculated (%): C 74.11, H 7.38; found C 74.15, H 7.20.

^{1}H-NMR (400 MHz), $CDCl_3$: 8.12 (d, ^{3}J = 8.7, 2H, ArH); 7.77 (d, ^{3}J = 8.1, 1H, ArH); 7.63 (s, 1H, ArH); 7.24 (s, 4H, ArH); 7.10 (d, ^{3}J = 6.0, 1H, ArH); 6.95 (d, ^{3}J = 8.7, 2H, ArH); 4.99 (s, OH); 4.02-4.00 (m, 2H, OCH_2); 1.82-1.80 (m, 2H, CH_2); 1.53-1.25 (m, 18H, CH_2); 0.86-0.88 (m, 3H, CH_3).

4-(4-n-Dodecyloxybenzoyloxy)phenyl 3-[4-(4-n-dodecyloxyphenoxycarbonyl)benzoate] Compound **IVi/12***:*

A mixture of 4-(4-n-dodecyloxyphenoxycarbonyl)benzoic acid **IId/12** (0.85 g, 2 mmol) and 10 ml thionyl chloride was refluxed for 4 h. Excess of thionyl chloride was removed by destillation under reduced pressure. Adding 20 ml toluene and following evaporation was realized twice to remove residues of thionyl chloride. The resulting 4-(4-n-dodecyloxyphenoxycarbonyl)benzoyl chloride was dissolved in dry toluene (20 ml) and added to a solution of 4-(4-n-dodecyloxybenzoyloxy)phenyl 3-hydroxybenzoate **IIIb/12** (1.03 g, 2 mmol) and triethylamine (0.25 g, 2.5 mmol) under stirring at 5 °C. The reaction mixture was stirred for 24 h at room temperature. The precipitate of triethylamine hydrochloride was separated. The filtrate was concentrated and the crude material purified by column chromatography with chloroform as eluant. Following crystallization from DMF/ethanol gave white crystals of compound **IVi/12,** yield 0.95 g, 50.4 %; melting behaviour see table 1. Elemental analysis: Mm 927.18 ($C_{58}H_{70}O_{10}$), calculated (%): C 75.13, H 7.61; found C 75.22, H 7.60

^{1}H-NMR (400 MHz), $CDCl_3$: 8.33 (s, 4H, ArH); 8.30-8.07 (m, 4H, ArH); 7.60-7.52 (m, 2H, ArH); 7.26 (s, 4H, ArH); 7.14-7.11 (m, 2H, ArH); 6.95 (d, ^3J = 8.9, 2H, ArH); 6.93 (d, ^3J = 8.9, 2H, ArH); 4.03 (t, ^3J = 6.5, 2H, OCH_2); 3.95 (t, ^3J = 6.5, 2H, OCH_2); 1.83-1.76 (m, 4H, CH_2); 1.55-1.26 (m, 36H, CH_2); 0.87 (t, ^3J = 6.8, 6H, CH_3)

IIId/12: ^{1}H-NMR (400 MHz), $CDCl_3$: 9.01-9.00 (m, 1H, ArH); 8.50 (d, ^{3}J = 8.0, 1H, ArH); 8.48 (d, ^{3}J = 7.9, 1H, ArH); 8.12 (d, ^{3}J = 8.9, 2H, ArH); 7.69 (t, ^{3}J = 7.8, 1H, ArH); 7.46-7.36 (m, 4H, ArH); 6.96 (d, ^{3}J = 9.1, 2H, ArH); 4.03 (t, ^{3}J = 6.6, 2H, OCH_2); 1.83-1.79 (m, 18H, CH_2); 0.87 (t, ^{3}J = 6.8, 3H, CH_3). White crystals, mp. 199 °C

IIIe/12: ^{1}H-NMR (400 MHz), $CDCl_3$: 8.32 (s, 4H, ArH); 8.01-7.96 (m, 2H, ArH); 7.56-7.50 (m, 2H, ArH); 7.13 (d, ^{3}J = 9.1, 2H, ArH); 6.93 (d, ^{3}J = 8.9, 2H, ArH); 3.95 (t, ^{3}J = 6.5, 2H, OCH_2); 1.80-1.76 (m, 2H, CH_2); 1.52-1.24 (m, 18H, CH_2); 0.87 (t, ^{3}J = 6.6, 3H, CH_3). White crystals, mp. 219.5 °C.

IVb/12: ^{1}H-NMR (400 MHZ) $CDCl_3$: 9.01 (t, ^4J = 1.7, 1H, ArH); 8.46 (dd, ^4J = 1.7, ^3J = 7.9, 2H, ArH); 8.13 (d, ^3J = 8.7, 4H, ArH); 7.68 (t, ^3J = 7.9, 1H, ArH); 7.31-7.26 (m, 8H, ArH); 6.96 (d, ^3J = 8.9, 4H, ArH); 4.03 (t, ^3J = 6.6, 4H, OCH_2); 1.85-1.77 (m, 4H, CH_2); 1.53-1.42 (m, 4H, CH_2); 1.37-1.24 (m, 32H, CH_2); 0.87 (t, ^3J = 6.6, 6H, CH_3).

IVd/12: ^{1}H-NMR (400 MHz), $CDCl_3$: 9.03 (t, ^4J = 1.7, 1H, ArH); 8.49 (dd, ^4J = 1.7, ^3J = 7.9, 2H, ArH); 8.29 (d, ^3J = 8.9, 4H, ArH); 7.73 (t, ^3J = 7.9, 1H, ArH); 7.39 (d, ^3J = 8.7, 2H, ArH); 7.11 (d, ^3J = 9.1, 2H, ArH); 6.92 (d, ^3J = 9.1, 2H, ArH); 3.95 (t, ^3J = 6.5, 4H, OCH_2); 1.81-1.74 (m, 4H, CH_2); 1.52-1.41 (m, 4H, CH_2); 1.32-1.23 (m, 32H, CH_2); 0.87 (t, ^3J = 6.6, 6H, CH_3).

IVe/12: ^{1}H-NMR (500 MHz), $CDCl_3$: 8.30-8.25 (m, 4H, ArH); 8.15-8.12 (m, 3H, ArH); 8.07 (t, ^4J = 1.9, 1H, ArH); 7.6 (t, ^3J = 7.9, 1H, ArH); 7.55-7.52 (m, 1H, ArH); 7.36 (d, ^3J = 8.9, 2H, ArH); 7.38 (d, ^3J = 8.9, 2H, ArH); 7.10 (d, ^3J = 9.0, 2H, ArH); 6.91 (d, ^3J = 9.0, 2H, ArH); 6.97 (d, ^3J = 8.9, 2H, ArH); 4.04 (t, ^3J = 6.6, 2H, OCH_2); 3.95 (t, ^3J = 6.6, 2H, OCH_2); 1.84-1.74 (m, 4H, CH_2); 1.50-1.20 (m, 36H, CH_2); 0.87 (t, ^3J = 6.9, 6H, CH_3).

IVf/12: ^{1}H-NMR (400 MHz), $CDCl_3$: 8.29 (d, ^3J = 8.7, 2H, ArH); 8.15-8.11 (m, 5H, ArH); 8.06 (t, ^3J = 1.9, 1H, ArH); 7.53-7.50 (m, 1H, ArH); 7.59 (t, ^3J = 7.8, 1H, ArH); 7.38 (d, ^3J = 8.9, 2H, ArH); 7.26 (s, 4H, ArH); 6.96 (d, ^3J = 8.9, 2H, ArH); 6.97 (d, ^3J = 9.0, 2H, ArH); 4.06-4.02 (m, 4H, OCH_2); 1.85-1.77 (m, 4H, CH_2); 1.53-1.42 (m, 4H, CH_2); 1.35-1.24 (m, 32H, CH_2); 0.87 (t, ^3J = 6.8, 6H, CH_3).

IVg/12: ^{1}H-NMR (400 MHz), $CDCl_3$: : 8.31 (s, 4H, ArH); 8.26 (d, ^3J = 8.7, 2H, ArH); 8.13 (d, ^3J = 8.9, 2H, ArH); 7.50 (t, ^3J = 8.2, 1H, ArH); 7.36 (d, ^3J = 8.7, 2H, ArH); 7.23-7.17 (m, 3H, ArH); 7.13 (d, ^3J = 8.9, 2H, ArH); 6.97 (d, ^3J = 9.1, 2H, ArH); 6.92 (d, ^3J = 9.1, 2H, ArH); 4.04 (t, ^3J = 6.6, 2H, OCH_2); 3.95 (t, ^3J = 6.6, 2H, OCH_2); 1.85-1.74 (m, 4H, CH_2); 1.40-1.23 (m, 32H, CH_2); 1.49-1.42 (m, 4H, CH_2); 0.87 (t, ^3J = 6.4, 6H, CH_3).

IVh/12: ^{1}H-NMR (400 MHz, $CDCl_3$): 9.02 (t, ^4J = 1.7, 1H, ArH); 8.46-8.49 (m, 2H, ArH); 8.28 (d, ^3J = 8.7, 2H,

ArH); 8.13 (d, ^3J = 9.0, 2H, ArH); 7.70 (t, ^3J = 7.7, 1H, ArH); 7.39 (d, ^3J = 8.9, 2H, ArH); 7.28-7.29 (m, 4H, ArH); 7.10 (d, ^3J = 8.4, 2H, ArH); 6.91-6.97 (m, 4H, ArH); 4.03 (t, ^3J = 6.7, 2H, OCH_2); 3.95 (t, ^3J = 6.6, 2H, OCH_2); 1.82-1.74 (m, 4H, CH_2); 1.52-1.24 (m, 36H, CH_2); 0.87 (t, ^3J = 6.9, 6H, CH_3).

IVj/12: ^{1}H-NMR (400 MHz), $CDCl_3$: 8.32 (s, 4H, ArH); 8.27 (d, ^3J = 8.7, 2H, ArH); 8.16-8.09 (m, 2H, ArH); 7.66-7.54 (m, 2H, ArH); 7.36 (d, ^3J = 8.7, 2H, ArH); 7.13 (d, ^3J = 8.9, 2H, ArH); 7.10 (d, ^3J = 8.9, 2H, ArH); 6.93 (d, ^3J = 8.9, 2H, ArH); 6.91 (d, ^3J = 8.9, 2H, ArH); 3.97-3.93 (m, 4H, OCH_2); 1.80-1.75 (m, 4H, CH_2); 1.53-1.25 (m, 36H, CH_2); 0.87 (t, ^3J = 6.7, 6H, CH_3).