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Thermotropic cubic and tetragonal phases made of rod-like molecules

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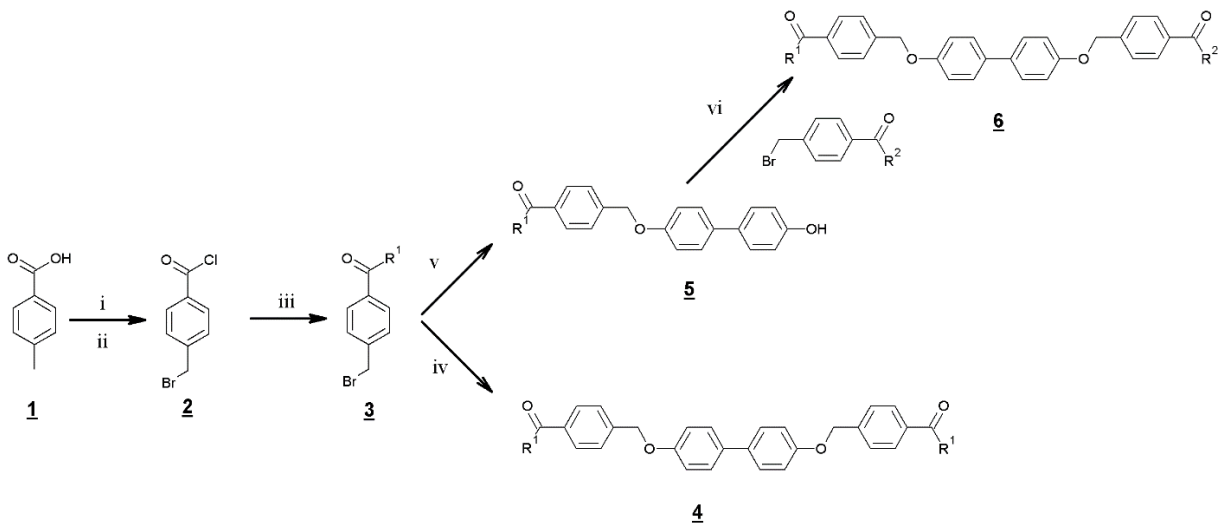
Synthesis and spectral characterization of studied compounds



Scheme S1. Synthesis scheme of rod-like mesogenic dimers. Reaction conditions: i) Br_2, hv; ii) $SOCl_2$, $CHCl_3$, reflux; iii) R^1OH, pyridine, toluene; iv) KI, K_2CO_3, 4,-4' – dihydroxybiphenol (0,5 eq), DMF; v) KI, K_2CO_3, 4,-4' – dihydroxybiphenol (2,5 eq), DMF; vi) KI, K_2CO_3, excess of alkyl 4-(bromomethyl)benzoate , DMF.

Preparation of 4-Bromomethyl-benzoyl chloride 2

To a dried 1000 mL two-neck round-bottom flask equipped with a stir bar and reflux condenser p-toluic acid **1** (34.04g, 0.25 mol) and CCl_4 (400 mL) was added. Solution was heated to reflux and then bromine solution (12.9 mL, 0.25 mol) in CCl_4 (20 mL) was added dropwise within 1.5h in the presence of visible light from 500W lamp. Slightly orange solution was cooled down and thionyl chloride (54.41 mL, 0.75 mol) was added afterwards stirred at reflux

for 2 h and then cooled. After the solvents were evaporated, the crude material was purified by distillation under lowered pressure yielding the pure product **2** as white crystals (68% yield). m.p: 33–34.

*Analytical data for compound **2**:*
^{1}H-NMR ($CDCl_3$) (δ, ppm): 8.12-8.11 (d, 2H), 8.09-8.06 (d, 2H), 4.63 (s, 2H).

Preparation of (R/S)-1-methylheptyl-4-(bromomethyl)-benzoate 3
To the acid chloride **2** (10.0g, 42.8 mmol) was dissolved in a dried toluene (130 mL) and pyridine (3.78 mL, 47.1 mmol) was added. The resulting solution was gently stirred at lowered temperature (3-5^{o}C) and the racemic 2-octanol (9.11 g, 70.0 mmol) was slowly added. The resulting suspension was further stirred gently at room temperature for 3 h. The white precipitate was filtrated and residue solution was evaporated; the crude material was purified by column chromatography (hexane/toluene = 2/8 as eluent) to give relevant ester **3** [R^1= [-$CH(CH_3)C_6H_{13}$] in 78% yield as a white solid.
The same procedure was applied to obtain compounds having other terminal chains. The following alcohols have been subjected to the esterification reaction with 4-Bromomethyl-benzoyl chloride to obtain proper benzyl bromide esters: (R)-2-octanol [substrate for final molecule 6/1 (R/RS) and 6/1 (R/R)], racemic 2-octanol [substrate for final molecule 6/1 (R/RS) and 6/1 (RS/RS)], racemic 2-undecanol [substrate for final molecule 9/1 (RS/RS)], racemic 2-dodecanol [substrate for final molecule 10/1 (RS/RS)], 5-nananol [substrate for final molecule 4/4], racemic 3-dodecanol 9/2 (RS/RS)].
Optically pure substrate: (R)-(−)-2-Octanol, 99% ([α]17/D −9.5°, neat) from Sigma-Aldrich has been used for synthesis of precursor of final compound **6/1 (R/R)**. The esterification reaction proceeds according to the SN2 mechanism, but not on the chiral carbon of (R)-2-octanol, thus neither racemization nor chirality inversion takes place and chirality of the substrate is completely preserved in the final product.

*Analytical data for compound **3*** ((R/S)-1-methylheptyl-4-(bromomethyl)-benzoate)
^{1}H-NMR ($CDCl_3$, 400MHz) δ8.04 (2H, d, J=8.2Hz); 7.46 (2H, d, J=8.2Hz); 5.15 (1H, m); 4.31 (2H,s); 1.81-1.70 (2H, m); 1.68-1.56 (3H, m); 1.47-1.23 (8H, m); 0.88 (3H, t, J=6.9Hz);

di-[(R/S)-1-methylheptyl]-4,4`-(4,4`-biphenyloxy)dibenzoate 4 (6/1(RS/RS))
To a gently heated solution – (45-50^{o}C), of 4,4'-dihydroxybiphenyl(11.14 g, 59.8 mmol), potassium iodide (14.61 g, 88.0 mmol) and potassium carbonate (14.59 g; 105.6 mmol) in 340mL of 1-methyl-2-pyrrolidinone a (R/S)-1-methylheptyl-4-(bromomethyl)-benzoate **3** (39,1 g, 119.6 mmol) was slowly added. The reaction mixture was further stirred for 24h at 120^{o}C. After that, the mixture was cooled down to a room temperature and poured into water with ice. Cream precipitate was dried and the crude product was chromatographed on silica gel using 1:1 mixture of toluene and hexane. The monoalkylated product 4aand dialkylated products were obtained. Yield of monoalkylated product 14%. Yield of dialkylated product 46%.
The same procedure was applied to obtain other di and monoalkylated derivatives of proper benzoyl bromides esters.

Analytical data for final compounds (*compounds **4** in Scheme S1.)*

6/1 (RS/RS)
^{1}H-NMR ($CDCl_3$, 400MHz): δ 8.10-8.05 (4H, m); 7.55-7.50 (4H,m); 7.50-7.44 (4H, m); 7.06-6.98
(4H, m); 5.22-5.12 (6H, m); 1.81-1.70 (4H, m); 1.68-1.56 (6H, m); 1.47-1.23 (16H, m); 0.95-0.83 (6H, m)
^{13}C-NMR ($CDCl_3$, 100MHz): δ 165.9; 157.6; 141.0; 130.5; 129.8; 126.9; 115.1; 71.8; 69.4; 36.1; 31.7; 29.2; 22.6; 14.1
Elemental analysis calculated for: $C_{44}H_{54}O_6$; C(77.84%), H(8.02%), O(14.14%). Found C(77.97%), H(7.93%).

6/1 (R/R)
^{1}H-NMR ($CDCl_3$, 400MHz): δ 8.10-8.05 (4H, m); 7.55-7.50 (4H,m); 7.50-7.43 (4H, m); 7.06-6.98
(4H, m); 5.22-5.11 (6H, m); 1.81-1.70 (4H, m); 1.67-1.56 (6H, m); 1.47-1.23 (16H, m); 0.95-0.83 (6H, m)
^{13}C-NMR ($CDCl_3$, 100MHz): δ 165.9; 157.6; 142.0; 133.8; 129.8; 127.0; 115.1; 71.8; 69.4; 36.1; 31.7; 29.2; 25.4; 22.6; 14.1
Elemental analysis calculated for: $C_{44}H_{54}O_6$; C(77.84%), H(8.02%), O(14.14%). Found C(77.90%), H(7.95%).

9/1 (RS/RS)
^{1}H-NMR ($CDCl_3$, 400MHz): δ 8.10-8.05 (4H, m); 7.55-7.50 (4H,m); 7.50-7.44 (4H, m); 7.06-6.98 (4H, m); 5.22-5.12 (6H, m); 1.81-1.71 (2H, m); 1.68-1.56 (3H, m); 1.47-1.23 (28H, m); 0.95-0.82 (6H, m)
^{13}C-NMR ($CDCl_3$, 100MHz): δ 165.9; 157.6; 141.0; 130.5; 129.8; 126.9; 115.1; 71.8; 69.4; 36.1; 32.0, 31.7; 29.2; 25.6, 24.1, 22.6; 14.1
Elemental analysis calculated for: $C_{50}H_{66}O_6$; C(78.70%), H(8.72%), O(12.58%). Found C(78.91%) H(8.73%).

10/1 (RS/RS)
^{1}H-NMR ($CDCl_3$, 400MHz): δ 8.10-8.05 (4H, m); 7.55-7.51 (4H,m); 7.50-7.43 (4H, m); 7.06-6.98 (4H, m); 5.22-5.12 (6H, m); 1.81-1.72 (2H, m); 1.67-1.56 (3H, m); 1.47-1.23 (30H, m); 0.95-0.83 (6H, m)
^{13}C-NMR ($CDCl_3$, 100MHz): δ 165.9; 157.5; 141.0; 130.1; 129.8; 127.0; 115.1; 71.8; 69.4; 36.2; 32.3, 31.7; 29.2; 25.8, 24.0, 22.6; 14.1
Elemental analysis calculated for: $C_{52}H_{70}O_6$; C(78.95%), H(8.92%), O(12.13%). Found ; C(79.13%); H(8.94%).

9/2 (RS/RS)
^{1}H-NMR ($CDCl_3$, 400MHz): δ 8.10-8.05 (4H, m); 7.55-7.50 (4H,m); 7.50-7.45 (4H, m); 7.05-6.99 (4H, m) 5.17 (4H, s); 5.13-5.04 (2H, m); 1.77-1.59 (8H, m); 1.44-1.18 (28H, m); 0.95 (6H, t, J=7.4 Hz), 0.87 (6H, t, J=7.6 Hz)
^{13}C-NMR ($CDCl_3$, 100MHz): δ 166.1; 157.6; 142.0; 130.4; 129.9; 127.8; 126.9; 115.1; 69.5; 33.7; 31.9; 29.5; 22.7; 14.1; 9.7
Elemental analysis calculated for: $C_{52}H_{70}O_6$; C(78.95%), H(8.92%), O(12.13%). Found C(79.09%) H(8.88%).

4/4
^{1}H-NMR ($CDCl_3$, 400MHz): δ 8.09-8.03 (4H, m); 7.54-7.43 (8H,m); 7.04-6.98 (4H, m); 5.20-5.11 (6H, m); 1.79-1.54 (8H, m); 1.47-1.20 (16H, m); 0.91-0.83 (12H, m)
^{13}C-NMR ($CDCl_3$, 100MHz): δ 165.9; 157.6; 141.9; 129.8; 127.8; 126.9; 115.11; 109.9; 71.8; 69.4; 36.0; 31.7; 29.5; 25.4; 22.7; 20.1; 14.1
Elemental analysis calculated for: $C_{46}H_{58}O_6$; C(78.15%), H(8.27%). Found ; C(78.31%), H(8.24%).

Preparation of (R/S)-1-methylpentyl-4-(4'-hydroxybiphenyl-4-yloxymethyl)benzoate 5
To a gently heated solution (45-50°C) of 4,4'-dihydroxybiphenyl (11.14 g, 59.8 mmol), potassium iodide (14.61 g, 88.0 mmol) and potassium carbonate (14.59 g; 105.6 mmol) in 340mL of 1-methyl-2-pyrrolidinone a (R/S)-1-methylheptyl-4-(bromomethyl)-benzoate **3** (11,51 g, 35.2 mmol) was slowly added. The reaction mixture was further stirred for 24h at 120°C. After that, the mixture was cooled to a room temperature and poured into water with ice. Brown precipitate was dried and the crude product was chromatographed on silica gel using a 1% methanol in chloroform – mixture as eluent. The monoalkylated product **5** and dialkylated products were obtained. Yield of monoalkylated product 41%.
The same synthetic procedure has been applied in reaction of excess of (R)-1-methylheptyl-4-(bromomethyl)-benzoate with (R/S)-1-methylpentyl-4-(4'-hydroxybiphenyl-4-yloxymethyl)benzoate **5** to obtain the final compound **6** (6/1 (R/RS)).

Analytical data for compound 5.
^{1}H-NMR ($CDCl_3$, 200MHz) δ8.08 (2H, d, J=8.4Hz); 7.55-7.36 (6H,m); 7.00 (2H, d, J=8.8); 6.89 (2H, d, J=8.6) 5.21-5.09 (3H, m); 1.82-1.70 (2H, m); 1.67-1.58 (3H, m); 1.47-1.22 (8H, m); 0.89 (3H, t, J=6.9Hz);

*Analytical data of final compound **6**:*

6/1 (RS/R)
^{1}H-NMR ($CDCl_3$, 400MHz): δ 8.10-8.05 (4H, m); 7.55-7.50 (4H,m); 7.50-7.44 (4H, m); 7.06-6.98 (4H, m); 5.22-5.12 (6H, m); 1.81-1.71 (4H, m); 1.69-1.56 (6H, m); 1.47-1.23 (16H, m); 0.94-0.84 (6H, m)
^{13}C-NMR ($CDCl_3$, 100MHz): δ 165.9; 157.6; 141.9; 133.8; 129.8; 127.8; 126.9; 115.1; 71.8; 69.4; 36.1; 31.7; 25.4; 22.6; 20.1; 14.1
Elemental analysis calculated for: $C_{44}H_{54}O_6$; C(77.84%), H(8.02%), O(14.14%). Found C(77.85%), H(8.04%).