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An investigation of the synthesis of chiral LCs based on the [1,2,3]-triazole ring

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The design and synthesis of chiral liquid crystalline compounds based on the [1,2,3]-triazole heterocycle using the click chemistry modular approach is presented. The target compounds showed LC phases of type SmA, SmC* and helical N* (cholesteric). Mesomorphic behaviour was determined by polarizing optical microscopy and differential scanning calorimetry. Contact experiments indicated a right-handed helix for the macrostructure of the cholesteric phase.

1. Introduction

Of crucial importance in organic synthesis is the reduction in the number of reaction steps and increase of chemical yield mainly for commercial purposes. Tandem [1], multi-component [2] and solid state [3] reactions as well as catalytic processes [4] have played a decisive role in this respect. In particular, the development of metal-catalysed cross-coupling reactions of organozincs, arylboronic acids and arylacetylenes with aryl halides have revolutionized the synthesis of liquid crystals [5]. Hundreds of different nematic, cholesteric and ferroelectric materials have been prepared using such approaches. In this context, cycloaddition reactions in organic chemistry are not only among the synthetically most useful reactions, they are also among the theoretically and mechanistically best understood reactions. Metallomesogens [6], cyclophanes [7], electroluminescent LC polymers [8], discotic LCs [9] and heterohelicenes [10] are some examples of self-organized materials that have been prepared using such a class of reactions. In addition, a great variety of five-membered heterocycles can be constructed using these powerful methods in a convergent manner from relatively simple precursors [11].

In a brief review of the specialized literature we have found no reports on LC compounds containing the five-membered ring [1,2,3]-triazole, only a few examples containing the regioisomeric [1,2,4]-triazole [12]. This gap in the literature is intriguing given that members bearing this *N*-heterocycle have been successfully applied in materials chemistry as dyes, corrosion inhibitors, photostabilizers and photographic materials [13]. A series of [1,2,3]-triazole derivatives as potentially mesomorphic chiral compounds was therefore sought, having the 1,3-dipolar cycloaddition reaction as a central step, which follows on from our more recent findings [14]. We are especially interested in chiral liquid crystals with helical structure, cholesteric (N*) and ferroelectric (SmC*).

2. Experimental

2.1. *Characterization*

^{1}H and ^{13}C NMR spectra were obtained with a Bruker AC-200F spectrometer at 200 and 50.4 MHz, respectively, using TMS as the internal standard. IR spectra were recorded using KBr discs with a Perkin-Elmer model 283 spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN system. Optical rotations were measured on a Perkin-Elmer 341 polarimeter at the sodium D line. The melting points, thermal transitions and mesomorphic textures were determined using an Olympus BX50 microscope in conjunction with a Mettler Toledo FP-90 heating stage and an exposure control unit PM-30. Differential scanning calorimetry (DSC) was carried out using Shimadzu equipment with a DSC-50 module.

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2.2. *Synthesis*

All reagents and chemicals were obtained from commercial sources and used without further purification unless otherwise noted. The organic solvents were of commercial grade quality except THF (HPLC grade) and all were dried by traditional methods. Analytical thin layer chromatography (TLC) was conducted on Merck aluminum plates with 0.2 mm of silica gel 60F-254.

2.2.1. (*S*)-(+)-2-Methylbutyl mesylate (1). To a three-necked flask (500 ml), fitted with a funnel, glass stopper and thermometer, dichloromethane (200 ml), TEA (53.9 ml, 0.39 mol) and (*S*)-2-methyl-1-butanol (30.8 ml, 0.28 mol) were transferred. The clear solution was cooled (0°C) and mesyl chloride (24.1 ml, 0.31 mol) was added dropwise. After complete addition the mixture was stirred for 2.5 h at 0°C and then poured onto crushed ice (200 ml). The phases were separated and the aqueous layer extracted with CH_2Cl_2 (2×50 ml). The combined organic extracts were washed using 5% HCl (2×50 ml) and saturated NaCl (50 ml) and then dried over sodium sulphate. Filtration, solvent evaporation and vacuum distillation yielded 39.5 g (84%) of **1** as a colourless liquid, b.p. 65°C (0.1 mmHg), $[\alpha]_D^{20} = +2.92$(neat). IR (film) ν_{max}/cm^{-1}: 3026, 2967, 2881, 1464, 1352, 1175, 958, 845, 529. ^1H NMR ($CDCl_3$) δ: 0.82 (m, 6H), 1.15 (m, 1H), 1.33 (m, 1H), 1.68 (m, 1H), 2.28 (s, 3H), 3.96 (m, 2H).

2.2.2. (*S*)-(+) 1-Azido-2-methylbutane (2). Compound **1** (2.92 g, 17.6 mmol) was suspended in DMF (20 ml). Sodium azide (2.28 g, 35.1 mmol) was added and the mixture held at 50°C for 25 h. The cold mixture was poured into water/ether (100 ml) and the phases separated. The aqueous layer was extracted with ether (2×30 ml) and the combined organics washed with solutions of $NaHCO_3$ (30 ml) and NaCl (30 ml), then dried over sodium sulphate. After filtration and solvent evaporation the residue was purified on a chromatographic column (silica gel, hexane/dichloromethane 9.2/0.8). Yield: 75%, colorless oil, $[\alpha]_D^{20} = +5.12$(neat). IR (film) ν_{max}/cm^{-1}: 2967, 2931, 2878, 2106, 1461, 1268. ^1H NMR ($CDCl_3$) δ: 0.92 (m, 6H), 1.14 (m, 1H), 1.37 (m, 1H), 1.63 (m, 1H), 3.17 (m, 2H).

2.2.3. 1-Ethynyl-4-benzyloxybenzene (3). *4-Benzyloxybromobenzene*: A mixture of 4-bromophenol (20.0 g, 0.116 mol), benzyl chloride (16.1 g, 0.127 mol), K_2CO_3 (47.9 g, 0.347 mol) and butanone (150 ml) was heated under reflux for 18 h. The cold mixture was filtered and the filtrate concentrated. The residue was recrystallized from ethanol giving 24.13 g (79%) of the alkylated product as a white solid, m.p. 62.5–62.8°C. IR (KBr) ν_{max}/cm^{-1}: 2887, 1586, 1484, 1452, 1377, 1288, 1257, 1169, 1041, 1025, 824.

4-(4-Benzyloxyphenyl)-2-methylbut-3-yn-2-ol: To a three-necked flask (100 ml), under an argon atmosphere, 4-benzyloxybromobenzene (10.0 g, 38.0 mmol), $PdCl_2(PPh_3)_2$ (0.260 g, 0.380 mmol), CuI (0.036 g, 0.19 mmol), triphenylphosphine (0.099 g, 0.38 mmol) and triethylamine (70 ml) were transferred, and the mixture was heated under reflux for 30 min. 2-Methyl-3-butyn-2-ol (6.2 ml, 57.0 mmol) was added dropwise, the reflux continued for 2.5 h and the cold mixture then filtered through a celite pad, washing with ether. Evaporation of the solvent provided a solid that was purified by recrystallization from heptane. Yield: 6.62 g (65%), white powder, m.p. 97.0–99.5°C. IR (KBr) ν_{max}/cm^{-1}: 3353, 2980, 2930, 1601, 1505, 1454, 1378, 1246 1163, 958, 831. ^1H NMR ($CDCl_3$) δ: 1.60 (s, 6H), 2.04 (s, 1H), 5.05 (s, 2H), 6.89 (d, J=8.4 Hz, 2H), 7.36 (d, J=8.4 Hz, 2H), 7.25 (m, 5H).

Alkynol deprotection: The alkynol prepared above was suspended in toluene (170 ml) and NaOH (1.69 g, 42.3 mmol) added. The mixture was slowly warmed for 3 h and acetone distilled off. After cooling the mixture was filtered through a celite pad and the toluene evaporated. The residue was recrystallized from aqueous ethanol furnishing 3.20 g (62%) of **3** as a yellow solid, m.p. 71.2°C. IR (KBr) ν_{max}/cm^{-1}: 3268, 2937, 2872, 1598, 1502, 1460, 1234, 1167, 1010, 831. ^1H NMR ($CDCl_3$) δ: 2.99 (s, 1H), 5.07 (s, 2H), 6.90 (d, J=8.6 Hz, 2H), 7.42 (d, J=8.6 Hz, 2H), 7.34 (m, 5H).

2.2.4. (2*S*)-4-(4-Benzyloxyphenyl)-1-(2-methyl-butyl)-1H-[1,2,3]triazole (4). The alkyne **3** (0.586 g, 2.82 mmol), CuI (0.053 g, 0.282 mmol) and TEA (0.04 ml, 0.282 mmol) were suspended in 1/1 ethanol/water (20 ml). To the heterogeneous and vigorously stirred mixture the chiral azide **2** (0.318 g, 2.82 mmol) was added dropwise, and a gentle reflux (60°C) maintained for 6 h. Water (30 ml) was added and the flask cooled in crushed ice; the precipitate was collected by filtration and washed with water. Recrystallization from heptane provided 0.508 g (64%) of **4**, m.p. 117.5–118.2°C. IR (KBr) ν_{max}/cm^{-1}: 3095, 2957, 2870, 1612, 1496, 1455, 1382, 1236, 1174, 1073, 1018, 827. ^1H NMR ($CDCl_3$) δ: 0.91 (m, 6H), 1.26 (m, 1H), 1.39 (m, 1H), 2.03 (m, 1H) 4.21 (m, 2H), 5.10 (s, 2H), 7.03 (d, J=8.6 Hz, 2H), 7.40 (m, 5H), 7.63 (s, 1H), 7.76 (d, J=8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.0, 16.8, 26.6, 35.9, 56.0, 70.0, 115.1, 119.1, 123.7, 126.9, 127.4, 128.0, 128.5, 136.8, 147.4, 158.7.

2.2.5. (2*S*)-(+)-4-[1-(2-Methylbutyl)-1H-[1,2,3]triazol-4-yl]phenol (5). To a solution of **4** (1.34 g, 4.17 mmol) in ethanol (20 ml) and cyclohexene (10 ml), 20% w/w $Pd(OH)_2/C$ (0.134 g) was added in small portions. After complete addition the mixture was heated under reflux for 5 h then cooled to r.t. and filtered through a celite® pad washing with ethanol. The filtrate was concentrated, furnishing 0.936 g (97%) of the analytically pure desired compound; m.p. 131.2–133.5°C, $[\alpha]_D^{20} = +7.8$ (*c* 1.02, $CHCl_3$). IR ν_{max}/cm^{-1} (KBr): 2960, 2924, 2813, 1613, 1499, 1465, 1391, 1276, 1216, 1173, 844, 800. ^1H NMR ($CDCl_3$) δ: 0.94 (m, 6H), 1.25 (m, 1H), 1.40 (m, 1H), 2.03 (m, 1H), 4.21 (m, 2H), 6.93 (d, J=8.5 Hz, 2H), 7.63 (s, 1H), 7.65 (d, J=8.5 Hz, 2H).

2.2.6. (2*S*)-(+)-4-[1-(2-Methylbutyl)-1H-[1,2,3]triazol-4-yl]-2-nitrophenol (6). The triazole **5** (0.200 g, 0.865 mmol) was suspended in concentrated acetic acid (7 ml), then concentrated HNO_3 (0.150 ml, 3.46 mmol) was added dropwise. The solution was stirred for 15 min and poured into an ice/water mixture (*c*. 20 ml). The yellow precipitate was collected by filtration, washing with portions of water, and drying. Yield: 0.212 g (88%), m.p. 109.6–111.4°C, $[\alpha]_D^{20} = +5.1$ (*c* 0.77, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 0.93 (m, 6H), 1.27 (m, 1H), 1.41 (m, 1H), 2.05 (m, 1H), 4,27 (m, 2H), 7.24 (d, J=7.5 Hz, 1H), 7.76 (s, 1H), 8.15 (d, J=7.5 Hz, 1H), 8.49 (s, 1H), 10,52 (s, 1H).

2.2.7. (2*S*)-1-Bromo-4-(2-methylbutoxy)benzene (7). To a round-bottom flask (50 ml), 4-bromophenol (3.0 g, 17.35 mmol), K_2CO_3 (4.79 g, 34.7 mmol) and DMF (20 ml) were transferred. The mixture was stirred at 60°C for 30 min and the mesylate **1** in DMF (5 ml) was then added dropwise. The mixture was stirred for 72 h at 75°C; the solid precipitate was filtered off, washing with ether (50 ml), and the filtrate partitioned in water (120 ml). The organic layer was extracted with portions of ether (3 × 40 ml) and dried over sodium sulphate. The residue after evaporation was purified on a chromatographic column (silica gel, hexanes) to furnish a clear yellow oil. Yield: 57%. ^1H NMR ($CDCl_3$) δ: 0.92 (t, 3H, J=7.3 Hz), 1.01 (d, 3H, J=6.8 Hz), 1.30 (m, 1H), 1.34 (m, 1H), 1.91 (m, 1H), 3.78 (m, 2H), 6.88 (d, 2H, J=8.8 Hz), 7.36 (d, 2H, J=8.8 Hz).

2.2.8. (2*S*)-4-Bromo-1-(2-methylbutoxy)-2-nitrobenzene (8). Prepared in the same way as **7** using 4-bromo-2-nitrophenol and the mesylate **1**. Light yellow oil; yield 68%, b.p. 136–143°C (0.2 mmHg). ^1H NMR ($CDCl_3$) δ: 0.91 (t, 3H, J=7.3 Hz), 1.01 (d, 2H, J=6.7 Hz), 1.30 (m, 1H), 1.54 (m, 1H), 1.86 (m, 1H), 3.88 (m, 2H), 6.95 (d, 1H, J=8.9 Hz), 7.57 (dd, 1H, J=8.9 Hz and 2.3 Hz), 7.90 (d, 1H, J=2.3 Hz).

Compounds **9** and **10** were prepared using the procedures described in § 2.2.3.

2.2.9. (2*S*)-1-Ethynyl-4-(2-methylbutoxy)benzene (9). Purified on a chromatographic column (silica gel, hexanes). Yellow oil; yield 79%. IR ν_{max}/cm^{-1} (KBr): 3290, 2108, 1600, 1530, 1430, 1350, 720. ^1H NMR ($CDCl_3$) δ: 0.86 (t, 3H, J=7.3 Hz), 0.91 (d, 3H, J=6,7 Hz), 1.11(m, 1H), 1.48 (m, 1H), 1.76 (m, 1H); 2.91 (s, 1H), 3.77 (m, 2H), 6.7 (d, 2H, J=8.7 Hz), 7.33 (d, 2H, J=8.7 Hz).

2.2.10. (2*S*)-4-Ethynyl-1-(2-methylbutoxy)-2-nitrobenzene (10). Purified on a chromatographic column (silica gel, hexanes/ethyl acetate 93/7). Yellow oil; yield 63%. IR ν_{max}/cm^{-1} (KBr): 3290, 2963, 2932, 2877, 1617, 1497, 1288, 1083, 820. ^1H NMR ($CDCl_3$) δ: 0.95 (t, 3H, J=7.3 Hz), 1.04 (d, 3H, J=6.7 Hz), 1.26 (m, 1H), 1.61 (m, 1H) 1.89 (m, 1H), 3.08 (s, 1H), 3.89 (m, 2H), 7.01 (d, 1H, J=8.7 Hz), 7.60 (d, 1H, J=8.7 Hz), 7,95 (s, 1H).

2.2.11. 4′-Bromobiphenyl-4-ol (11). *Friedel–Crafts acylation*: To a three-necked flask (250 ml) fitted with a thermometer, condenser and addition funnel, 4-bromobiphenyl (20 g, 85.8 mmol) and dichloromethane (120 ml) were transferred. After cooling (−2°C), anhydrous $AlCl_3$ (14 g, 103.0 mmol) was added in portions. The dark green solution was stirred and acetyl chloride (7.3 ml, 103.0 mmol) was added dropwise. After complete addition, the solution was stirred at 0°C the heated under reflux for 2 h. The cold solution was poured into a beaker and concentrated HCl (80 ml) and water (80 ml) were carefully added. Dichloromethane was evaporated and the precipitated collected by filtration and washed with portions of water. The dried solid was recrystallized from *n*-heptane giving 13.21 g (56%) of the 1-(4′-bromobiphenyl-4-yl)-ethanone as a pale yellow solid, m.p. 119.1–123.6°C. IR ν_{max}/cm^{-1} (KBr): 1672, 1603, 1387, 1358, 1264, 1079, 1001, 604.

Baeyer-Villiger oxidation: CH_2Cl_2 (250 ml), MCPBA (29.09 g, 168.56 mmol) and the aryl ketone described above (13.21 g, 48.05 mmol) were transferred to a 250 ml three-necked flask fitted with a dropping funnel, condenser and glass stopper. Freshly distilled trifluoroacetic acid (8 ml) was added dropwise to the suspension at 0°C. The vessel was protected from light and left at room temperature for 48 h. The filtrate was cooled in an ice-water bath and a saturated solution of sodium bisulphite (100 ml) was added. The white precipitate was

collected. The filtrate was submitted to aqueous standard work-up and dried over sodium sulphate. Filtration and evaporation of the solvent gave 140 g of an orange solid, m.p. 127.9–130.9°C. ^{1}H NMR ($CDCl_3$) δ: 2.32 (s, 3H), 7.15 (d, J=8.5 Hz, 2H), 7.41 (d, J=8.5 Hz, 2H) 7.54 (d, J=8.6 Hz, 2H), 7.55 (d, J=8.6 Hz, 2H). IR ν_{max}/cm^{-1} (KBr): 1750, 1476, 1370, 1204, 1068, 997, 908, 823.

Hydrolysis of the acetyl group: The ester discribed above (14.0 g, 48.0 mmol) was suspended in methanol (75 ml), water (60 ml) and KOH (4.0 g, 72.1 mmol). The mixture was heated under reflux for 1 h and then cooled to room temperature. The solid was added to water (150 ml) and concentrated HCl was added (*c*. pH=5). The precipitate was collected by filtration, washed with water, and dried. Yield: 10.7 g (90%), m.p. 165.2–166.9°C. IR ν_{max}/cm^{-1} (KBr): 3394, 1605, 1594, 1482, 1260, 1198, 999, 831, 728.

2.2.12. 4′-*n*-Decyloxy-4-ethynylbiphenyl (12). This compound was prepared using the same sequence as described for **3**. m.p. 105.6–107.6°C. IR ν_{max}/cm^{-1} (KBr): 3286, 2955, 2919, 2850, 1605, 1493, 1472, 1289, 1254, 1029, 825. ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, 2H), 1.27 (m, 14H), 1.83 (q, 2H), 3.11 (s, 1H) 3.99 (t, 2H), 6.96 (d, J=8.8 Hz, 2H), 7.49 (m, 6H).

2.2.13. (2*S*)-(+)-4-[1-(2-Methylbutyl)-1H-[1,2,3]triazol-4-yl]phenyl 4-*n*-decyloxybenzoate (13). 4-*n*-Decyloxybenzoic acid (0.377 g, 1.35 mmol) and phenol **5** (0.314 g, 1.35 mmol) were suspended in CH_2Cl_2 (25 ml). To this mixture, DCC (0.308 g, 1.49 mmol) and DMAP (0.014 g, 0.135 mmol) were added while stirring, and the agitation maintained for 30 h at room temperature. The white precipitate was filtered off, washing with CH_2Cl_2 (30 ml). The filtrate was concentrated and the residue purified on a chromatographic column (silica gel, hexanes/dichloromethane 1/1, then neat dichloromethane) to give a white powder. Yield: 74%, $[\alpha]_D^{20} = +4.6$(c 1.08, $CHCl_3$). IR ν_{max}/cm^{-1} (KBr): 3080, 2922, 2852, 1725, 1607, 1506, 1463, 1270, 1203, 1166, 1069, 845. ^{1}H NMR ($CDCl_3$) δ: 0.93 (m, 9H), 1.28 (m, 16H), 1.28 (q, 2H), 2.04 (m, 1H), 4.05 (t, 2H), 4.26 (m, 2H), 6.97 (d, J=8.2 Hz, 2H), 7.29 (d, J=8.4 Hz, 2H), 7.72 (s, 1H), 7.89 (d, J=8.2 Hz, 2H), 8.15 (d, J=8.4 Hz, 2H). Anal: calcd for $C_{30}H_{41}N_3O_3$, C 73.29, H 8.41, N 8.55; found C 72.81, H 8.52, N 8.46%.

Compounds **14**, **15** and **16** were prepared using the same general procedure as described for **4**.

2.2.14. (2*S*)-(+)-4-(4′-*n*-Decyloxybiphenyl-4-yl)-1-(2-methylbutyl)-1H-[1,2,3]triazole (14). This compound was synthesized using the alkyne **12** and the azide **2** in a 3/1 mixture of ethanol/water. It was purified by recrystallization from heptane. Yield: 45%, white powder, m.p. 173.4°C, $[\alpha]_D^{20} = +9.1$(c 1.09, $CHCl_3$). IR ν_{max}/cm^{-1} (KBr): 3099, 2920, 2852, 1603, 1485, 1460, 1251, 1203, 815. ^{1}H NMR ($CDCl_3$) δ: 0.93 (m, 9H), 1.28 (m, 16H), 1.79 (q, J=6.5 Hz, 2H), 2.04 (m, 1H), 4.00 (t, J=6.5 Hz, 2H), 4.26 (m, 2H), 6.97 (d, J=8.7 Hz, 2H), 7.55 (d, J=8.7 Hz, 2H), 7.62 (d, J=8.2 Hz, 2H), 7.74 (s, 1H), 7,88 (d, J=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.7, 14.7, 17.5, 23.3, 26.7, 27.3, 29.9, 30.0, 30.2, 32.5, 36.6, 56.7, 68.7, 77.0, 77.6, 78.3, 115.4, 120.4, 126.6, 127.6, 128.5, 129.6, 133.5, 141.1, 148.0, 159.5. Anal: calcd for $C_{29}H_{41}N_3O$, C 77.1, H 9.23, N 9.39; found C 77.56, H 9.26, N 9.50%.

2.2.15. (2*S*)-1-(4-*n*-Decyloxyphenyl)-4-[4-(2-methylbutoxy)phenyl]-1H-[1,2,3]triazole (15). This compound was synthesized using the alkyne **9** and 1-azido-4-(*n*-decyloxy)benzene in a 1/1 mixture of ethanol/water. It was purified by recrystallization from heptane. Yield: 90%, white powder, $[\alpha]_D^{20} = +7.7$(c 1.03, $CHCl_3$). IR ν_{max}/cm^{-1} (KBr): 3133, 2920, 2850, 1614, 1522, 1495, 1264, 1247, 1042, 828, 724. ^{1}H NMR ($CDCl_3$) δ: 0.96 (m, 9H), 1.28 (m, 16H), 1.82 (m, 3H), 3.83 (m, 2H), 4.00 (t, 2H, J=6.5 Hz), 6.97 (d, 2H, J=7.5 Hz), 7.01 (d, 2H, J=7.5 Hz), 7.65 (d, 2H, J=8.7 Hz); 7.80 (d, 2H, J=8.7 Hz), 8.01 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 11.3, 14.0, 16.4, 22.6, 25.0, 25.9, 26.1, 29.1, 29.3, 29.5, 31.8, 34.6, 37.9, 66.3, 68.3, 72.8, 114.7, 115.1, 116.8, 121.9, 122.7, 126.9, 130.2, 148.0, 159.2, 159.4. Anal: calcd for $C_{29}H_{41}N_3O_2$, C 75.12, H 8.91, N 9.06; found C 75.53, H 8.96, N 9.39%.

2.2.16. (2*S*)-1-(4-*n*-Decyloxyphenyl)-4-[4-(2-methylbutoxy)-3-nitrophenyl]-1H-[1,2,3]triazole (16). This compound was synthesized using the alkyne **10** and 1-azido-4-(*n*-decyloxy)benzene in a 1/1 mixture of ethanol/water. It was purified by recrystallization from isopropanol. Yield: 72%, light yellow powder, $[\alpha]_D^{20} = +5.9$(c 1.07, $CHCl_3$). IR ν_{max}/cm^{-1} (KBr): 3146, 2954, 2921, 2848, 1566, 1518, 1256, 1166, 827. ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, 3H, J=7.8 Hz), 0.98 (t, 3H, J=7.4 Hz), 1.07 (d, 3H, J=6.6 Hz), 1,28 (m, 16H), 1.82 (m, 3H), 3.98 (m, 4H); 7.02 (d, 2H, J=8.8 Hz), 7.15 (d, 2H, J=8.8 Hz), 7.65 (d, 1H, J=8.8 Hz), 8.12 (s, 1H), 8.15 (d, 1H, J=8.8 Hz), 8.27 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 11.5, 14.1, 16.3, 22.6, 25.8, 25.9, 29.1, 29.3, 29.5, 31.8, 34.6, 68.5, 74.4, 114.8, 115.3, 117.7, 122.0, 122.7, 122.9, 130.0, 131.2, 139.7, 145.9, 152.4, 159.6. Anal: calcd for $C_{29}H_{40}N_4O_4$, C 68.48, H 7.93, N 11.01; found C 68.64, H 8.31, N 11.15%.

2.2.17. (2*S*)-(+)-4-[1-(2-Methylbutyl)-1H-[1,2,3]triazol-4-yl]phenyl 5-(4-*n*-decyloxyphenyl)isoxazole-3-carboxylate (17). To a round bottom flask (50 ml) 5-(4-*n*-decyloxyphenyl)isoxazole-3-carboxylic acid (0.255 g, 0.739 mmol), dichloromethane (20 ml) and thionylchloride (0.06 ml, 0.88 mmol) were transferred. The mixture was heated under reflux for 4 h; all volatiles were then removed on a rotary evaporator giving the crude acid chloride. This was redissolved in CH_2Cl_2 (20 ml) and cooled in an ice/water bath. The phenol **5** (0.170 g, 0.739 mmol) in CH_2Cl_2 (5 ml) and TEA (0.5 ml) was added dropwise. After stirring for 14 h at r.t., the mixture was poured into ice/water (*c*. 30 ml) and submitted to the standard workup. The residue after concentration was purified by recrystallization from ethanol to give a white powder. Yield: 41%, $[\alpha]_D^{20} = +3.8$(*c* 1.08, $CHCl_3$). IR ν_{max}/cm^{-1} (KBr): 3125, 3082, 2925, 2852, 1752, 11615, 1507, 1455, 1270, 1229, 1114, 986, 814. ^{1}H NMR ($CDCl_3$) δ: 0.96 (m, 9H), 1.28 (m, 16H), 1.81 (q, 2H), 2.05 (m, 2H), 4.02 (t, 2H), 4.26 (m, 2H), 6.92 (s, 1H), 7.00 (d, J=8.3 Hz, 2H), 7.34 (d, J=8.2 Hz, 2H), 7.74 (s, 1H), 7.77 (d, J=8.2 Hz, 2H), 7.91 (d, J=8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.6, 14.7, 17.5, 23.3, 26.6, 27.3, 29.7, 29.9, 30.2, 32.5, 36.6, 56.7, 68.9, 77.0, 77.6, 78.3, 99.3, 115.7, 119.6, 120.7, 122.5, 127.5, 128.2, 129.8,147.3, 150.4, 156.9, 159.1, 162.0, 172.9. Anal: calcd for $C_{33}H_{42}N_4O_4$, C 70.94, H 7.58, N 10.03; found C 70.73, H 7.77, N 10.03%.

2.2.18. (2*S*)-4-[1-(2-Methylbutyl)-1H-[1,2,3]triazol-4-yl]-2-nitrophenyl 5-(4-*n*-decyloxyphenyl)isoxazole-3-carboxylate (18). This compound was prepared using the procedure described for **17** using 5-(4-*n*-decyloxyphenyl)isoxazole-3-carboxylic acid and the phenol **6**. Purification was carried out on a chromatographic column (silica gel, hexanes/dichloromethane 4/1). Yield: 56%, pale yellow powder, m.p. 170.1°C, $[\alpha]_D^{20} = +14.9$(*c* 0.16, $CHCl_3$). IR ν_{max}/cm^{-1} (KBr): 3125, 2959, 2917, 2849, 1762, 1611, 1524, 1452, 1356, 1261, 1225, 1176, 1112, 1070, 832. ^{1}H NMR ($CDCl_3$) δ: 0.94 (m, 9H), 1.28 (m, 16H), 1.78 (m, 2H), 2.04 (m, 1H), 4.02 (t, 2H), 4.28 (m, 2H), 6.94 (s, 1H), 7.00 (d, J=8.8 Hz, 2H), 7.49 (d, J=8.5 Hz, 1H), 7.77 (d, J=8.8 Hz, 2H), 7.88 (s, 1H), 8.8 (dd, J=8.5 Hz and J=2 Hz, 1H), 8.57 (d, J=2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 11.0, 14.1, 16.8, 22.6, 25.9, 26.6, 29.1, 29.3, 29.5, 31.8, 35.9, 56.3, 68.2, 98.5, 115.1, 118.8, 120.8, 122.8, 125.7, 127.6, 130.7, 131.7, 141.6, 142.5, 144.5, 155.4, 157.8, 161.3, 172.5. Anal: calcd for $C_{33}H_{41}N_5O_6$, C 65.65, H 6.85, N 11.60; found C 65.36, H 6.91, N 10.76%.

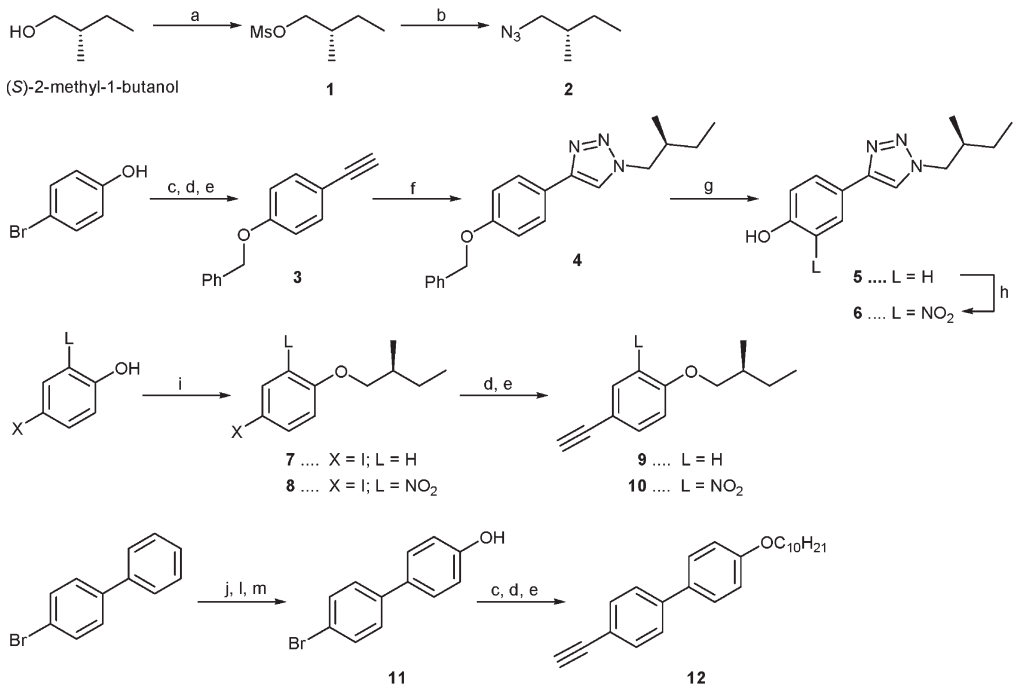
2.2.19. (2*S*)-(+)-4-[1-(2-Methylbutyl)-1H-[1,2,3]triazol-4-yl]phenyl 4′-*n*-decyloxybiphenyl-4-carboxylate (19). This compound was prepared with the procedure described for **13**, using 4′-*n*-decyloxy-4-biphenylcarboxylic acid and the phenol **5**. Purification was carried out by recrystallization from butanone. Yield: 65%, white powder, $[\alpha]_D^{20} = +2.8$(*c* 1.04, $CHCl_3$). IR ν_{max}/cm^{-1} (KBr): 3071, 2924, 2852, 1730, 1601, 1496, 1465, 1280, 1193, 1076, 821. ^{1}H NMR ($CDCl_3$) δ: 0.93 (m, 9H), 1.28 (m, 16H), 1.81 (q, 2H), 2.05 (m, 1H), 4.01 (t, 2H), 4.22, (m, 2H), 7.00 (d, J=8.6 Hz, 2H), 7.30 (d, J=8.5 Hz, 2H), 7.59 (d, J=8.6 Hz, 2H), 7.69 (d, J=8.3 Hz, 2H), 7.72 (s, 1H), 7.90 (d, J=8.5 Hz, 2H), 8.24 (d, J=8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.0, 14.1, 16.8, 22.7, 26.0, 26.7, 29.3, 29.5, 31.9, 36.0, 56.1, 68.1, 115.0, 119,9, 122.2, 126.6, 126.8, 127.3, 128.4, 130.7, 131.9, 146.0, 150.8, 159.6. Anal: calcd for $C_{36}H_{45}N_3O_3$, C 76.16, H 7.99, N 7.40; found C 75.78, H 8.07, N 7.54%.

2.2.20. (2*S*)-4-[1-(2-Methylbutyl)-1H-[1,2,3]triazol-4-yl]-2-nitrophenyl 4′-*n*-decyloxybiphenyl-4-carboxylate (20). This compound was prepared with the procedure described for **17** using 5-(4-*n*-decyloxyphenyl) isoxazole-3-carboxylic acid and the phenol **6**. Purification was carried out by recrystallization from aqueous ethanol. Yield: 66%, white powder $[\alpha]_D^{20} = 4.9$(*c* 1.0, $CHCl_3$). IR ν_{max}/cm^{-1} (KBr): 2921, 2852, 1739, 1604, 1531, 1338, 1255, 1220, 1080, 883, 831. ^{1}H NMR ($CDCl_3$) δ: 0.98 (m, 9H), 1.28 (m, 16H), 1.82 (q, 2H), 2.07 (m, 1H), 4.02 (t, 2H), 4.30 (m, 2H), 7.00 (d, J=8.4 Hz, 2H), 7.47 (d, J=8.4 Hz, 1H), 7,60 (d, J=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 11.7, 14.8, 17.5, 23.3, 26.7, 27.3, 30.0, 30.2, 32.5, 36.6, 57.0, 68.8, 115.7, 116.3, 121.4, 123.2, 126.6, 126.9, 127.4, 129.1, 130.5, 131.7, 132.0, 132.4, 142.8, 144.3, 145.5, 147.3, 160.3, 164.9. Anal: calcd for $C_{36}H_{44}N_4O_5$, C 70.56, H 7.24, N 9.14; found C 70.80, H 7.41, N 9.24%.

3. Results and discussion

3.1. *Synthesis*

Scheme 1 shows the synthesis of the key intermediates of the [1,2,3]-triazole containing mesogens. Chiral aliphatic azide **2** was prepared by nucleophilic displacement from (*S*)-2-methylbutanol mesylate **1**. Triple bonds were constructed from the corresponding aryl bromides by palladium/copper-catalysed cross-coupling (Sonogashira–Tohda–Hagihara coupling) [15] with mebynol (2-methyl-3-butyn-2-ol) and subsequent deprotection, thus furnishing **8**, **9**, **10** and **12**. In order to obtain the desired 1,4-disubstituted [1,2,3]-triazole **4**, the 1,3-dipolar cycloaddition reaction between acetylene **3** and chiral azide **2** was accomplished. This type of 1,3-dipolar cycloaddition of organic azides to triple bonds is



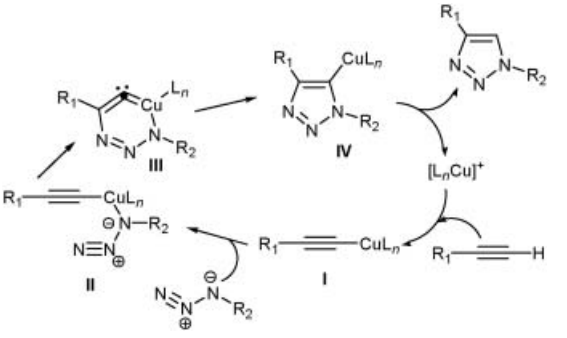
Reagents: a. Mesyl chloride, CH_2Cl_2, TEA; b. NaN_3, DMF; c. RX, K_2CO_3, butanone; d. 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA, e. NaOH, toluene; f. CuI, TEA, **2**, Ethanol/water (1:1); g. 20% w/w Pd/C, cyclohexene, ethanol; h. HNO_3, HOAc; i. K_2CO_3, **1**, DMF; j. $AlCl_3$, CH_3COCl, CH_2Cl_2; l. MCPBA, CF_3CO_2H, CH_2Cl_2; m. KOH, MeOH/H_2O.

Scheme 1. Synthesis of the key intermediates of the [1,2,3]-triazole ring-containing mesogens.

also known as 'click chemistry'. If the cycloaddition is thermally conducted, a 1/1 mixture of the 1,4- and 1,5-regioisomers is usually obtained [11]. In order to improve the 1,4-regioselectivity, reactions are carried out catalytically using Cu(I) or Cu(II) salts and sodium ascorbate [16], using water as the solvent [17] or even in encapsulated systems [18]. Three reaction systems were tested in order to improve both the 1,4-selectivity and chemical yield of **4** [14]. Best results were achieved using a modified system with copper(I) iodide as the catalyst and triethylamine (TEA) as the additive in a 1/1 ethanol/water mixture. The catalytic mechanism has been investigated in detail by Sharpless *et al.* [17*a*, 19] and a catalytic cycle proposed see scheme 2.

Since copper(I) readily binds to terminal alkynes the polarization of the terminal triple bond by covalently bound copper(I) catalyses the cycloaddition. Based on density functional theory calculations Sharpless pointed out that the energetics disfavour a concerted [2+3] cycloaddition (I→IV) tending towards a stepwise process (I→II→III→IV).

Using our methodology only one product was obtained from the 1,3-dipolar cycloaddition of two possible regioisomers. The product was characterized as the desired 1,4-disubstituted [1,2,3]-triazole **4** by NMR



Scheme 2. Catalytic cycle proposed by Sharpless *et al.* for Cu^I-catalysed synthesis of 1,4-disubstituted [1,2,3]-triazoles.

experiments based on the strong NOE effect observed between the triazole proton and the methyl group from the chiral chain, as shown in figure 1. In addition, this structural assignment was confirmed by X-ray experiments [14].

As a continuation of the synthetic procedures the synthetic target compounds were prepared according to scheme 3 either by esterification (**13**, **17**–**20**) or by 1,3-dipolar cycloaddition (**14**–**16**). The aryl azide was synthesized by diazotization from the corresponding

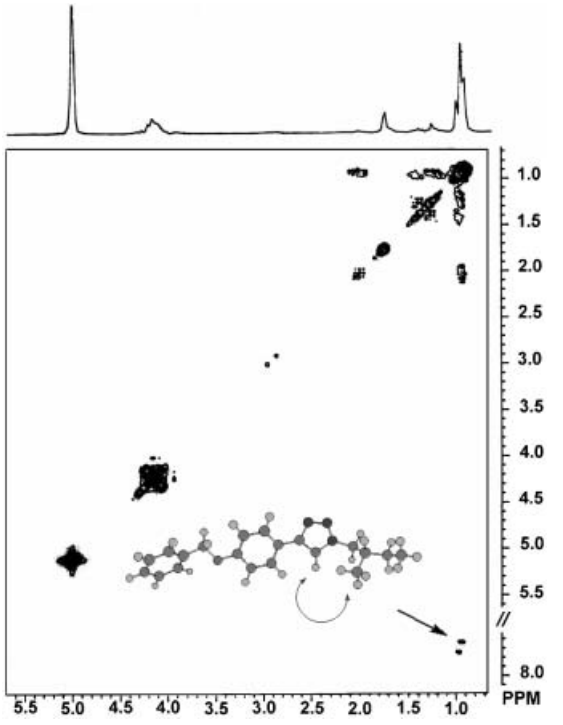


Figure 1. Partial 2D NOESY spectrum of **4**. The NOE indicated by an arrow confirms the 1,4-substitution shown as an AM1 minimized structure.

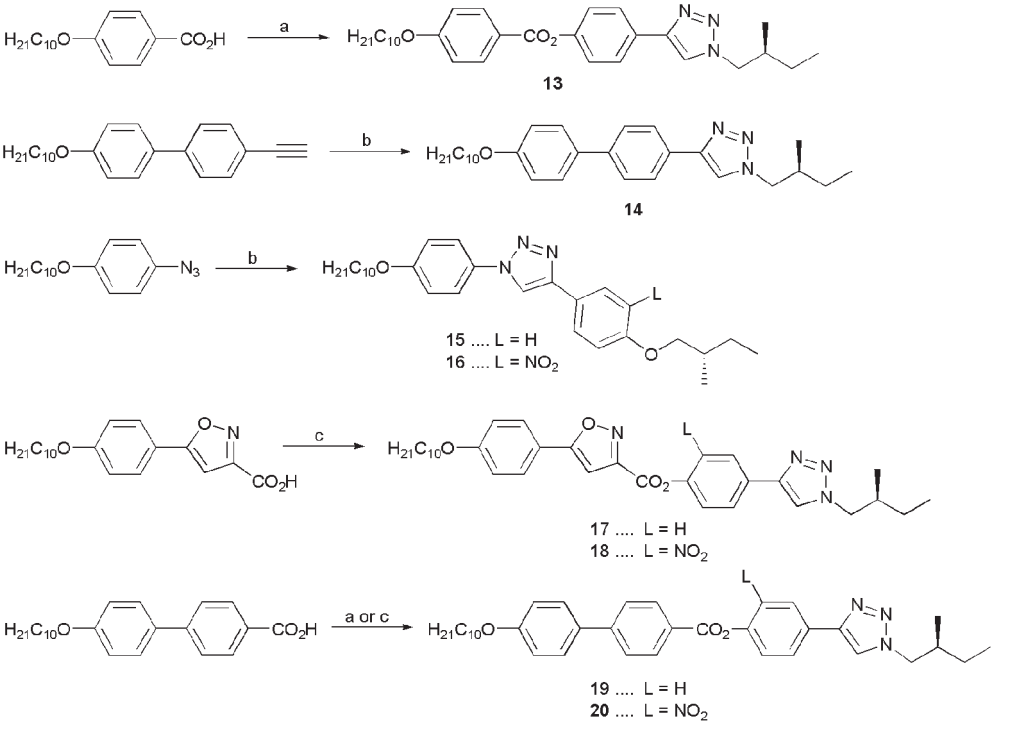
4-*n*-decyloxyaniline and the carboxylic acids by previously reported methods [20].

3.2. *Mesomorphic properties*

Thermal properties of the final compounds were investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The results are given in table 1.

The typical DSC thermogram and polarized microphotographs for the compounds under study are shown in chart figures 2 and 3 (*a*) respectively.

In order to aid an analysis of their mesomorphic behaviour, the target compounds were grouped into two sets, schemes 4 and 5; a bar graph, chart figure 4, was obtained. For compounds where the [1,2,3]-triazole heterocycle was placed at the end of the rigid core (scheme 4), the number of aromatic rings was found to be related to the appearance of mesophases. Shorter cores containing three rings (compounds **13** and **14**) did not display any liquid crystalline phase. The [1,2,3]-triazole heterocycle causes a bending of the core (*c.* 148.9°) and consequently a linearity deviation that seems detrimental to the mesomorphic packing. On the other hand, on increasing the core length to four rings the anisometry was restored and N* and SmC* phases



Scheme 3. Synthesis of the target compounds.

Table 1. Thermal and thermodynamic properties of final compounds **13**–**20**: determined by DSC (5°C min^{-1}) during second cycle.

Compound	Transition temperatures/°C [transition enthalpies ΔH/kJ mol^{-1}]
13	Cr 135.6 I (heating)
14	Cr 173.4 I (heating)
15	Cr 136.4 [18.8] SmA 150.8 [3.93] I (heating) I 146.8 [−3.82] SmA 129.3 [−19.0] Cr (cooling)
16	CrI 62.6 [11.6] CrII 151.1 [32.9] I (heating) I 146.3 [−0.27] (SmA) 144.9 [−32.6] CrII 56.5 [−10.3] CrI (cooling)
17	Cr 155.4 [34.5] N* 182.1 [1.49] I (heating) I 178.2 [−1.67] N* 145.1 [−33.1] Cr (cooling)
18	Cr 170.1 I (heating)
19	Cr 187.9 [39.1] SmC* 204.6 [2.51] N* 238.2 [1.29] I (heating) I 236.6 [−1.51] N* 202.6 [−2.56] SmC* 172.5 [−38.7] Cr (cooling)
20	CrI 105.4 [1.71] CrII 129.3 [27.8] N* 175.3 [1.58] I (heating) I 172.8 [−1.91] N* 115.4 [−26.6] CrII 103.1 [−4.45] (cooling)

[a]Temperatures for compounds **13**, **14** and **18** taken only from optical microscopy observations.

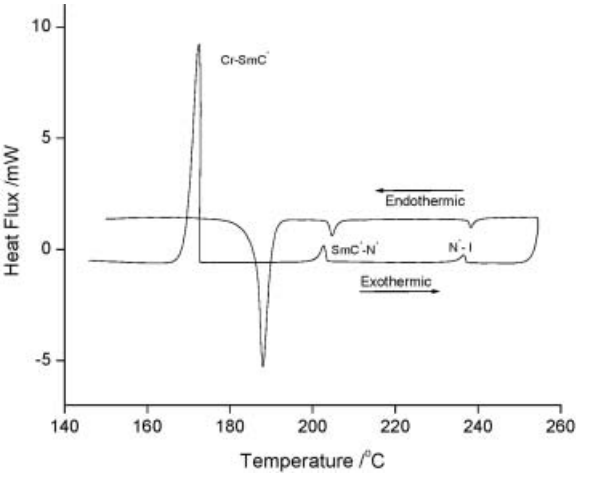


Figure 2. Thermogram of **19** during the second cycle at 5°C min^{-1} showing the heating and cooling curves.

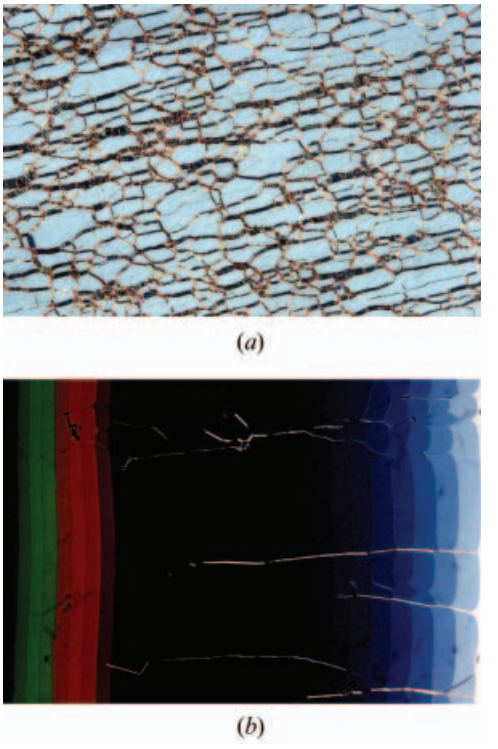
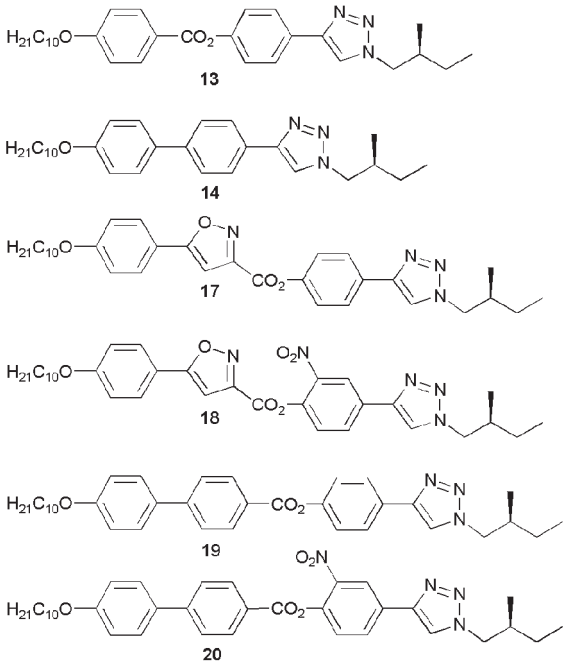


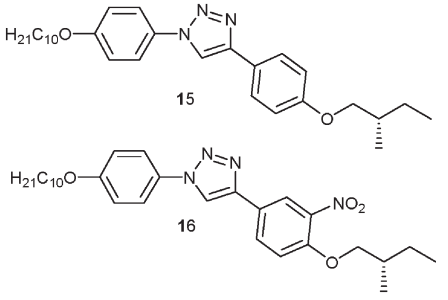
Figure 3. Photomicrographs: (*a*) Grandjean texture of N* phase of compound **19** at 211.9°C (33×), (*b*) contact preparation between **17** (right) and the laevo-rotatory standard N* material cholesteryl benzoate (left) at 162.0°C (33×); the contact region (middle) shows a continuous change in pitch without diverging, indicating the same twist direction.

(compounds **17**, **19** and **20**) a rose. With the introduction of the lateral nitro group *meta* to the triazole ring, the SmC* presents in **19** disappeared completely in **20**. The main factor contributing to this may be the van der Waals volume contributed by the nitro group, which reduces the dipolar interactions which lead to smectic phases. The strong dipole moment is insufficient to keep the molecular packing in layers and only the N* was maintained in **21**. This steric effect was even more pronounced when one of the benzene rings present in **20** was substituted by the heterocycle 3,5-disubstituted isoxazole (compound **18**). In this situation all mesomorphic behaviour was lost and **18** is an ordinary solid that melts to the isotropic liquid at 179°C.

Displacing the [1,2,3]-triazole ring to a central core position (scheme 5), the melting point is substantially lowered (approx. 37°C) as seen when comparing, for instance, the related compounds **14** and **15**. In addition, this geometry seems to favour the smectic phases, especially SmA. In order to achieve an even greater



Scheme 4. Compounds bearing the 1,4-disubstituted [1,2,3]-triazole ring at the core end.



Scheme 5. Compounds bearing the 1,4-disubstituted [1,2,3]-triazole ring at the core centre.

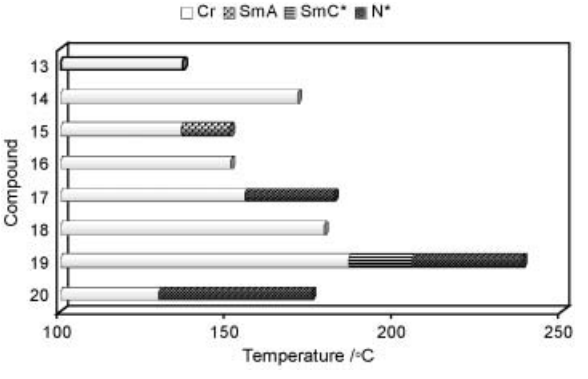


Figure 4. Comparative thermal behaviour of the [1,2,3]-triazole containing anisometric compounds.

lowering of the melting point and to obtain a ferroelectric SmC*, the nitro group was again used (compound **16**). Unfortunately, this attempt was unsuccessful since the enantiotropic SmA phase was transformed into a short monotropic one and surprisingly the melting point increased by about 15°C due to the non-laterally substituted **14**.

3.3. *Determination of helical twist direction of the N* phase by contact experiments*

Figure 3 (*b*) illustrates a contact preparation used to establish the helical twist direction of the N* phase of **17**. A laevo-rotation is indicated which corresponds, by definition, to a right-handed helix (RH-helix). For N* an empirical relation was established between the helical ordering of the phase and the chirality in the flexible chain [21]. According the *S*ol-*R*el, *S*ed-*R*od rules, helical twist direction and the rotation direction of plane polarized light depend strongly on the absolute spatial configuration of the chiral centre (*R* or *S*) and the distance separating the chiral centre from the rigid core (odd or even number of atoms). However, on applying such a set of rules to the molecular system of **17**, one would expect a dextro-rotation or right-handed helix (RH-helix). This result is not surprising because although such guidelines work well in predicting the helical twist direction in simple a N* without electron-withdrawing groups at the chiral centre [22], in SmC* [23] materials (with some modifications) and in optically active poly-(3,4-diakoxythiophenes) [24] they fail, as exemplified by pitch inversion in cholesterics and chirality on a larger scale [25].

4. Conclusions

Using the click chemistry modular approach a series of compounds containing the heterocycle [1,2,3]-triazole have been prepared with the Huisgen Cu(I)-catalysed cycloaddition as a crucial step. The method used selectively produced the desired 1,4-disubstituted regioisomer that was characterized by NMR experiments and single crystal XRD. Final compounds having four rings in the rigid core and the triazole in a terminal position showed smectic and nematic mesophases. In these cases the introduction of nitro *meta* to the triazole was detrimental to the liquid crystalline phases. On displacing the [1,2,3]-triazole to a central position of the core, only the SmA phase was observed along with lowered melting points. Contact experiments for N* derivatives revealed a laevo-rotation that corresponds to a right-handed helix.

Acknowledgments

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