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Preliminary communication

Novel ferroelectric liquid crystals based on optically active propargylic alcohols

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Some new calamitic chiral mesogens (2,5-diphenyl-1,3,4-thiadiazoles, 2,5-diphenylpyrimidines and a biphenylyl benzoate) incorporating the 1-alkylpropynyl moiety have been synthesized as enantiomerically enriched materials (ee *c.* 87%) and/or as racemates. Their liquid crystalline properties were studied by polarizing microscopy, differential scanning calorimetry and electro-optical investigation. Thereby it was found that most of the new compounds exhibit smectic C phases. The spontaneous polarization ($\mathbf{P}_s$) of the optically active materials was measured to be around 10 nC cm^{-2}.

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It is well known that mesogens made from optically active molecules can form chiral mesophases showing ferroelectricity [1]. In recent years, ferroelectric and antiferroelectric liquid crystals have attracted considerable interest because of their unique properties and their potential technical applications [2, 3]. Consequently a large variety of different structures have been chosen for novel chiral liquid crystal materials. Both the rigid cores and the side chains, usually incorporating the molecular chirality, have been varied. Although enantiomerically enriched alkyn-3-ols are easy available via enantioselective reduction of appropriate alkyn-3-ones, only a few examples of liquid crystals incorporating this propynyl moiety are known from the patent literature [4]. We wish to report here the synthesis and mesomorphic properties of some new ferroelectric liquid crystal materials incorporating such a propargylic moiety.

The synthetic route is outlined in figure 1. Racemic oct-1-yn-3-ol was first oxidized to give oct-1-yn-3-one using CrO_3 (Jones reagent) [5]. Enantioselective reduction with (*R*)-Alpine-Borane® afforded (*R*)-oct-1-yn-3-ol in 87% ee after oxidative work-up [6]. The enantiomeric purity of this compound was determined by derivatizing it with (*S*)-α-methoxy-α-trifluormethylphenylacetyl chloride [(*R*)-MTPACl] and analysing the resulting (*S*)-MTPA-esters by ^{19}F NMR and ^{1}H NMR spectroscopy (Mosher's method) [7].

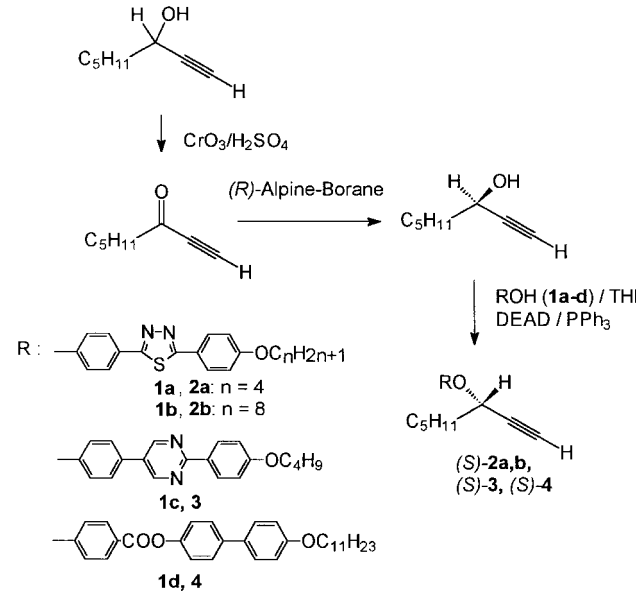

Figure 1. Synthesis of propargyl aryl ethers **2**–**4**.

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Finally (*R*)-oct-1-yn-3-ol was appended to the promesogenic phenols **1a–d** [8, 9] by the Mitsunobu reaction to afford the enantiomerically enriched propargylic ethers **2–4** with inversion of the configuration at the stereogenic centre [10]. Although we were not able to determine the optical purity of the propargylic ethers (*S*)-**2–4** directly by spectroscopic or chromatographic methods, we estimated the enantiomeric excess of the compounds synthesized to be around 87% on the assumption that the configuration at the stereogenic centre is completely inverted following the mechanistic aspects of the Mitsunobu reaction [10].

Phase transition temperatures were determined by optical microscopy between crossed polarizers and were checked by differential scanning calorimetry (see the table).

All compounds except the butoxy substituted derivative (*S*)-**2a** display (chiral) nematic and (chiral) smectic C mesophases, whereas compound (*S*)-**2a** exhibits only a broad cholesteric mesophase. The chiral nematic phases appear with the typical Grandjean texture and the chiral smectic C phases show a fan-shaped texture with helicoidal stripes on slow cooling and give the schlieren texture on stressing; we were therefore able to classify these phases from textural observation.

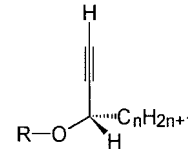
In order to evaluate the influence of the ethynyl group on the mesomorphic properties, the propargyl ether (*S*)-**4** is compared with the methyl branched compound **5** [11] which has the same structure of the rigid core and a comparable total length of the molecule.

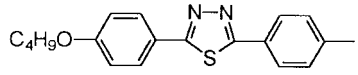
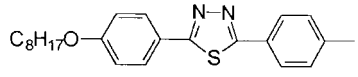
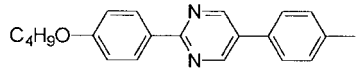
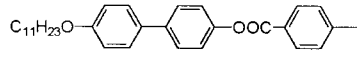
C 78 SmC* 103 N* 117.5 I

Both compounds have the same phase sequence. The clearing temperature of the ethynyl branched compound is slightly enhanced in comparison with the methyl branched molecule. The influence of this structural variation on the stability of the SmC phase is significantly smaller. It seems, that the disturbance of mesophase formation by branching of the molecule is less pronounced in the case of the ethynyl group. Probably, being one carbon atom longer, but slim, the –C≡C–H group allows a better packing of the molecules than the shorter, but—due to its tetrahedral arrangement of hydrogens—more bulky CH_3 group.

Compounds (*S*)-**2b**, (*S*)-**3** and (*S*)-**4** exhibiting the SmC* phase were submitted to electro-optical investigation, and a ferroelectric switching process was observed. The switching behaviour was studied by applying a triangular voltage (peak to peak 20 V) to a 4 μm EHC-cell providing a homogeneous alignment of the sample. The spontaneous polarization ($\mathbf{P}_s$) was determined as a function of temperature (see figure 2). The maximal values for the pyrimidine derivative (*S*)-**3** and the

Table Transition temperatures *T*/°C and corresponding enthalpy values ΔH/kJ mol^{-1} (lower lines) of compounds (*S*)-**2** to (*S*)-**4** and *rac*-**2c**.



Compound	*R*	*n*	Transition temperatures *T*/°C (Enthalpy values ΔH/kJ mol^{-1})
(*S*)-**2a**		5	Cr 78/83[a] N* 133 I (21.6) (1.0)
(*S*)-**2b**		5	Cr 57/63[a] SmC* 96 N* 123 I (25.5) (1.0) (0.9)
rac-**2c**		13	Cr 65 SmC 113 N 118 I (30.0) (0.5) (1.9)
(*S*)-**3**		5	Cr 77/92[a] SmC* 102 N* 150 I (12.8) (0.3) (0.7)
(*S*)-**4**		5	Cr 52 SmC* 96 N* 131 I (29.6) (1.6) (1.4)

[a] Different crystalline modifications.

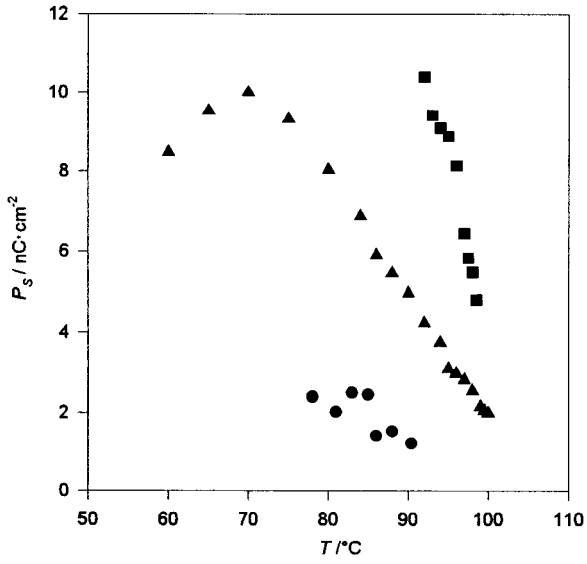


Figure 2. Spontaneous polarization ($\mathbf{P}_s$/nC cm^{-2}) of compounds (*S*)-**2b**, (●) (*S*)-**3** (■), (*S*)-**4** (▲) vs. temperature (*T*/°C).

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biphenylyl benzoate (*S*)-**4** were about 10 nC cm^{-2}. The spontaneous polarization of the thiadiazole derivative (*S*)-**2b** was significantly smaller (2.5 nC cm^{-2}) than for the other two compounds. Comparison of the ethynyl branched derivative (*S*)-**3** with the related methyl branched compound **5** revealed that the value of the spontaneous polarization of the ethynyl derivative is lower than that for the related methyl branched mesogen **5**.

Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on a VARIAN Unity (500 MHz). Phase transition temperatures were measured using a METTLER FP 82 HT hot stage and control unit in conjunction with a NIKON Optiphot-2 polarizing microscope, and were confirmed by differential scanning calorimetry using a PERKIN ELMER DSC-7. Microanalyses were performed using a Carlo-Erba 1102 and Leco CHNS-932 elemental analyser. Thin layer chromatography was performed on MERCK TLC aluminum sheets (silica gel 60 F_{254}). Column chromatography was carried out with silica gel from MERCK (0.040–0.063 mm or 0.063–0.20 mm. (*R*)-oct-1-yn-3-ol was synthesized according to [6*b*]; 87% ee (Mosher's method).

The preparation procedure for the propargylic ethers was as follows. For 2-(4-butoxyphenyl)-5-{4-[(1*S*)-1-pentyl-2-propynyloxy]phenyl}-1,3,4-thiadiazole, (*S*)-**2a**, a solution of (*R*)-oct-1-yn-3-ol (50 mg, 0.40 mmol), dry triphenylphosphine (105 mg, 0.40 mmol) and 4-[5-(4-butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenol **1a** [8] (90 mg, 0.27 mmol) in dry tetrahydrofuran (10 ml) was placed in a flask (20 ml) equipped with magnetic stirrer, rubber septum, gas inlet and gas outlet, under an atmosphere of argon. The solution was cooled to 0°C (external cold bath) and diethyl azodicarboxylate (DEAD, 65 µl, 70 mg, 0.40 mmol, ALDRICH) was added dropwise via a syringe. During the addition the solution was vigorously stirred and the temperature was maintained at 0°C. After the addition was complete, the cold bath was removed and the mixture was stirred at room temperature until thin layer chromatography indicated complete consumption of the phenol. Then the solvent was evaporated (18 mbar, 30°C) and the resulting solid residue was dissolved in chloroform (1–2 ml) and purified by flash chromatography (chloroform/methanol 20 : 1, 30 cm × 1, 5 cm, R_f 0.7). The resulting white solid was recrystallized twice from ethanol (2 ml) to afford (*S*)-**2a** as a white crystalline solid. Yield 30 mg (25%); $[\alpha]_D^{20}$: −120.52 (c = 0.9 in $CHCl_3$). Found (calculated for $C_{26}H_{30}N_2O_2S$): C 71.6 (71.86), H 7.0 (6.96), N 6.4 (6.45), S 7.4 (7.38%). ^{1}H NMR (500 MHz, $CDCl_3$, *J*/Hz): δ_H = 7.92 (d, 2H, *J* 9.0, Ar–H), 7.89 (d, 2H, *J* 9.0, Ar–H), 7.09 (d, 2H, *J* 8.8, Ar–H), 6.96 (d, 2H, *J* 9.0, Ar–H), 4.77 (dt, 1H, ^3J 6.3, ^4J 1.95, CH_2CH), 4.02 (t, 2H, *J* 6.6, OCH_2), 2.50 (d, 1H, ^4J 1.95, C≡CH), 2.0–1.93 (m, 2H, CH_2), 1.8 (m, 2H, CH_2), 1.60–1.54 (m, 4H, CH_2), 1.38–1.32 (m, 4H, CH_2), 0.98 (t, 3H, *J* 7.5, CH_3), 0.91 (t, 3H, *J* 6.9, CH_3).

The other compounds were prepared in an analogous manner.

(*S*)-**2b**: $[\alpha]_D^{20}$: −71.38 (c = 0.83 in $CHCl_3$). Found (calculated for $C_{30}H_{38}N_2O_2S$): C 73.4 (73.43), H 7.8 (7.81), N 5.55 (5.71), S 6.4 (6.53%). ^{1}H NMR (500 MHz, $CDCl_3$, *J*/Hz): δ_H = 7.92 (d, 2H, *J* 8.7, Ar–H), 7.90 (d, 2H, 9.0, Ar–H), 7.09 (d, 2H, *J* 9.0, Ar–H), 6.96 (d, 2H, *J* 8.8 Ar–H), 4.77 (dt, 1H, CH_2CH), 4.0 (t, 2H, OCH_2, *J* 6.6), 2.50 (d, 1H, ^4J 1.95, C≡CH), 2.0–1.93 (m, 2H, CH_2), 1.80 (q, 2H, CH_2), 1.60–1.25 (m, 16H, CH_2), 0.91 (t, 3H, *J* 7.5, CH_3), 0.88 (t, 3H, *J* 6.9, CH_3).

rac-**2c**. Found (calculated for $C_{38}H_{54}N_2O_2S$): C 75.7 (75.70), H 8.7 (9.03), N 4.55 (4.65), S 5.3 (5.32%). ^{1}H NMR (500 MHz, $CDCl_3$, *J*/Hz): δ_H = 7.92 (d, 2H, *J* 9.0, Ar–H), 7.90 (d, 2H, *J* 9.0, Ar–H), 7.09 (d, 2H, *J* 9.0, Ar–H), 6.96 (d, 2H, *J* 9.0, Ar–H), 4.77 (dt, 1H, CH_2CH), 4.0 (t, 2H, *J* 6.6, OCH_2), 2.50 (d, 1H, ^4J 1.95, C≡CH), 2.0–1.94 (m, 2H, CH_2), 1.8 (m, 2H, CH_2), 1.60–1.20 (m, 32H, CH_2), 0.88 (t, 3H, *J* 7.5, CH_3), 0.86 (t, 3H, *J* 6.9, CH_3).

(*S*)-**3**: $[\alpha]_D^{20}$: −56.83 (c = 0.63 in $CHCl_3$). Found (calculated for $C_{28}H_{32}N_2O_2$): C 78.5 (78.47), H 7.5 (7.53), N 6.5 (6.54%). ^{1}H NMR (500 MHz, $CDCl_3$, *J*/Hz): δ_H = 8.94 (s, 2H, Ar–H), 8.42 (d, 2H, *J* 8.8, Ar–H), 7.54 (d, 2H, *J* 8.6, Ar–H), 7.14 (d, 2H, *J* 8.8 Ar–H), 7.0 (d, 2H, *J* 8.8, Ar–H), 4.76 (dt, 1H, *J* 6.3, *J* 2.1, CH_2CH), 4.04 (t, 4H, *J* 6.5, OCH_2), 2.50 (d, 1H, *J* 2.1, C≡CH),

2.01–1.94 (m, 2H, CH_2), 1.8 (m, 2H, CH_2), 1.6–1.2 (m, 8H, CH_2), 0.99 (t, 3H, *J* 7.3, CH_3), 0.87 (t, 3H, *J* 7.0, CH_3).

(*S*)-**4**: $[\alpha]_D^{20}$: −62.13 (*c* = 2.09 in $CHCl_3$). Found (calculated for $C_{38}H_{48}O_4$): C 80.1 (80.24), H 8.4 (8.51%). ^{1}H NMR (500 MHz, $CDCl_3$, *J*/Hz): δ_H = 8.16 (d, 2H, *J* 8.8, Ar–H), 7.56 (d, 2H, *J* 8.8, Ar–H), 7.48 (d, 2H, *J* 8.6 Ar–H), 7.22 (d, 2H, *J* 8.6, Ar–H), 7.08 (d, 2H, *J* 8.9, Ar–H), 6.95 (d, 2H, *J* 8.6, Ar–H), 4.81 (dt, 1H, *J* 4.6, *J* 2.1, CH_2CH), 3.98 (t, 2H, *J* 6.5, OCH_2), 2.50 (d, 1H, *J* 2.1, C≡CH), 2.01–1.94 (m, 2H, CH_2), 1.8 (m, 2H, CH_2), 1.63–1.2 (m, 22H, CH_2), 0.91 (t, 3H, *J* 7.1, CH_3), 0.87 (t, 3H, *J* 7.0, CH_3).

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