New chiral side chains for ferro- and antiferro-electric liquid crystals derived from the preen-gland wax of the domestic goose†

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(2*R*,4*R*,6*R*,8*R*)-2,4,6,8-Tetramethyldecanoic acid and (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanol, as well as the (2*R*,4*R*,6*R*,8*R*) and the (2*S*,4*R*,6*R*,8*R*) diastereomers of 4,6,8-trimethyldecan-2-ol, have been obtained from the preen-gland wax of the domestic goose. Starting from these alkanols and alkanoic acid, novel ferro- and antiferro-electric liquid crystals bearing four methyl branchings in the chiral side chain have been synthesized and their mesomorphic and electro-optical properties have been investigated. The results obtained are compared with the properties of the respective chiral (*S*)-2-methyldecanoic acid, (*S*)-decan-2-ol and (*S*)-2-methyldecanol derivatives. The compounds with four methyl branchings in the chiral side chain are found to exhibit lower melting points, broader SmC* phase ranges, higher values of spontaneous polarization and larger tilt angles in comparison to the respective compound with only one methyl branching.

Many physical properties which are used in modern applications of liquid crystals depend entirely on the presence of chiral molecules, *e.g.* the helical structure of cholesteric and some smectic phases, the ferroelectricity of uniformly tilted smectic phases and the antiferroelectricity of alternating tilted smectic phases.[1] Moreover, in certain systems high chirality causes the induction of novel phases (Blue phases, Twist Grain Boundary phases, Q phases *etc.*)[1,2] Several chiral phases possess frustrated structures displaying competition between chiral forces and the tendency of the molecules to pack in a space-filling arrangement. For a better understanding of the chiral forces as well as for electro-optical applications the development of new chiral liquid crystals plays an important role. However, the design of novel structures is restricted by the available chiral moieties, which can be obtained either by enantioselective reactions or by using the natural chiral pool.

A novel natural source of chiral mono-, di-, tri- or tetramethyl branched alkanoic acids is the preen-gland wax of poultry.[3] For example, the wax of the domestic goose consists of about 90% octadecyl (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanoate,[4,5] so that after transesterification and Spaltrohr distillation large quantities of methyl (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanoate are obtained,[6] which can be transformed into the free acid by standard methods. As recently shown, methyl (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanoate can also be transformed into (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanol and further into (4*R*,6*R*,8*R*)-4,6,8-trimethyldecan-2-ol, from which both the (2*R*,4*R*,6*R*,8*R*) and the (2*S*,4*R*,6*R*,8*R*) diastereomers can be isolated by column chromatography.[7] These tetramethylalkanols, as well as (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanoic acid, are promising chiral side chains for the design of novel liquid crystals.

Here we present the first ferro- and antiferro-electric liquid crystals having tetramethylalkyl groups in the chiral side chain. In order to study the influence of the additional optically active methyl branchings, the respective chiral 2-methyldecanoic acid, decan-2-ol and 2-methyldecanol derivatives have also been synthesized. Polymorphy, phase transition temperatures and electro-optical properties (spontaneous polarization, optical tilt angles and switching times) of the novel ferro- and antiferro-electric liquid crystals are discussed.

Experimental

Synthesis

Methyl (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanoate was obtained by transesterification and Spaltrohr distillation of the preen gland-wax of the domestic goose. According to the reaction scheme shown in Scheme 1, the methyl ester was transformed into the free acid **1f** as well as into (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanol **1b**, which was partially further transformed into the (2*R*,4*R*,6*R*,8*R*) and the (2*S*,4*R*,6*R*,8*R*) diastereomers **1d** and **1e** of 4,6,8-trimethyldecan-2-ol. All these tetramethylalkanols, as well as (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanoic acid, were obtained with a diastereomeric excess of more than 99%.[6,7] Compounds **1b**, **1d**, **1e** and **1f**, as well as the commercially available compounds (purchased from the Japan Energy Corporation) (*S*)-2-methyldecanol **1a**, (*S*)-decan-2-ol **1c** and (*S*)-2-methyldecanoic acid **1g**, were then used as chiral starting materials for the synthesis of three series of liquid crystalline products. These series differ by the linking group between mesogenic core and chiral side chain. Within each series, the number and the position of the chiral methyl branchings are varied. As outlined in Scheme 2, compounds **2a**–**d** were synthesized by esterification of 4-benzyloxybenzoic acid with the chiral alkanols **1a**–**d**, followed by hydrogenation to remove the benzyloxy protecting group and finally esterification of the obtained phenols with 4′-octyloxybiphenyl-4-carboxylic acid. The respective liquid crystalline ethers **3a**–**d** were obtained by a reaction between 4-hydroxyphenyl 4′-octyloxybiphenyl-4-carboxylate and the chiral alkanols **1a**–**c** and **1e** in the presence of diethylazodicarboxylate (DEAD) and triphenylphosphine[8] (see Scheme 3). Compound **4c** was synthesized by esterification of the acid chloride of **1g** with 4-hydroxyphenyl 4′-octyloxybiphenyl-4-carboxylate (see Scheme 3), whereas compound **4d** could not been obtained optical pure in a similar way. Compound **4d** was synthesized by esterification of **1f** with 4-hydroxyphenyl 4′-octyloxybiphenyl-4-carboxylate in the presence of dicyclohexylcarbodiimide (DCC). All products were purified by

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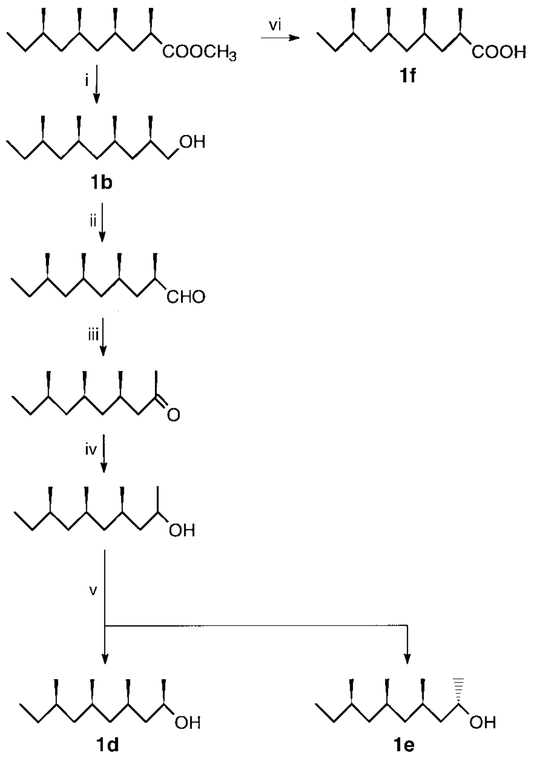
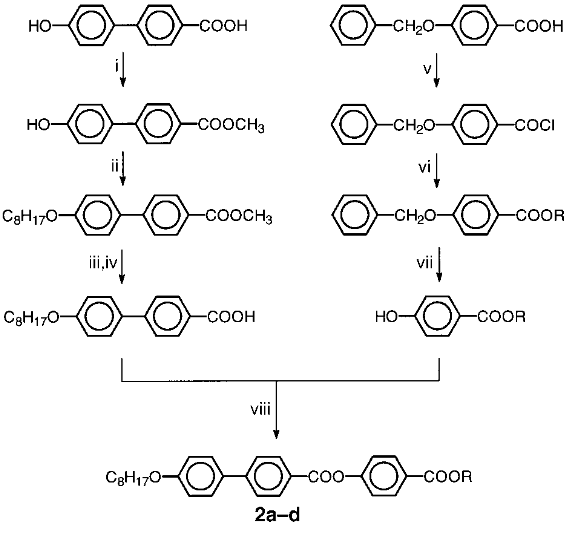
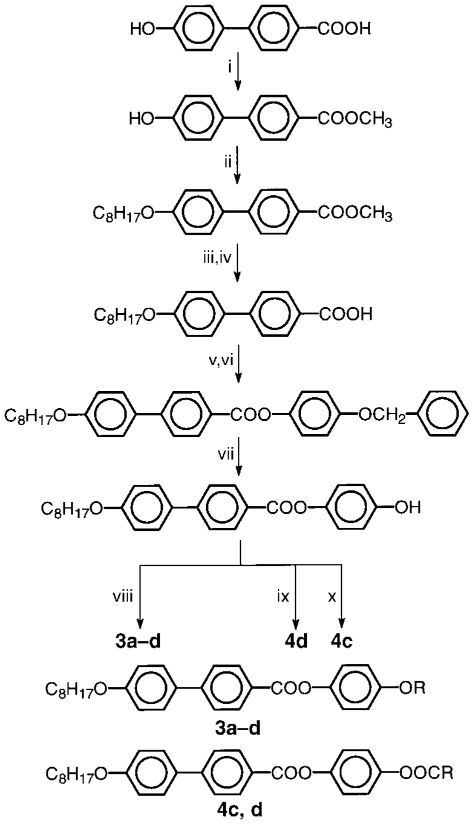
† Presented in part at the 5th International Conference on Liquid Crystals, Cambridge, 1995.



Scheme 1 *Reagents and conditions*: i, $LiAlH_4$; ii, PCC, CH_2Cl_2; iii, 2,2′-bipyridyl–Cu complex, DABCO, Bu^tOH, air; iv, methyloxazaborolidine, BH_3–THF, THF; v, column chromatography [silica gel, CH_2Cl_2–Pr^i_2O (9 : 1)]; vi, NaOH, dioxane



Scheme 2 *Reagents and conditions*: i, MeOH, H_2SO_4; ii, K_2CO_3, $C_8H_{17}Br$, DMF; iii, KOH, EtOH; iv, HCl; v, $SOCl_2$; vi, ROH (**1a**–**d**); vii, H_2, Pd; viii, DCC, CH_2Cl_2



Scheme 3 *Reagents and conditions*: i, MeOH, H_2SO_4; ii, K_2CO_3, $C_8H_{17}Br$, DMF; iii, KOH, EtOH; iv, HCl; v, $SOCl_2$; vi, 4-$BnOC_6H_4OH$, pyridine; vii, H_2, Pd; viii, ROH (**1a**–**c**,**e**), DEAD, PPh_3, THF; ix, **1f**, DCC; x, RCOCl (from **1g** and $SOCl_2$)

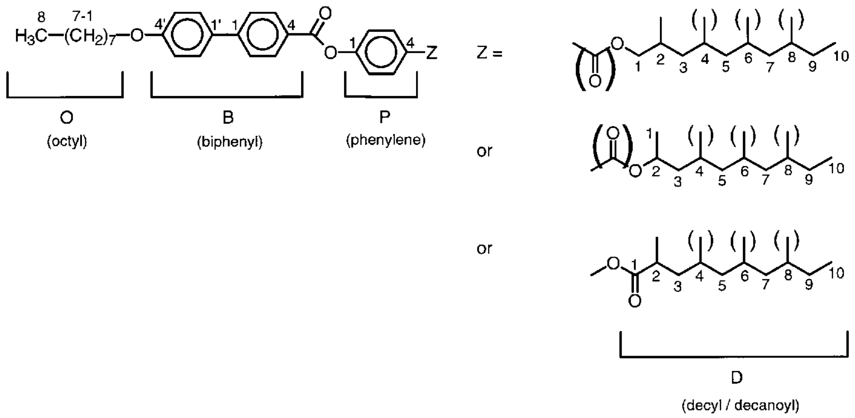
chromatography, followed by recrystallization until the transition temperatures remained constant. The structure of the products was confirmed by ^1H and ^{13}C NMR experiments (Bruker ARX-400, AM-400 and DPX-300; 9.4 and 7.0 T, respectively) and, in case of compounds **2d**, **3d** and **4d**, additionally by IR (Perkin-Elmer PE 257) and mass (Varian MAT 44F) spectroscopy. Signal assignments in the ^{13}C NMR spectra were achieved by DEPT-135 experiments,[9] by two-dimensional ^{13}C, ^1H COSY[10] and COLOC[10] experiments for **2a**, **3b** and **4d** and by comparison with literature data.[6,7] These assignments were then transferred to the remaining compounds while considering the usual substituent effects on chemical shifts[11] and attempting maximum internal consistency. The purity of the products was checked by TLC and HPLC (pump: Knauer HPLC pump 64, column: Nucleosil 120-5 C18, solvent: methanol, detector: Severn Analytical SA 6503 at 303 nm) and their optical purity was characterized by measuring the optical rotation (Perkin-Elmer polarimeter 241). All compounds were found to be of high purity (HPLC purity above 99%).

The synthesis of compound **2c** has already been described;[12] however no detailed information about the physical properties of this compound were reported.

Synthesis of 2a–d

A synthetic procedure for **2d** is given as an example. Dicyclohexylcarbodiimide (DCC) (1.24 g, 6 mmol) was added at room temperature to a solution of 4′-octyloxybiphenyl-4-carboxylic acid (0.98 g, 3 mmol), (1*R*,3*R*,5*R*,7*R*)-1,3,5,7-tetramethylnonyl 4-hydroxybenzoate (0.95 g, 3 mmol) and 4-dimethylaminopyridine (DMAP) (0.06 g, 0.5 mmol) in dry dichloromethane (50 ml), and the mixture was stirred for 24 h. After filtration the solvent was evaporated and the resulting product was purified by chromatography over silica gel using dichloromethane as the eluent (R_f 0.70), followed by recrystallization from ethanol until the transition temperature remained constant. Yield: 1.34 g (71%); $\nu(CCl_4)/cm^{-1}$ 2955, 2925, 2871, 2854, 1735, 1715, 1604, 1504; *m*/*z* 628.5 (M^+); ^1H and ^{13}C NMR data are given in Tables 1 and 2; $[\alpha]^{20}_D$ −0.30 (*c* 5, $CHCl_3$) (**2b**, −2.36; **2c**, +18.29; **2d**, −18.68).

Table 1 ^1H NMR data for compounds **2a–d**, **3a–d** and **4c–d** (400 or 300 MHz; $CDCl_3$; Me_4Si)



proton	2a	2b	2c	2d	3a	3b	3c	3d	4c	4d
	chemical shift (multiplicity, coupling constant)[a,b]									
O1	4.01 (t,6.6)	4.01 (t,6.6)	4.01 (t,6.6)	4.01 (t,6.6)	4.01 (t,6.6)	4.01 (t,6.6)	4.01 (t,6.5)	4.01 (t,6.6)	4.01 (t,6.6)	4.01 (t,6.6)
O2	1.81 (qi,7.0)	1.82 (qi,7.0)	1.81 (qi,7.0)		1.81 (qi,7.0)	1.88 (qi,7.0)	1.81 (qi,7.0)		(qi,7.0)	1.80
O8	0.89† (t,6.9)		0.89† (t,6.9)		0.89† (t,6.9)	0.89 (t,*ca.* 7)	0.89† (t,6.9)		0.89† (t,6.9)	0.89 (t,6.9)
B2	7.69 (8.4)	7.70 (8.3)	7.69 (8.4)	7.69 (8.4)	7.67 (8.3)	7.67 (8.4)	7.67 (8.3)	7.68 (8.5)	7.68 (8.4)	7.68 (8.4)
B3	8.23	8.23	8.23	8.22	8.22	8.22	8.21	8.22	8.22	8.22
B2′	7.59 (8.7)	7.59 (8.7)	7.59 (8.7)	7.59 (8.7)	7.59 (8.7)	7.58 (8.7)	7.58 (8.6)	7.58 (8.8)	7.59 (8.7)	7.58 (8.7)
B3′	7.00	7.00	7.00	7.00	7.00	6.99	6.99	7.00	7.00	7.00
P2	7.31 (8.6)	7.32 (8.6)	7.30 (8.6)	7.31 (8.7)	7.12 (9.0)	7.12 (9.0)	7.11 (8.9)	7.12 (9.0)	7.24‡ (9.0)	7.24† (9.0)
P3	8.13	8.13	8.12	8.12	6.93	6.93	6.91	6.92	7.13‡	7.13†
D1	4.22 (dd,10.7,5.8) 4.12 (dd,10.7,6.7)	4.25 (dd,10.7,5.0) 4.09 (dd,10.7,6.8)	1.34 (d,6.3)	1.35 (d,6.1)	3.82 (dd,8.9,5.8) 3.72 (dd,8.9,6.8)	3.84 (dd,8.9,5.0) 3.70 (dd,8.9,6.8)	1.30 (d,*ca.* 6)	1.30 (d,*ca.* 6)		
D2	1.93 (oct,6.4)	2.06 (oct,6.5)	5.16 (sext,6.3)	5.28 (m)	1.93 (oct,6.4)	2.04 (oct,6.5)	4.32 (sext,6.0)	4.43 (m)	2.69 (sext,7.0)	2.82 (dqd,9.8,6.9,4.9)
D10	0.88† (t,6.9)		0.88† (t,6.9)		0.88† (t,6.9)	0.85 (t,7.3)	0.88† (t,6.9)		0.88† (t,6.9)	0.85 (*t,ca.* 7)
D2-*Me*	1.02 (d,6.7)	1.04 (d,6.6)			1.02 (d,6.7)	1.04 (d,6.8)			1.30 (d,6.9)	1.31 (d,6.9)

[a] Coupling constants (J) are given in Hz; qi = quintet, sext = sextet, oct = octet. Footnote symbols (†,‡) indicate interchangeable assignments. For the B and P protons, which are parts of AA′XX′ spin systems, the N values ($J_{AX}+J_{AX'}$) are given in parentheses. [b] Further signals: **2a**: δ 1.52–1.27 (m); **2b**: δ 1.71–0.81 (m); **2c**: δ 1.73–1.26 (m); **2d**: δ 1.90–0.80 (m); **3a**: δ 1.54–1.21 (m); **3b**: δ 1.68–0.82 (m); shifts assigned by 2D experiments: δ 1.64 (m, D4), 1.60 (m, D6), 1.47 (m, D3), 1.46 (m, O3), 1.43 (m, D8), 1.38 (m, D9), 1.36, 1.32 (m, O4, O5), 1.30 (m, O7), 1.28 (m, O6), 1.22 (m, D5, D7), 1.05 (m, D9), 0.98 (m, D3), 0.90, 0.86 (m, D5, D7), 0.90 (d, 6.6, D4-*Me*), 0.85 (d, 6.6, D8-*Me*), 0.83 (d, 6.5, D6-*Me*); **3c**: δ 1.73–1.28 (m); **3d**: δ 1.87–0.83 (m); **4c**: δ 1.86–1.28 (m); **4d**: δ 1.96–0.83 (m); shifts assigned by 2D experiments: δ 1.90 (ddd, 13.9, 9.7, 4.3, D3), 1.66 (m, D4), 1.63 (m, D6), 1.46 (m, O3)1.43 (m, D8), 1.36 (m, D9), 1.36, 1.32 (m, O4, O5), 1.30 (m, O7), 1.28 (m, O6), 1.23 (m, D5), 1.20 (m, D7), 1.16 (m, D3), 1.08 (m, D9), 0.97 (m, D5), 0.96 9d, 6.5, D4-*Me*), 0.90 (m, D7), 0.85 (d, *ca.* 7, D6-*Me*, D8-*Me*).

Synthesis of 3a–d

A synthetic procedure for **3d** is given as an example. 4-Hydroxyphenyl 4′-octyloxybiphenyl-4-carboxylate (1.26 g, 3 mmol), triphenylphosphine (0.79 g, 3 mmol) and (2*S*,4*R*,6*R*,8*R*)-4,6,8-trimethyldecan-2-ol **1e** (0.4 g, 2 mmol) were dissolved in dry tetrahydrofuran (50 ml). While the temperature was kept at 0 °C, diethyl azodicarboxylate (DEAD) (0.52 g, 3 mmol) was added dropwise under a nitrogen atmosphere and stirring was continued for 36 h at room temperature. Afterwards the solvent was removed and the resulting product was purified by chromatography over silica gel using dichloromethane as the eluent (R_f 0.90), followed by recrystallization from ethanol until the transition temperature remained constant. Yield: 0.64 g (53%); $\nu(CCl_4)/cm^{-1}$ 2954, 2926, 2870, 2854, 1733, 1606, 1504; m/z 600.5 (M^+); ^1H and ^{13}C NMR data are given in Tables 1 and 2; $[\alpha]^{20}_D+3.05$ (c 5, $CHCl_3$) (**3b**, −2.02; **3c**, −2.11; **3d**, −3.44).

Synthesis of 4c

4-Hydroxyphenyl 4′-octyloxybiphenyl-4-carboxylate (1.26 g, 3 mmol) was dissolved in dry pyridine (50 ml) and (*S*)-2-methyldecanoyl chloride (0.71 g, 3 mmol) was added while the temperature was kept at 0 °C. Stirring was continued for 16 h at room temperature. After hydrolysis in an excess of diluted HCl, the product was extracted into dichloromethane (3 × 150 ml). The combined dichloromethane solutions were washed with water (200 ml) and dried ($MgSO_4$). The solvent was removed and the resulting product purified by chromatography over silica gel using dichloromethane as the eluent (R_f 0.71), followed by recrystallization from ethanol until the

Table 2 ^{13}C NMR data for compounds **2a–d**, **3a–d** and **4c–d** (101 or 75 MHz; $CDCl_3$)

	chemical shift[a]									
carbon	**2a**	**2b**	**2c**	**2d**	**3a**	**3b**	**3c**	**3d**	**4c**	**4d**
O1	68.2	68.2	68.3	68.2	68.2	68.2	68.2	68.2	68.2	68.2
O2	29.3	29.3	29.3	29.3	29.3	29.3	29.3	29.3	29.3	29.3
O3	26.1	26.1	26.1	26.1	26.1	26.1	26.1	26.1	26.1	26.1
O4	29.3†	29.3†	29.3†	29.3†	29.3†	29.3†	29.3†	29.3†	29.3†	29.3†
O5	29.4†	29.4†	29.4†	29.4†	29.4†	29.4†	29.4†	29.4†	29.4†	29.4†
O6	31.9‡	31.8	31.9	31.9	31.9‡	31.9	31.9	31.9	31.9‡	31.9
O7	22.7	22.7	22.7	22.7	22.7	22.7	22.7	22.7	22.7	22.7
O8	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1
B1	146.3	146.3	146.3	146.3	145.9	145.9	145.9	145.9	146.1	146.1
B2	126.7	126.6	126.7	126.7	126.6	126.6	126.6	126.6	126.6	126.6
B3	130.8	130.8	130.8	130.8	130.7	130.7	130.7	130.7	130.7	130.8
B4	127.1	127.0	127.1	127.1	127.7	127.7	127.7	127.7	127.3	127.4
B4-*C*O	164.6	164.6	164.7	164.7	165.5	165.5	165.5	165.5	165.0	165.0
B1′	131.9	131.8	131.9	131.9	132.1	132.0	132.1	132.0	131.9	132.0
B2′	128.4	128.4	128.4	128.4	128.4	128.4	128.4	128.4	128.4	128.4
B3′	115.1	115.0	115.1	115.1	115.0§	115.0	115.0	115.0	115.0	115.1
B4′	159.7	159.7	159.7	159.7	159.6	159.6	159.6	159.6	159.6	159.7
P1	154.7	154.7	154.6	154.6	144.4	144.3	144.3	144.3	148.3	148.4
P2	121.8	121.8	121.7	121.8	122.4	122.4	122.5	122.5	122.6§	122.6‡
P3	131.2	131.2	131.2	131.1	115.2§	115.1	116.6	116.5	122.5§	122.5‡
P4	128.2	128.1	128.6	128.5	157.1	157.1	156.0	156.2	148.3	148.4
P4-*C*O	166.0	165.9	165.5	165.5						
D1	70.1	69.8	20.1	20.6‡	73.7	73.5	19.8	20.4‡	175.3	175.3
D2	32.8	30.2	72.0	70.0	33.2	30.7	74.6	72.4	39.7	37.7
D3	33.5	41.4	36.1	43.1	33.6	41.3	36.6	44.1	33.8	41.3
D4	26.9	27.6‡	25.5	26.7	27.0	27.7	25.6	26.6	27.3	28.5
D5	29.9†	44.7	29.5†	45.0	30.0†	44.7‡	29.7†	44.9	29.6†	45.6
D6	29.6†	27.5‡	29.5†	27.4	29.6†	27.5	29.6†	27.4	29.5†	27.4
D7	29.3†	45.7	29.5†	45.5	29.4†	45.6‡	29.3†	45.7	29.3†	45.0
D8	31.8‡	31.5	31.9	31.6	32.0‡	31.6	31.9	31.6	31.8‡	31.6
D9	22.7	28.8	22.7	29.1	22.7	28.9	22.7	29.0	22.7	29.1
D10	14.1	11.2	14.1	11.2	14.1	11.2	14.1	11.2	14.1	11.2
Me-D2	17.1	18.3			17.1	18.3			17.0	18.3
Me-D4		20.9		20.6‡		21.1		20.7‡		20.5
Me-D6		20.9		21.0‡		21.0		20.7‡		20.8
Me-D8		20.0		19.9		20.0		20.0		20.0

[a] Footnote symbols (†,‡,§) indicate interchangeable assignments.

transition temperature remained constant. Yield: 1.18 g (67%); ^1H and ^{13}C NMR data are given in Tables 1 and 2; $[\alpha]^{20}_D + 8.60$ (*c* 5, $CHCl_3$).

Synthesis of 4d

Dicyclohexylcarbodiimide (DCC) (0.70 g, 3.4 mmol) was added at room temperature to a solution of 4-hydroxyphenyl 4′-octyloxybiphenyl-4-carboxylate (0.71 g, 1.7 mmol), (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanoic acid **1f** (0.82 g, 3.4 mmol) and 4-dimethylaminopyridine (DMAP) (0.27 g, 2.2 mmol) in dry dichloromethane (50 ml), and the mixture was stirred for 24 h. After filtration, the reaction mixture was washed twice with a solution of 5% citric acid in water (50 ml) and once with water (50 ml). The organic phase was dried (Na_2SO_4), the solvent removed and the resulting product purified by chromatography over silica gel using dichloromethane as the eluent (R_f 0.81), followed by recrystallization from ethanol until the transition temperature remained constant. Yield: 0.42 g (39%); $\nu(CCl_4)/cm^{-1}$ 2954, 2925, 2870, 2854, 1756, 1732, 1604, 1504; *m*/*z* 628.5 (M^+); ^1H and ^{13}C NMR data are given in Tables 1 and 2; $[\alpha]^{20}_D - 10.53$ (*c* 5, $CHCl_3$).

Equipment and methods

Phase transition temperatures were determined optically by observing the textural changes with a polarizing microscope. Transition enthalpies were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7. Miscibility studies were carried out by the contact method and, in one case, by choosing specific concentrations. For these investigations both enantiomers of 4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (**MHPOBC**)[13] have been used as reference compounds. Commercially available test cells (E.H.C.) with a layer spacing of 10 μm were used for the electro-optical investigations. The spontaneous polarization was measured by the triangular wave method. Optical tilt angles were obtained by an extrapolation of the switching angles to zero field. Switching times, defined as the rise time from 10 to 90% transmission, were determined by measuring the optical response to an applied electric field (rectangular wave) at a field strength of ±10 V μm^{-1} (compounds **2a**–**d**, **3a**–**d** and **4c**) or ±20 V μm^{-1} (compound **4d**).

Results

Liquid crystalline properties

Textural observations and miscibility studies have been carried out in order to determine the liquid crystalline properties of the compounds of series **2**–**4**. On cooling from the isotropic phase for all compounds the SmA phase appears showing characteristic textures (planar oriented region: focal-conic fan texture, homeotropic oriented regions: no texture). On further cooling a phase transition into the SmC phase occurs: in the planar oriented region the focal-conic fan texture of the SmA phase transforms into a broken focal-conic fan texture and in the homeotropic regions a schlieren texture appears. Below the SmC phase, most of the compounds show a direct transition into a higher ordered smectic phase (denoted as SmIII phase in the following text, probably SmI) which exhibits either a broken focal-conic fan texture with thin round coloured bands or a schlieren texture. In the other two compounds, a SmC_A

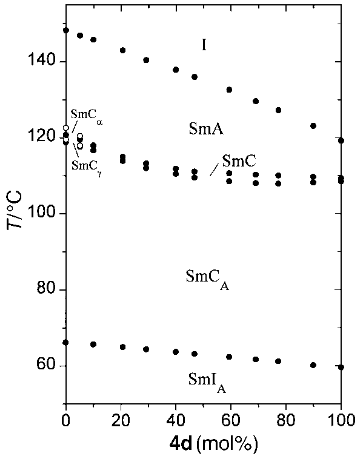


Fig. 1 Phase diagram between (*R*)-**MHPOBC** and **4d**

phase occurs between the SmC and the higher ordered smectic phase SmI$_A$. At the transition from the SmC to the SmC$_A$ phase the number of chirality lines in the broken focal-conic fan texture strongly decreases and the number of chevron defects strongly increases. The SmC–SmC$_A$ phase transition is also indicated by an inversion of the helical twist sense which can be observed in the schlieren texture. Moreover, in the supercooled region of three compounds a transition into a high ordered smectic phase SmIV can clearly be observed by the formation of a mosaic texture.

The classification of the SmA, SmC, SmC$_A$ and SmI$_A$ phases was confirmed by miscibility studies. As an example, the phase diagram between the compounds **4d** and (*R*)-**MHPOBC**, which has been investigated in more detail, is shown in Fig. 1. The SmA, SmC, SmC$_A$ and SmI$_A$ phases of (*R*)-**MHPOBC** are uninterruptedly miscible, with the respective smectic modifications of **4d** confirming thereby the phase sequence SmI$_A$–SmC$_A$–SmC–SmA for compound **4d**.

Polymorphy, phase transition temperatures and transition enthalpies of the liquid crystalline products are shown in Table 3 [NB: compounds with different linking groups X are distinguished by different numbers (**2**–**4**), whereas the letters (**a**–**d**) label the kind of the chiral side chain]. As can be seen, the introduction of three additional methyl branchings leads to a decrease of the melting points of about 10 K for series **2** and **4** and 25 K for series **3**, as well as to about 30 K lower clearing temperatures, resulting in a smaller liquid crystalline phase range for the tetramethyl derivatives. However, the SmC temperature range increases slightly in the case of series **2** and **4** and by more than a factor of three in case of series **3**. The largest SmC phase ranges are observed in series **2**, ranging from 47 to 62 K.

In the two compounds **2c** and **4d**, an alternating tilted SmC$_A$ phase occurs in a broad temperature range. With respect to the appearance of this SmC$_A$ phase the influence of the three additional methyl branchings is puzzling. Whereas in series **2** the SmC$_A$ phase of the 2-methyldecanol derivative **2c** is replaced by a SmC phase in the respective tetramethyl derivative **2d**, the opposite effect is observed in series **4**.

Electro-optical properties

All compounds of series **2**–**4** (see Table 3) show ferroelectric switching in the SmC and SmIII phases. To characterize the ferroelectric properties the temperature dependence of spontaneous polarization, optical tilt angle and switching time (τ_{10-90} at $E\pm10$ V μm^{-1}) of the SmC phases have been measured. In two of the compounds (**2c**, **4d**) the ferroelectric smectic modifications (SmC, SmIII) are almost replaced by antiferroelectric phases. For both antiferroelectric phases (SmC$_A$ and SmI$_A$) of compounds **2c** and **4d**, a 'tristate' switching has been observed, confirming the antiferroelectric nature of these phases. In order to allow a comparison to the electro-optical properties of the SmC phases of the other compounds, in the temperature range of the antiferroelectric SmC$_A$ phases polarization and optical tilt angle of the field induced ferroelectric states, as well as the rise time from 10 to 90% transmission for the direct switching between the two ferroelectric switching states, have been determined. Since no switching was observed for the SmC$_A$ phase of compound **4d** at $E\pm10$ V μm^{-1}, the switching times of this compound were measured at $E\pm20$ V μm^{-1}.

For the compounds of series **2** the results of the electro-optical investigations are shown in Figs. 2–4. Both tetramethyl derivatives (**2b**, **2d**) are found to exhibit two to three times higher values of spontaneous polarization in comparison to their respective reference compound (**2a**, **2c**) with only one chiral methyl branching. Additionally, an increase of the optical tilt angle by about a factor of 1.5 is observed; *e.g.* 50 K below

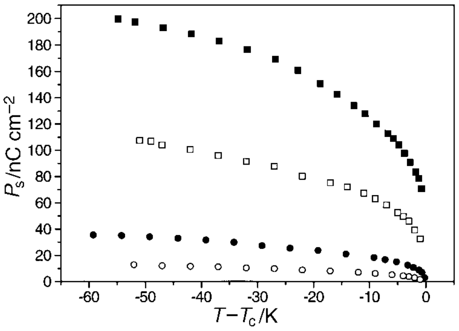


Fig. 2 Temperature dependence of spontaneous polarization of compounds **2**; (○) **2a**, (●) **2b**, (□) **2c** and (■) **2d**

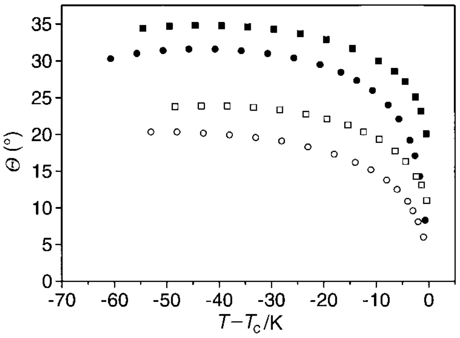


Fig. 3 Temperature dependence of the tilt angle of compounds **2**; (○) **2a**, (●) **2b**, (□) **2c** and (■) **2d**

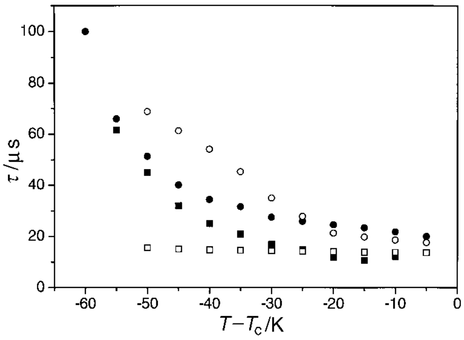
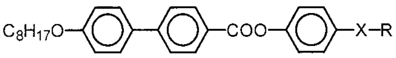


Fig. 4 Temperature dependence of the switching time of compounds **2**; (○) **2a**, (●) **2b**, (□) **2c** and (■) **2d**

Table 3 Polymorphy, phase transition temperatures and transition enthalpies of the liquid crystalline products



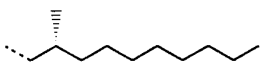
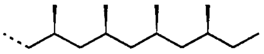
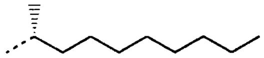
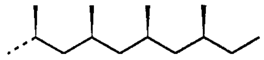
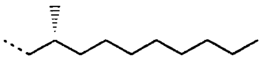
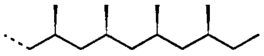
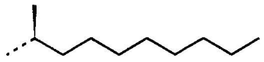
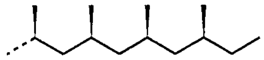
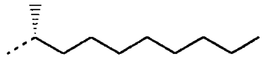
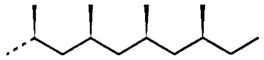
compound	X	R	transition temperatures/°C [enthalpies/kJ mol^{-1}]
2a	CO_2		Cr 66.4 (SmIII 54.5) SmC 108.0 SmA 164.1 I [30.6] [1.02] [0.00] [6.24]
2b	CO_2		Cr 53.9 SmIII 54.0 SmC 115.7 SmA 134.3 I [22.9] [0.80] [0.00] [7.08]
2c	CO_2		Cr 62.8 (SmI$_A$ 62.5) SmC$_A$ 109.3 SmC 113.4 SmA 140.4 I [29.4] [1.50] [0.021] [0.00] [5.83]
2d	CO_2		Cr 53.5 (SmIII 38.0) SmC 94.8 SmA 102.1 I [19.9] [0.43] [0.50] [1.98]
3a	O		Cr 84.4 (SmIV 56.6) SmIII 101.6 SmC 107.9 SmA 164.4 I [31.2] [1.96] [2.96] [0.00] [7.04]
3b	O		Cr 55.1 (SmIV 44.7) SmIII 80.6 SmC 104.6 SmA 133.6 I [18.8] [1.84] [2.40] [0.00] [4.80]
3c	O		Cr 65.2 SmIII 81.3 SmC 94.5 SmA 144.2 I [23.5] [2.16] [0.00] [6.07]
3d	O		Cr 41.6 SmIII 49.5 SmC 90.4 SmA 116.3 I [22.7] [1.04] [0.00] [4.22]
4c	O_2C		Cr 62.6 (SmIV 58.5) SmIII 91.7 SmC 136.1 SmA 157.5 I [26.1] [1.66] [2.72] [0.00] [5.48]
4d	O_2C		Cr 56.3 SmI$_A$ 59.5 SmC$_A$ 108.5 SmC 109.4 SmA 119.2 I [23.2] [1.32] [0.12] [0.28] [2.68]

Table 4 Spontaneous polarization, optical tilt angles and switching times of the compounds of series **3** at 5, 10, 20, 30 and 40 K below the SmA–SmC transition temperature

compound	$T-T_c$/K	P_s/nC cm^{-2}	θ(°)	τ/μs
3a	−5	1.8	9.1	22.3
3b	−5	5.1	17.7	48.6
3b	−10	6.8	20.4	70.0
3b	−20	8.8	22.5	90.0
3c	−5	24.4	11.1	9.6
3c	−10	32.6	13.5	9.9
3d	−5	49.2	19.0	12.3
3d	−10	63.6	23.0	13.8
3d	−20	82.8	26.3	18.4
3d	−30	93.3	27.5	25.5
3d	−40	97.9	27.2	45.8

Table 5 Spontaneous polarization, optical tilt angles and switching times of the compounds of series **4** at 5, 10, 20, 30 and 40 K below the SmA–SmC transition temperature

compound	$T-T_c$/K	P_s/nC cm^{-2}	θ(°)	τ/μs
4c	−5	8.0	18.0	17.6
4c	−10	10.7	21.5	19.1
4c	−20	13.9	24.5	21.3
4c	−30	16.2	25.9	22.9
4c	−40	18.0	26.5	26.4
4d	−5	25.6	27.1	12.4[a]
4d	−10	29.6	29.6	14.4[a]
4d	−20	35.7	32.2	20.2[a]
4d	−30	41.0	33.5	32.9[a]
4d	−40	44.3	33.8	62.1[a]

[a] Measured at a field strength of ±20 V μm^{-1}.

the SmA–SmC transition temperatures, optical tilt angles of about 30° for the tetramethyl derivatives are measured, compared to about 20° for the reference compounds. Thus the strong increase of the spontaneous polarization can not only be attributed to an increase of the polarization–tilt angle coupling constant (as expected for the introduction of three additional chiral centres), but is also caused by the remarkable increase of the tilt angle. Although the spontaneous polarization of the tetramethyl derivatives are much higher, their switching times are of the same order. In the vicinity of the higher ordered smectic phase (probably SmI), an exponential increase of the switching times is observed for the SmC phases of compounds **2a**, **2b** and **2d**, whereas the switching time of the SmC$_A$ phase of compound **2c** remains almost constant close above the transition to the SmI$_A$ phase.

For the electro-optical properties of the compounds of series **3**, similar results are obtained (see Table 4). Again, the tetramethyl derivatives are found to exhibit nearly two times larger optical tilt angles and two to three times higher values of spontaneous polarization in comparison to their respective reference compounds.

In series **4** only two compounds with the (first) chiral centre in the α-position have been synthesized. The electro-optical properties of compounds **4c** and **4d** are summarized in Table 5. As in series **2** and **3**, the introduction of the additional methyl branchings leads to a remarkable increase of the optical tilt angle and of the spontaneous polarization. In comparison to the respective compounds of series **2**, whose molecular structures differ only by the direction of the ester group between the mesogenic core and the chiral side chain, the spontaneous polarization of compounds **4c** and **4d** is reduced by about a factor of five.

Conclusion

Starting from the natural source of the preen-gland wax of poultry, novel ferro- and antiferro-electric liquid crystals bearing tetramethylalkyl chains have been synthesized. In comparison to the respective compounds with only one methyl branching, lower melting points and broader SmC phase ranges are exhibited which favour the tetramethyl derivatives for use in broad range SmC room temperature mixtures. According to the electro-optical investigations, the introduction of the additional methyl branchings leads to an increase of the spontaneous polarization and the optical tilt angle. The use of new chiral tetramethylalkyl side chains seems to be promising, especially for the development of new materials for device applications where switching angles of 45° are required (*e.g.* for deformed helix ferroelectric liquid crystal displays[14,15] or for antiferroelectric liquid crystal displays).[16]

The authors thank the Deutsche Forschungsgemeinschaft (Sfb 335) for financial support.

References

1 J. W. Goodby, A. J. Slaney, C. J. Booth, I. Nishiyama, J. D. Vuijk, P. Styring and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1994, **243**, 231.

2 A.-M. Levelut, D. Bennemann, G. Heppke and D. Lötzsch, *Mol. Cryst. Liq. Cryst.*, in the press.

3 J. Jacob, *Fortschr. Chem. Org. Naturst.*, 1976, **34**, 373.

4 K. E. Murray, *Aust. J. Chem.*, 1962, **15**, 510.

5 G. Odham, *Ark. Kemi*, 1963, **21**, 379.

6 M. Morr, V. Wray, J. Fortkamp and R. D. Schmid, *Liebigs Ann. Chem.*, 1992, 433.

7 M. Morr, C. Proppe and V. Wray, *Liebigs Ann.*, 1995, 2001.

8 O. Mitsonubu, *Synthesis*, 1981, 1.

9 D. M. Doddrell, D. T. Pegg and M. R. Bendall, *J. Magn. Reson.*, 1982, **48**, 323.

10 W. R. Croasmun and R. M. K. Carlson, *Two-Dimensional NMR Spectroscopy. Applications for Chemists and Biochemists*, VCH, Weinheim, 2nd edn., 1994.

11 H.-O. Kalinowski, S. Berger and S. Braun, *^{13}C-NMR-Spektroskopie*, Thieme, Stuttgart 1984.

12 A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa and H. Takazoe, *J. Mater. Chem.*, 1994, **4**, 997.

13 A. D. L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.*, 1988, **27**, L729.

14 J. Fünfschilling and M. Schadt, *J. Appl. Phys.*, 1989, **66**, 3877.

15 A. G. H. Verhulst and G. Cnossen, *Ferroelectrics*, 1996, **179**, 141.

16 K. Nakamura, A. Takeuchi, N. Yamamoto, Y. Yamada, Y.-I. Suzuki and I. Kawamura, *Ferroelectrics*, 1996, **179**, 131.

Paper 7/04503D; *Received* 26*th June*, 1997