49. Ferroelectric Liquid Crystals

Part 2[1])

Chiral Phenyl Benzoates Incorporating a *trans*-1,4-Disubstituted Cyclohexane Ring

by **Stephen M. Kelly*** and **Richard Buchecker**

Zentrale Forschungseinheiten, *F. Hoffmann-La Roche & Co. AG*, CH–4002 Basel

(22.XII.87)

About forty novel phenyl benzoates also incorporating a *trans*-1,4-disubstituted cyclohexane ring and a chiral centre have been prepared. The dependence of the liquid-crystal transition temperatures of this new class of compounds on lateral substituents, diverse central linkages, chain lengths, and position of the chiral centre has been studied systematically. The synthesis and liquid-crystal transition temperatures of these new compounds are described in detail.

Introduction. – Current, commercially available electro-optic display devices based on standard liquid-crystal technology have fairly long response times (ms) [2][3]. This is a serious disadvantage for many applications, where liquid-crystal displays would otherwise be suitable. Prototype electro-optic display devices using ferroelectric liquid crystals have been shown to have exceptionally fast response times (µs) [4][5]. The successful commercial realisation of displays based on this principle would open up the possibility of many new applications in the electronics industry.

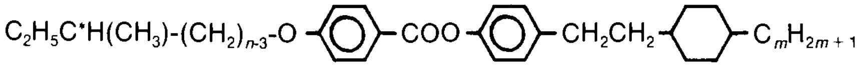
The ferroelectric substances required for these displays must exhibit a broad spectrum of narrowly defined physical properties [6–9]. A chiral smectic C mesophase ($^*S_c$) and a smectic A mesophase (S_A) are essential [10][11] over a wide temperature range (*e.g.*,–30°–+70°). Further requirements are a negative dielectric anisotropy ($\Delta\varepsilon$), a small birefringence (Δn), a sufficiently large spontaneous polarisation (Ps) and a low rotational viscosity (η) [6–9]. No single substance can satisfy all these specifications simultaneously, so mixtures of suitable components are needed. Each component must, however, be chemically, thermally, photo- and electrochemically stable. At least, one component must incorporate a chiral centre.

The most successful attempts to produce suitable substances have involved the synthesis of esters [9–16] some having lateral substituents [13–16] and biphenyl-cyclohexanes [8][17]. The synthesis of a new class of different substances has been undertaken, and the results of these investigations are described below. The influence of lateral substituents, various central linking units, optically active centres and chain-lengths on the nature and temperature range of the liquid-crystal mesophases of this new class of substances **1–12** have been investigated systematically (see *Tables 1–7*).

---

[1]) 'Ferroelectric Liquid Crystals', Part 1: [1].

Table 1. *Transition Temperatures* [C°] *and Enthalpies of Fusion* [Kcal · mol^{-1}] *for Compounds* **1**



1

n	m	C-S/Ch	S$_3$-S$_2$	S$_2$-*S$_c$^{a})	*S$_c$-Ch	Ch-I	ΔH(Kcal · mol^{-1})
4	3	81	–	–	–	146	
6	3	82	–	–	–	149	5435
8	3	73	–	(61)	77	144	
4	5	74	–	–	–	130	
6	5	66	–	–	–	137	
8	5	58	–	59	93	140	4767
4	7	66	–	–	–	131	5237
6	7	62	–	70	75	136	1988
8	7	42	44	69	103	136	5967

[a]) ( ) Indicates a monotropic transition temp.

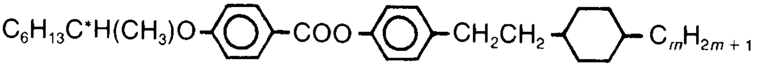
The desired chiral intermediates were all prepared from commercially available (–)-(*S*)-2-methyl-1-butanol (*Fluka, puriss.* > 99.5% pure; $[\alpha]_D^{20}=-6.6\pm0.3$) according to literature methods [6][10][12–14][19]. The desired phenyl benzoates **1–12** (see *Tables 1–7*) were prepared by a number of modified literature methods (see *Exper. Part*).

Results and Discussion. – The liquid-crystal transition temperatures and some enthalpies of fusion (ΔH) of the 4-[2-(*trans*-4-alkylcyclohexyl)ethyl]phenyl 4-alkoxybenzoates **1**, where the alkoxy chain contains an (+)-(*S*)-chiral centre, are recorded in *Table 1*.

The esters **1** exhibit a chiral nematic mesophase (Ch) at relatively low temperatures for three-ring compounds. This is a consequence of the presence of two non-linear linking units (COO and C_2H_4). Smectic mesophases are observed for homologues with a combined C-chain length of at least 11 CH_2 units ($n+m \geqslant 11$). The smectic phases (S$_3$,S$_2$,*S$_c$) are then observed at relatively high temperatures, which increase with increasing chain length. Similar effects have also been found for other smectic mesogens. The melting points (C-S, C-Ch) are irregular as expected, but show a general tendency to decrease with increasing chain length. The ΔH values are average for liquid crystals in general. The esters **1** represent the first liquid crystals incorporating a 1,4-disubstituted cyclohexane ring, which also exhibit a chiral smectic C mesophase. The 1,4-disubstituted cyclohexane ring is otherwise known to strongly induce the smectic **B** mesophase [25–30].

The liquid-crystal transition temperatures and some ΔH values of the compounds **2** incorporating an (+)-(*S*)-(1-methylheptyl)oxy chain are listed in *Table 2*.

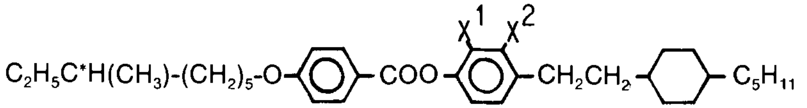
Table 2. *Transition Temperatures* [C°] *and Enthalpies of Fusion* [Kcal · mol^{-1}] *for Compounds* **2**



2

m	C-Ch	Ch-I	ΔH
3	40	74	6470
5	28	78	6080
7	49	83	

Table 3. *Transition Temperatures* [C°] *and Enthalpies of Fusion* [Kcal · mol^{-1}] *for Compounds* 3



3

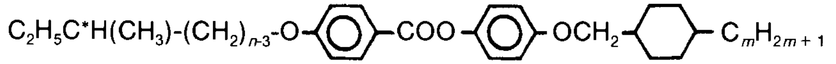
X^1	X^2	C-S/Ch/I	S_2-*S_c	*S_c-Ch[a])	Ch-I	ΔH
H	H	58	59	93	140	4767
Br	H	57	–	–	97	
CN	H	80	–	(50)	120	
CN	CN	123	–	(113)	(116)	6485

[a]) ( ) Indicates a monotropic transition temp.

The esters **2** exhibit only chiral nematic phases and no smectic phases. The melting points (C-Ch) and clearing points (Ch-I) are exceptionally low for three-ring materials. This is a direct consequence of the close proximity of the chiral centre to the Ph ring. It has been generally observed [18–20] that the more a lateral substituent in the C-chain of a mesogen is situated closer to the central core of the molecule, the lower are the observed liquid-crystal transition temperatures.

The effect of several lateral substituents on the liquid-crystal transition temperatures of one homologue ($n = 8$; $m = 5$) of the esters **3** is shown in *Table 3*. The presence of a Br-atom is seen to decrease the clearing point (Ch-I) substantially (–43°), whereas the melting point (C-Ch) remains virtually unchanged (–1°). Smectic phases have been totally eliminated. A CN group decreases the clearing point to a lesser extent (–20°), but leads to a substantial increase in the melting point (+22°). A monotropic chiral smectic C phase (*S_c) could be observed. This represents a substantial decrease (–43°) in the corresponding transition temperature (*S_c-Ch) of the analogous, non-substituted ester **3** ($X^1 = X^2 = H$). The presence of a second CN group induces a large increase (+65°) in melting point (C-I), a substantial increase (+20°) in the smectic transition temperature (*S_c-Ch), and a moderate decrease (–24°) in the clearing point (Ch-I).

Table 4. *Transition Temperatures* [°C] *and Enthalpies of Fusion* [Kcal · mol^{-1}] *for Compounds* 4



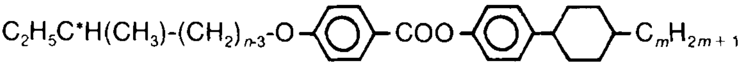
4

$C_2H_5C^*H(CH_3)$-$(CH_2)_{n-3}$-O-C$_6$H$_4$-COO-C$_6$H$_4$-OCH_2-C$_6$H$_{10}$-C_mH_{2m+1}

n	m	C-S/Ch	S_3-S_2[a])	S_2-*S_c[a])	*S_c-Ch[a])	Ch-I	ΔH
4	3	92	–	–	–	144	5510
6	3	79	–	–	–	148	5345
8	3	83	(61)	(68)	94	145	6889
4	5	88	–	–	–	141	5533
6	5	86	–	(44)	(85)	148	6242
8	5	73	(34)	(65)	108	146	5648
4	7	67		(63)	(65)	136	
6	7	70	–	77	93	142	8143
8	7	72	–	74	115	142	

[a]) ( ) Indicates a monotropic transition temp.

Table 5. *Transition Temperatures* [°C] *and Enthalpies of Fusion* [Kcal·mol^{-1}] *for Compounds* **5**



5

n	m	C-S/Ch	S_2-*S_c[a])	*S_c-Ch[a])	Ch-I	ΔH
4	3	113	–	–	168	5262
6	3	80	–	–	170	5978
8	3	85	(63)	86	163	8975
4	5	100	–	–	161	5562
6	5	85	(74)	(80)	165	9204
8	5	75	(65)	106	163	4297

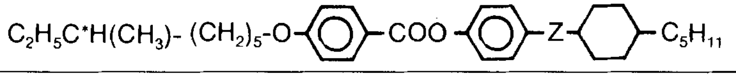
[a]) ( ) Indicates a monotropic transition temp.

The liquid-crystal transition temperatures of the compounds **4** are collated in *Table 4*. The esters **4** are identical with the esters **1**, except that a CH_2 group has been replaced by an O-atom. The result is that the liquid-crystal transition temperatures (C-S/Ch, S_3-S_2, S_2-*S_c, *S_c-Ch, Ch-I) of the esters **4** are all marginally higher (+12°, 3.5°, 0.5°, 6.5°, 4.5°, respectively) than those of the analogous esters **1** with exactly the same C-chains. ΔH values are also correspondingly higher (+8.36 Kcal·mol^{-1}).

The liquid-crystal transition temperatures and ΔH values of the esters **5**, which only contain *one* linking unit, are listed in *Table 5*. Comparison of the data in *Table 5* for **5** with those in *Table 1* for the corresponding esters **1** containing an additional CH_2CH_2 linking unit, reveals that the liquid-crystal transition temperatures (C-S, C-Ch, S_2-*S_c, *S_c-Ch, Ch-I) of the former compounds are consistently higher on average (23°, 2.5°, 4.0°, 26°, respectively) than those of the latter materials. This may be explained by the additional rigidity and linearity of the direct bond as compared to the CH_2CH_2 linkage [25–31]. The ΔH values are also correspondingly higher (+1.195 Kcal·mol^{-1}, on average). It should be noted that, due to the larger increase (+23°) in the melting point than in the chiral smectic C transition temperature (+4°), only one enantiotropic smectic C mesophase could be observed for the six homologues prepared.

The liquid-crystal transition temperatures of five phenyl benzoates **1** and **4**–**7** incorporating a *trans*-1,4-disubstituted-cyclohexane ring and identical C-chains and only differing in the nature of one central linking unit (Z) are recorded in *Table 6*. The most striking

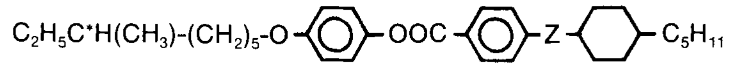
Table 6. *Transition Temperatures* [°C] *for Compounds of Structure:*



Compound	Z	C-S/Ch	S_2-*S_c[a])	*S_c-Ch[a])	Ch-I
1	CH_2CH_2	58	59	93	140
4	OCH_2	73	–	108	146
5	–	75	(65)	106	163
6	O–OC	66	80	112	186
7	CO–O	85	–	(68)	148

[a]) ( ) Indicates a monotropic transition temp.

Table 7. *Transition Temperatures* [°C] *for Compounds of Structure:*



Compound	Z	C-S_B	S_B-S_A	S_A-Ch/I	Ch-I
8	CH_2CH_2	103	107	145	–
9	OCH_2	91	96	155	–
10	–	65	111	156	163
11	OOC	61	91	166	180
12	COO	78	88	123	148

feature of the data in *Table 6* is their similarity, despite large differences in the rigidity, linearity, and polarisability of the five linkages investigated. The combination of two ester (COO) groups in **7** seems to be the least favorable combination. The high melting point and low smectic transition temperature lead to the only monotropic chiral smectic C phase observed for the esters studied. The nature of the second central linking unit (Z) seems to play no rôle in determining the nature of the liquid-crystal mesophases observed.

The liquid-crystal transition temperatures of the phenyl benzoates **8**–**12** are listed in *Table 7*. The esters **8**–**12** are constitutional isomers of the esters **1** and **4**–**7** (see *Table 6*) the only difference being the direction of the first ester (COO) linking unit (not Z). This small change leads to the complete disappearance of the chiral smectic C phase and to the appearance of smectic A and B phases instead. For the esters **8** and **9**, the chiral nematic phase also completely disappears. However, it should be noted that the clearing point (Ch-I) of the esters **1** and **4**–**7** are very similar to those (S_A-I, Ch-I) of their constitutional isomers **8**–**12** and in the cases **10** and **12** are even identical. The other liquid-crystal transition temperatures differ to varying extents, but no general trends can be identified. This demonstrates once again the difficulty in predicting the nature and magnitude of liquid-crystal transitions even for apparently very similar systems.

The authors thank the following colleagues for the measurement and interpretation of the various spectra: Dr. *W. Arnold* (NMR), *W. Meister* (MS), Dr. *M. Grosjean* (IR), *M. F. Wild* and Mr. *B. Halm* (DTA) and Mrs. *J. Kohler* (optical rotation).

Experimental Part

(Mr. *U. Wyss* is thanked for competent technical assistance)

General. The liquid-crystal transition temp. of the compounds **1**–**12** (*Tables 1–7*) were determined by optical microscopy using a *Leitz Ortholux II POL-BK* microscope in conjunction with a *Mettler FP 82* heating stage and *FP 80* control unit. All the monotropic liquid-crystal phases could be observed using a microscope, and no virtual values (extrapolated) had to be determined. When necessary, the *Mettler* stage could be cooled (< –20°) by allowing N_2, cooled by liquid N_2, to pass through the stage at a controlled rate. The liquid-crystal transition temp. and enthalpies were also determined using a *Mettler DTA TA 2000*. The purity of the compounds was determined by TLC, GC, and DTA analysis. A *Perkin Elmer 8310* gas chromatograph and *GP-100* graphics printer were used. Precoated TLC plates (4 cm × 8 cm, SiO_2 *SIL G/UV*$_{254}$, layer thickness 0.25 mm; *Macheray-Nagel*, Düren, Germany) were utilised. Column chromatography was carried out using silica gel *60* (230–400 mesh ASTM). Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Reactions were carried out under N_2, unless H_2O was present as solvent or reagent. All temp. were measured externally, unless otherwise stated. The ^{1}H-NMR spectra were recorded at 60 MHz *(Varian T-60)*, 80 MHz *(Bruker WP-80)*, or 270 MHz *(Bruker HX-270)*. Mass spectra were recorded on a *MS 9* (*AEZ*, Manchester) spectrometer. DMAP = 4-(Dimethylamino)pyridine, DCC = *N,N'*-dicyclohexylcarbodiimide.

*4-[2-(*trans*-4-Pentylcyclohexyl)ethyl]phenyl 4-{[(*S*)-6-Methyloctyl]oxy}benzoate* (**1**; *n* = 8, *m* = 5). A soln. of 4-{[(*S*)-6-methyloctyl]oxy}benzoic acid (0.25 g, 0.0009 mol), 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol (0.26 g, 0.0009 mol), DMAP (0.02 g), DCC (0.23 g, 0.0011 mol), and CH_2Cl_2 (25 ml) was stirred at r.t. overnight and then filtered to remove the precipitate. The solvent was removed from the filtered soln. and the solid residue purified by column chromatography using toluene. The ester thus obtained was crystallised from AcOEt, until constant transition temp. were obtained (see *Tables 1* and *2* for the liquid-crystal transition temp. of this ester and other homologues prepared using this method). $[\alpha]_D^{20}$ = +0.028 (*c* = 1.0, $CHCl_3$). IR (KBr): 1740*s*, 1610*s*, 1510*s*, 1280*s*, 1160*s*, 1080*m*, 850*m*. MS: 520 ($M^{+\cdot}$).

*4-[2-(*trans*-4-Pentylcyclohexyl)ethyl]phenol.* A soln. of BBr_3 (2.6 g, 0.011 mol) and anh. CH_2Cl_2 (50 ml) was added dropwise to a soln. of 2-(*trans*-4-pentylcyclohexyl)-1-(4-methoxyphenyl)ethane [25] (2 g, 0.007 mol) and anh. CH_2Cl_2 (50 ml) under anh. conditions at 0°. The solution was stirred for a further 1 h at r.t. and added to H_2O. The org. phase was separated off, and the aq. phase was shaken with CH_2Cl_2 (3 × 50 ml). The combined org. layers were washed with 10% Na_2CO_3 soln. (50 ml) and H_2O (2 × 500 ml), and then dried ($MgSO_4$). The filtered soln. was evaporated under reduced pressure. The residue was crystallised from hexane to yield the pure (99.4%) product (1.8 g, 95%). M.p. 101–2°. IR (KBr): 3350*s*, 1610*m*, 1510*s*, 1240*s*, 825*m*. MS: 274 ($M^{+\cdot}$).

*4-[2-(*trans*-4-Propylcyclohexyl)ethyl]phenol* was prepared using the same method (99%). M.p. 99–100° ([26]: 98–99°). IR (KBr): 3400*s*, 1600*s*, 1510*s*, 1445*m*, 1420*m*, 1230*s*, 820*m*. MS: 246 ($M^{+\cdot}$).

*4-[2-(*trans*-4-Heptylcyclohexyl)ethyl]phenol* was prepared using the same method (95%). M.p. 95–96° ([26]: 95–96°). IR (KBr): 3400*s*, 1600*s*, 1510*s*, 1450*m*, 1225*s*, 820*m*. MS: 394 ($M^{+\cdot}$).

*4-([(*S*)-6-Methyloctyl]oxy)benzoic Acid.* A soln. of (*S*)-1-bromo-6-methyloctane (5 g, 0.024 mol), 4-hydroxybenzoic acid (2.2 g, 0.016 mol), anh. KOH (1.8 g, 0.032 mol), EtOH (80 ml), and H_2O (10 ml) was heated under reflux overnight, 25% (*v*/*v*) HCl (50 ml) was added to the cooled soln. and the resultant soln. was heated under reflux for a further 3 h. A precipitate was formed, which was filtered off from the cooled mixture, washed with H_2O, pressed dry, and crystallised from EtOH, until constant liquid-crystal transition temp. were obtained for the pure (99%) acid (1.6 g, 38%; C-Ch, 126.5°; Ch-I, 128°). IR (KBr): 2650*w*, 1700*s*, 1600*s*, 1510*s*, 1250*s*, 850*m*. MS: 236 ($M^{+\cdot}$).

The following acids could be prepared by the same method:

*4-{[(*S*)-2-Methylbutyl]oxy}benzoic Acid* (35%): m.p. 114–115°. $[\alpha]_D^{20}$ = +0.110 (*c* = 1.0; $CHCl_3$). IR (KBr): 2250*m*, 1680*s*, 1610*s*, 1510*m*, 1260*s*, 850*m*. MS: 208 ($M^{+\cdot}$).

*4-{[(*S*)-4-Methylhexyl]oxy}benzoic Acid* (45%): C-Ch, 119.5°; Ch-I, 125°. $[\alpha]_D^{20}$ = +0.088 (*c* = 1.0; $CHCl_3$). IR (KBr): 2640*w*, 1700*s*, 1610*s*, 1505*m*, 1250*s*, 850*m*. MS: 236 ($M^{+\cdot}$).

*4-{[(*S*)-1-Methylheptyl]oxy}benzoic Acid* (21%): m.p. 64–65°. $[\alpha]_D^{20}$ = +0.103 (*c* = 1.0; $CHCl_3$). IR (KBr): 2920*s*, 1680*s*, 1610*s*, 1510*m*, 1360*m*, 1180*m*, 1040*w*, 850*m*. MS: 250 ($M^{+\cdot}$).

*4-{[(*R*)-1-Methylheptyl]oxy}benzoic Acid* (39%): m.p. 64–65°. $[\alpha]_D^{20}$ = −0.105 (*c* = 1.0; $CHCl_3$). IR (KBr): 2920*s*, 1680*s*, 1610*s*, 1510*m*, 1360*m*, 1180*m*, 1040*w*, 850*m*. MS: 250 ($M^{+\cdot}$).

*(*S*)-1-Bromo-6-methyloctane.* A soln. of *Grignard* reagent (0.9 mol; prepared in the usual way from 0.9 mol Mg and 0.9 mol (*S*)-1-bromo-2-methylbutane) and anh. THF (1000 ml) was added dropwise to a soln. of 1,4-dibromobutane (142 g, 0.67 mol), 0.1M Li_2CuCl_4 (32 ml), and anh. THF (500 ml) cooled *via* an ice/MeOH bath. After completion of the addition, the mixture was allowed to attain r.t. and was stirred overnight. The mixture was decomposed with 25% H_2SO_4 and the org. layer separated off. The aq. layer was shaken with EtO_2 (3 × 200 ml) and the combined org. layers were washed with H_2O (2 × 1000 ml) and dried ($MgSO_4$). The filtered soln. was evaporated under vacuum and the liquid residue distilled under reduced pressure (b.p. 95–96°/15 Torr) to yield pure (99.9%) product (48 g, 35%). $[\alpha]_D^{20}$ = +0.072 (*c* = 1.0, $CHCl_3$). IR (film): 2930*s*, 2856*s*, 1460*s*, 1378*m*, 1241*m*, 647*m*. MS: 177, 179 ($M^{+\cdot} - C_2H_5$), 149, 151 ($M^{+\cdot} - C_4H_9$).

*(*S*)-1-Bromo-2-methylbutane.* Br_2 (46 g, 0.284 mol) was added dropwise to a mixture of (*S*)-2-methylbutanol (50 g, 0.568 mol; *Fluka*, puriss., > 99.5%; $[\alpha]_D^{20}$ = −6.6 ± 0.3) and red P (3.9 g, 0.125 mol) maintained at 110°, so that a gentle reflux was observed. The mixture was maintained at this temp. for a further 30 min, then the temp. was raised to 150°, and the raw product distilled off. The mixture was allowed to cool, H_2O was added, and the distillation continued, until no more org. material could be collected. The org. layer from the combined fractions was separated off and washed with dil. $NaHCO_3$ (2 × 100 ml) and H_2O (2 × 500 ml), and dried ($CaCl_2$). The filtered liquid was distilled to yield pure (99.9%) bromide (42.5 g, 49.5%). B.p. 120–121° ([19]: 121°). $[\alpha]_D^{20}$ = +0.041 (*c* = 1.0, $CHCl_3$; [19]: +0.039). IR (film): 2933*s*, 2876*s*, 1229*s*. MS: 121, 123 ($M^{+\cdot} - C_2H_5$), 71 ($M^{+\cdot}$ − Br).

(S)-1-Bromo-4-methylhexane. A mixture of (*S*)-4-methylhexanol (16 g, 0.138 mol), red P (0.030 mol), and Br_2 (11 g, 0.069 mol) was allowed to react and then worked up as described above to yield pure (98%) bromide (24.5 g, 99%). B.p. 74–76°/12 Torr ([19]: 170/760 Torr). $[\alpha]_D^{20} = +0.10$ (c = 1.0, $CHCl_3$; [19]: +0.076). IR (film): 2929*s*, 2874*s*, 1462*m*, 1378*m*, 1247*m*, 1210*w*, 643*m*, 462*s*. MS: 149, 151 ($M^{+\cdot} - C_2H_5$).

(S)-4-Methylhexanol. A soln. of (*S*)-4-methylhexanoic acid (19 g, 0.146 mol) and anh. Et_2O (100 ml) was added dropwise to a mixture of $LiAlH_4$ (9.7 g, 0.256 mol) and anh. Et_2O. A strongly exothermic reaction was observed. The mixture was heated under reflux overnight. After decomposition of the complex and excess of hydride in the normal way [28], the org. layer was separated off and the aq. layer was shaken with EtO_2 (2 × 250 ml). The combined org. layers were washed with H_2O (2 × 500 ml) and dried ($MgSO_4$). The filtered soln. was evaporated under vacuum to yield a liquid residue, which was distilled under reduced pressure to yield pure (98%) alcohol (16.2 g, 96%). B.p. 72–75°/12 Torr ([19]: 108°/20 Torr). $[\alpha]_D^{20} = +0.075$ (c = 1.0, $CHCl_3$; [19]: +0.076). IR (film): 3336*s*, 2933*s*, 2874*s*, 1461*m*, 1378*m*, 1061*m*, 472*s*. MS: 98 ($M^{+\cdot} - H_2O$).

(S)-4-Methylhexanoic Acid. A soln. of diethyl (*S*)-2-(2-methylbutyl)malonate (70 g, 0.3 mol), anh. KOH (68 g, 1.2 mol), and H_2O (70 ml) was heated under reflux for 2 h. A soln. of conc. H_2SO_4 (60 ml) and H_2O (160 ml) was added carefully to the cooled soln. and then heated under reflux for 4 h. A layer of org. material was formed, which was separated off from the cooled mixture. The aq. layer was shaken with Et_2O (3 × 150 ml) and the combined org. layers washed with ice-cold H_2O (1 × 500 ml) and dried ($MgSO_4$). After filtration and removal of the solvent, the liquid residue distilled under reduced pressure to yield pure (96%) acid (35 g, 88%). B.p. 124°/12 Torr ([19]: 134°/25 Torr).

Diethyl (S)-2-(2-Methylbutyl)malonate. (*S*)-2-Methylbutyl *p*-toluenesulfonate (116 g, 0.479 mol) was added dropwise to a soln. of diethyl malonate (92 g, 0.575 mol) and freshly prepared 2M NaOEt (240 ml). An emulsion was formed initially which disappeared gradually during the addition of the *p*-toluenesulfonate. The soln. was heated at 100°. More EtOH (100 ml) was added to help liquify a thick orange emulsion, which had formed after a few min at this temp. The mixture was, thus, heated overnight. The excess EtOH was distilled off, H_2O (300 ml) was added, and the org. layer was separated off. The aq. layer was extracted with EtO_2 (2 × 200 ml), the combined org. layers were washed with H_2O (2 × 500 ml) and dried ($MgSO_4$). After filtration and removal of the solvent, the liquid residue was distilled under reduced pressure to yield pure (99.7%) product (74 g, 67%). B.p. 124°/13 Torr ([14]: 200°/18 Torr).

(S)-2-Methylbutyl p-*Toluenesulfonate.* A soln. of TsCl (200 g, 1.05 mol) and anh. pyridine (200 ml) was added dropwise to a soln. of (*S*)-2-methylbutanol (44 g, 0.50 mol; *Fluka*) and anh. pyridine (200 ml) cooled *via* an ice-bath so that the internal temp. did not rise above 5°. A white precipitate formed during the next 5 h, while the mixture was stirred and cooled *via* the ice-bath. H_2O (1000 ml) was added, and the resultant soln. was stirred for a further 4 h and then shaken with Et_2O (3 × 200 ml). The combined org. layers were washed with 2M HCl (2 × 500 ml), H_2O (1 × 500 ml), dil. $NaHCO_3$ (1 × 500 ml), H_2O (1 × 500 ml), and dried ($MgSO_4$). TLC indicated single-spot material. After removal of the drying agent by filtration and the solvent by evaporation under reduced pressure, the raw product (116 g, 96%) was used immediately in the next reaction without further purification.

*2,3-Dicyano-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-{[(S)-6-Methyloctyl]oxy}benzoate* (**3**; $X^1 = X^2$ = CN) was prepared from the esterification of 4-{[(*S*)-6-methyloctyl]oxy}benzoic acid and 2,3-dicyano-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol as described above for **1** (see *Table 3* for the liquid-crystal transition temp.). $[\alpha]_D^{20} = +0.025$ (c = 0.9, $CHCl_3$). IR (KBr): 2215*m*, 1735*s*, 1605*s*, 1510*m*, 1250*s*, 1170*s*, 1050*s*, 850*m*. MS: 324 ($C_{21}H_{28}N_2O^+$).

*2,3-Dicyano-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol.* A homogeneous mixture of finely powdered 2-(*trans*-4-pentylcyclohexyl)-1-(2,3-dicyano-4-butyloxyphenyl)ethane [32] (2.2 g, 0.006 mol), crushed anh. $AlCl_3$ (1.4 g, 0.011 mol), and analar NaCl (0.3 g, 0.006 mol) was heated at an oil-bath temp. of 150° for 40 min. TLC indicated complete absence of starting material. The molten raw product was added carefully to H_2O (250 ml) and the mixture shaken with CH_2Cl_2 (3 × 50 ml) and dried ($MgSO_4$). The filtered soln. was evaporated under reduced pressure. The solid residue was purified by column chromatography using toluene/AcOEt 4:1 and crystallisation from EtOH to yield pure phenol (0.6 g, 30%). M.p. 100–2°. IR (KBr): 3250*s*, 2220*s*, 2215*s*, 1580*m*, 1490*s*, 1310*s*, 1175*m*, 850*m*. MS: 324 ($M^{+\cdot}$).

*2-Cyano-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-{[(S)-6-Methyloctyl]oxy}benzoate* (**3**; X^1 = CN; X^2 = H). A soln. of *2-bromo-4-[2-(*trans*-4-pentylcyclohexyl)etyhl]phenyl 4-{[(S)-6-methyloctyl]oxy}benzoate* (**3**; X^1 = Br; X^2 = H; 2.0 g, 0.003 mol), anh. CuCN (0.5 g, 0.005 mol), and 1-methyl-2-pyrrolidone (50 ml) was heated at 185° for 3 h. The cooled mixture was added to a 15% NH_4OH soln. and stirred for 30 min. The mixture was shaken with Et_2O (3 × 50 ml) and the combined org. layers were washed with H_2O (2 × 250 ml) and dried ($MgSO_4$). After removal of the solvent under reduced pressure, the solid residue was purified by column chromatography using toluene/hexane 1:1 and crystallisation from EtOH until constant transition temp. were obtained (see *Table 3* for the liquid-crystal transition temp.). IR (KBr): 2220*m*, 1730*s*, 1610*s*, 1510*m*, 1260*s*, 1170*m*, 850*m*. MS: 247 ($C_{16}H_{23}O_2^+$).

*2-Bromo-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-{[(S)-6-Methyloctyl]oxy}benzoate* (**3**; X^1 = Br; X^2 = H). A soln. of 2-bromo-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol (0.67 g, 0.0019 mol), 4-{[(*S*)-6-methyloctyl]oxy}benzoic acid (0.5 g, 0.0019 mol), DCC (0.47 g, 0.0022 mol) DMAP (0.05 g), and CH_2Cl_2 was stirred at r.t. overnight. The mixture was worked up and purified as described above to yield pure ester (see *Table 3* for the liquid-crystal transition temp.). $[\alpha]_D^{20}$ = +0.031 (*c* = 1.0, $CHCl_3$). IR (KBr): 1730*s*, 1270*s*, 1170*s*, 1065*s*, 850w. MS: 247 ($C_{16}H_{23}O_2^+$), 185, 187 ($C_7H_6OBr^+$), 121 ($C_7H_5O_2^+$).

*2-Bromo-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol.* Br_2 (1.6 g, 0.01 mol) was added dropwise to a soln. of 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol (2.7 g, 0.01 mol) and CH_2Cl_2 (50 ml) at 0°. The red colour disappeared immediately on addition, and a regular flow of HBr was observed. After the addition, the resultant soln. was stirred for 1 h at r.t., then washed with 10% $NaHSO_4$ soln. (50 ml) and H_2O (2 × 500 ml), and dried ($MgSO_4$). The solvent was removed from the filtered soln. under slightly reduced pressure to yield crude product which was crystallised from hexane at 0° to yield pure (97%) phenol (3.4 g, 96%). M.p. 53–4°. IR (KBr): 3419*s*, 2913*s*, 2849*s*, 1606*w*, 1492*s*, 819*m*. MS: 352, 354 ($M^{+\cdot}$).

*4-[(*trans*-4-Pentylcyclohexyl)methoxy]phenyl 4-{[(S)-6-Methyloctyl]oxy}benzoate* (**4**; *n* = 8, *m* = 5) was prepared from the esterification of 4-{[(*S*)-6-methyloctyl]oxy}benzoic acid and 4-[(*trans*-4-pentylcyclohexyl)methoxy]phenol as described above for **1** (see *Table 6* for the liquid-crystal transition temp.). $[\alpha]_D^{20}$ = +0.026 (*c* = 1.0, $CHCl_3$). IR (KBr): 1730*s*, 1610*s*, 1510*s*, 1170*s*, 820*w*. MS: 522 ($M^{+\cdot}$).

*4-[(*trans*-4-Pentylcyclohexyl)methoxy]phenol.* A mixture of (*trans*-4-pentylcyclohexyl)methyl bromide [25][28] (5 g, 0.02 mol), hydroquinone (11 g, 0.10 mol), anh. K_2CO_3 (11 g, 0.08 mol), and $CH_3COC_2H_5$ (100 ml) was heated under reflux overnight. The cooled mixture was added to H_2O and shaken with Et_2O (3 × 50 ml). The combined org. layers were washed with H_2O (500 ml) and dried ($MgSO_4$). After removal of the solvent under reduced pressure, the crude product was purified by chromatography using toluene/AcOEt 4:1 and crystallisation from hexane to yield pure (99.9%) phenol (2.75 g, 50%). M.p. 102–3°. IR (KBr): 3417*m*, 2913*s*, 2849*s*, 1606*w*, 1493*s*, 819*m*. MS: 276 ($M^{+\cdot}$).

*4-(*trans*-4-Pentylcyclohexyl)phenyl 4-{[(S)-6-Methyloctyl]oxy}benzoate* (**5**; *n* = 8, *m* = 5) was prepared by the esterification of 4-{[(*S*)-6-methyloctyl]oxy}benzoic acid and 4-(*trans*-4-pentylcyclohexyl)phenol [26] as described above for **1** (see *Table 6* for the liquid-crystal transition temp.). $[\alpha]_D^{20}$ = 0.024 (*c* = 1.0, $CHCl_3$). IR (KBr): 1730*s*, 1605*s*, 1510*s*, 1275*s*, 1170*s*, 1080*s*, 850*m*. MS: 247 ($C_{16}H_{23}O_2^+$), 153 ($C_{12}H_{21}O^+$), 121 ($C_7H_5O_2^+$).

*4-{[(*trans*-4-Pentylcyclohexyl)carbonyl]oxy}phenyl 4-{[(S)-6-Methyloctyl]oxy}benzoate* (**6**) was prepared by the esterification of *trans*4-pentylcyclohexane-1-carboxylic acid [19][30] and 4-hydroxyphenyl 4-{[(*S*)-6-methyloctyl]oxy}benzoate as described above for **1** (see *Table 6* for the liquid-crystal transition temp.). IR (KBr): 1748*s*, 1725*s*, 1604*s*, 1506*s*, 1256*s*, 1169*s*, 1081*m*, 815*m*. MS: 247 ($C_{16}H_{23}O_2^+$), 121 ($C_7H_5O_2^+$).

4-Hydroxyphenyl 4-{[(S)-6-Methyloctyl]oxy}benzoate. A soln. of 4-{[(*S*)-6-methyloctyl]oxy}benzoyl chloride (2.5 g, 0.009 mol; prepared from the corresponding acid using $SOCl_2$), 4-hydroquinone (1.1 g, 0.009 mol), anh. pyridine (2 ml), and anh. toluene (20 ml) was heated under reflux for 1 h. The cooled mixture was then added to cold, dil. HCl and shaken with CH_2Cl_2 (3 × 50 ml). The combined org. layers were washed with H_2O and dried ($MgSO_4$). After filtration and removal of the solvent, the solid residue was purified by column chromatography using toluene/AcOEt 4:1 and crystallisation from EtOH to yield pure phenol (2 g, 59%). M.p. 74–75°.

*4-{[(*trans*-4-Pentylcyclohexyl)oxy]carbonyl}phenyl 4-{[(S)-6-Methyloctyl]oxy}benzoate* (**7**) was prepared by the esterification of 4-{{{[(*S*)-6-methyloctyl]oxy}carbonyl}oxy}benzoic acid and *trans*-4-pentylcyclohexanol [33] as described above for **1** (see *Table 6* for the liquid-crystal transition temp.). IR (KBr): 1731*s*, 1708*s*, 1603*s*, 1510*m*, 1262*s*, 1164*s*, 1064*s*, 847*w*. MS: 247 ($C_{16}H_{23}O_2^+$), 121 ($C_7H_5O_2^+$).

4-{{4-{[(S)-6-Methyloctyl]oxy}benzoyl}oxy}benzoic Acid. Jones reagent (3 ml) was added dropwise to a soln. of 4-formylphenyl 4-{[(*S*)-6-methyloctyl]oxy}benzoate (1.4 g, 0.004 mol) and acetone (25 ml) cooled *via* an ice-bath. A precipitate was formed almost immediately after completion of the addition. The mixture was stirred at r.t. for a further 2 h and then poured onto ice (100 g) and stirred for 20 min. The solid was filtered off, washed with H_2O pressed dry, and crystallised from EtOH to yield pure (99%) acid (0.75 g, 51%; C-*S_c, 144°; *S_c-Ch, 192°; Ch-I, 219°). IR (KBr): 2999*m*, 1732*s*, 1692*s*, 1257*s*, 844*m*. MS: 247 ($C_{16}H_{23}O_2^+$), 121 ($C_7H_5O_2^+$).

4-Formylphenyl 4-{[(S)-6-Methyloctyl]oxy}benzoate. A soln. of 4-{[(*S*)-6-methyloctyl]oxy}benzoic acid (1 g, 0.004 mol), 4-hydroxybenzaldehyde (0.5 g, 0.004 mol), DCC (1 g, 0.005 mol), DMAP (0.04 g), and CH_2Cl_2 (50 ml) was stirred at r.t. overnight. The resulting mixture was worked up as described above for **1**. Column chromatography using toluene as solvent and crystallisation from hexane at 0° yielded pure aldehyde (1.4 g, 98%; C-S_A, 37°; S_A-Ch, 45°; Ch-I, 47°). $[\alpha]_D^{20}$ = +0.441 (*c* = 1.0, $CHCl_3$). IR (KBr): 2738*w*, 1732*s*, 1701*s*, 1511, 1268*s*, 1170*s*, 1067*m*, 846*m*. MS: 247 ($C_{16}H_{23}O_2^+$).

4-{[(S)-6-Methyloctyl]oxy}phenyl 4-[2-(trans-4-pentylcyclohexyl)ethyl]benzoate (**8**) was prepared by esterification of 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]benzoic acid and 4-{[(*S*)-6-methyloctyl]oxy}phenol as described above for **1** (see *Table 7* for the liquid-crystal transition temp.). $[\alpha]_D^{20} = 0.046$ (c = 1.0, $CHCl_3$). IR (KBr): 1735*s*, 1610*m*, 1510*s*, 1275*s*, 1200*s*, 1080*s*, 810*w*. MS: 520 ($M^{+\cdot}$).

4-{[(S)-6-Methyloctyl]oxy}phenol. A mixture of (*S*)-1-bromo-6-methyloctane (15 g, 0.073 mol), hydroquinone (40 g, 0.362 mol), anh. K_2CO_3 (40 g, 0.210 mol), and DMF (250 ml) was heated at 50° for *ca.* 48 h. The cooled mixture was added to H_2O (500 ml) and shaken with CH_2Cl_2 (3 × 150 ml). The combined org. layers were washed with H_2O (2 × 500 ml) and dried ($MgSO_4$). After filtration and removal of the solvent, the raw product was purified by column chromatography using toluene/AcOEt 4:1 and crystallisation from hexane to yield pure (99.9%) phenol (11.5 g, 67%). M.p. 39–40°. $[\alpha]_D^{20} = +0.064$ (c = 1.0, $CHCl_3$). IR (KBr): 3400*s*, 1620*w*, 1510*s*, 1240*s*, 1110*m*, 830*s*. MS: 236 (M^{+}).

The following phenols could be prepared using the same method:

4-{[(S)-2-Methylbutyl]oxy}phenol (22%). M.p. 42–43°. $[\alpha]_D^{20} = +0.093$ (c = 1.0; $CHCl_3$). IR (KBr): 3300*s*, 2920*s*, 1250*s*, 1160*m*, 1030*s*, 830*s*. MS: 180 (M^{+}).

4-{[(S)-2-Methylhexyl]oxy}phenol (55%). $[\alpha]_D^{20} = +0.078$ (c = 1.0; $CHCl_3$). IR (film): 3280*s*, 1600*w*, 1500*s*, 1225*s*, 1020*m*, 830*s*. MS: 208 (M^{+}).

*4-[2-(*trans*-4-Pentylcyclohexyl)ethyl]benzoic Acid.* A soln. of methyl 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]benzoate [35] (16 g, 0.051 mol), anh. KOH (16 g, 0.286 mol), EtOH (160 ml), and H_2O (100 ml) was heated at 75° overnight. A white precipitate was observed, 25% HCl (600 ml) was added slowly to the cooled (ice) mixture. The raw product was filtered off from the soln., washed with small volumes of H_2O, pressed dry, and then crystallised from EtOH to yield pure (99.7%) acid (15.2 g, 99%; C-N, 202°; N-I, 235°). IR (KBr): 2920*s*, 2840*s*, 1680*s*, 1610*m*, 1280*m*. MS: 302 (M^{+}).

*4-{[(S)-6-Methyloctyl]oxy}phenyl 4-[(*trans*-4-Pentylcyclohexyl)methoxy]benzoate* (**9**) was prepared by the esterification of 4-[(*trans*-4-pentylcyclohexyl)methoxy]benzoic acid and 4-{[(*S*)-6-methyloctyl]oxy}phenol as described above for **1** (see *Table 7* for the liquid-crystal transition temp.). $[\alpha]_D^{20} = +0.024$ (c = 1.0, $CHCl_3$). IR (KBr): 1735*s*, 1610*m*, 1510*s*, 1260*m*, 1200*s*, 1060*w*. MS: 522 (M^{+}).

*4-[(*trans*-4-Pentylcyclohexyl)methoxy]benzoic Acid.* A mixture of (*trans*-4-pentylcyclohexyl)methyl bromide [26][30] (1.5 g, 0.006 mol), 4-hydrobenzoic acid (0.8 g, 0.005 mol), anh. K_2CO_3 (2.8 g, 0.02 mol), and $CH_3CO_2C_2H_5$ (100 ml) was heated under reflux overnight. The cooled mixture was added to H_2O (500 ml). The resultant mixture was shaken with Et_2O (3 × 50 ml) and the combined org. layers were washed with H_2O (2 × 250 ml) and dried ($MgSO_4$). After removal of the solvent under reduced pressure, the solid residue was crystallised from EtOH (until the liquid-crystal transition temp. were constant) to yield pure (99.8%) acid (0.85 g, 56%; C-N, 205°; N-I, 240°). IR (KBr): 2609*w*, 1677*s*, 1603*s*, 1514*m*, 1262*s*, 1172*s*, 1029*m*, 651*m*. MS: 304 (M^{+}).

*4-{[(S)-6-Methyloctyl]oxy}phenyl 4-(*trans*-4-Pentylcyclohexyl)benzoate* (**10**) was prepared by the esterification of 4-(*trans*-4-pentylcyclohexyl)benzoic acid and 4-{[(*S*)-6-methyloctyl]oxy}phenol as described for **1** (see *Table 7* for the liquid-crystal transition temp.). $[\alpha]_D^{20} = +0.029$ (c = 1.0, $CHCl_3$). IR (KBr): 1740*s*, 1610*m*, 1510*s*, 1200*s*, 1070*s*, 850*w*. MS: 492 (M^{+}).

*4-(*trans*-4-Pentylcyclohexyl)benzoic Acid.* A soln. of 4-(*trans*-4-pentylcyclohexyl)benzonitrile (50 g, 0.2 mol), 50% (*v*/*v*) H_2SO_4 (300 ml), and glacial AcOH (900 ml) was heated at 120° overnight. The precipitated product, filtered off from the reaction soln. upon cooling to r.t., was washed with small volumes of H_2O, pressed dry, and then crystallised from EtOH to yield pure (98.5%) acid (42.5 g, 74%; C-N, 180.5°; N-I, 266.5; [34]: C-N, 180°; N-I, 265°). IR (KBr): 2670*w*, 1681*s*, 1608*m*, 858*w*. MS: 274 (M^{+}).

*4-{[(S)-6-Methyloctyl]oxy}phenyl 4-{[(*trans*-4-Pentylcyclohexyl)carbonyl]oxy}benzoate* (**11**) was prepared by esterification of 4-{[(*trans*-4-pentylcyclohexyl)carbonyl]oxy}benzoic acid and 4-{[(*S*)-6-methyloctyl]oxy}phenol as described for **1** (see *Table 7* for the liquid-crystal transition temp.). $[\alpha]_D^{20} = +0.031$ (c = 1.0, $CHCl_3$). IR (KBr): 1741*s*, 1601*m*, 1507*s*, 1243*s*, 1162*s*, 1072*s*. MS: 536 (M^{+}).

*4-{[(*trans*-4-Pentylcyclohexyl)carbonyl]oxy}benzoic Acid. Jones* reagent (3 ml) was added dropwise to a soln. of 4-{[(*trans*-4-pentylcyclohexyl)carbonyl]oxy}benzaldehyde (2.2 g, 0.007 mol) and anh. acetone (25 ml) cooled *via* an ice-bath. A precipitate was formed almost immediately after completion of the addition. The mixture was stirred at r.t. for a further 2 h and then poured onto ice (100 g) and stirred for 20 min. The solid was filtered off, washed with H_2O, pressed only, and crystallised from EtOH to yield pure (99%) acid (1.3 g, 56%; C-N, 220°; N-I, 234°). IR (KBr): 2927*w*, 1751*s*, 1680*s*, 1604*m*, 1508*w*, 1292*s*, 1163*s*, 1016*w*. MS: 181 ($C_{12}H_{21}O^+$), 138 ($C_7H_6O_3$).

*4-{[(*trans*-4-Pentylcyclohexyl)carbonyl]oxy}benzaldehyde.* A soln. of 4-*trans*-pentylcyclohexane-1-carboxylic acid [33] (1.5 g, 0.008 mol), 4-hydroxybenzaldehyde (0.92 g, 0.008 mol), DCC (1.8 g, 0.009 mol), DMAP (0.04 g), and CH_2Cl_2 (50 ml) was stirred at r.t. overnight. The resulting mixture was worked up as described above. Column chromatography using toluene/AcOEt 4:1 and crystallisation from hexane at 0° yielded pure aldehyde (2.2 g, 96%; C-N, 38°; N-I, 54°). IR (KBr): 2740*w*, 1749*s*, 1700*s*, 1599*s*, 1210*s*, 859*m*. MS: 302 (M^{+}).

*4-{[(S)-6-Methyloctyl]oxy}phenyl 4-(*trans*-Pentylcyclohexyl) Terephthalate* (**12**). A soln. of 4-{[(*S*)-6-methyloctyl]oxy}phenyl 4-(chloroformyl)benzoate (1.0 g, 0.003 mol), *trans*-4-pentylcyclohexanol [33] (0.42 g, 0.003 mol), pyridine (1 ml), and toluene (50 ml) were heated under reflux for 1 h. The cooled mixture was worked up and purified as described above to yield pure ester (see *Table 7* for the liquid-crystal transition temp). $[\alpha]_D^{20} = +0.028$ ($c = 1.0$, $CHCl_3$). IR (KBr): 1717*s*, 1601*w*, 1506*s*, 1249*s*, 1194*s*, 1016*m*, 810*w*. MS: 536 (M^{+}).

4-{[(S)-6-Methyloctyl]oxy}phenyl 4-(Chloroformyl)benzoate. A soln. of 4-{[(*S*)-6-methyloctyl]oxy}phenol (0.6 g, 0.003 mol), terephthaloyl dichloride (0.5 g, 0.003 mol), pyridine (1 ml), and toluene (50 ml) were stirred at r.t. overnight. After filtration to remove inorg. material, the solvents were removed under vacuum and the resulting solid residue (1.0 g, 98%) used in the next reaction without further purification.

REFERENCES

[1] S. M. Kelly, R. Buchecker, H.-J. Fromm, M. Schadt, *Ferroelectrics*, in press.
[2] M. Schadt, W. Helfrich, *Appl. Phys. Lett.* **1971**, *18*, 127.
[3] T. J. Scheffer, J. Nehring, *Appl. Phys. Lett.* **1984**, *10*, 1021.
[4] N. A. Clark, S. T. Lagerwall, *Appl. Phys. Lett.* **1980**, *36*, 899.
[5] N. A. Clark, M. A. Handschy, S. T. Lagerwall, *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 213.
[6] G. W. Goodby, T. M. Leslie, 'Liquid Crystals and Ordered Fluids', Plenum Press, New York, 1984, Vol. 4, and ref. cit. therein; J. W. Goodby, *Ferroelectrics* **1983**, *49*, 275.
[7] C. Escher, *Kontakte* **1986**, *2*, 3.
[8] T. Geelhar, C. Escher, E. Bohm, 17 Freiburger Arbeitstagung, 1987.
[9] D. M. Walba, S. C. Slater, W. N. Thurmes, N. A. Clark, M. A. Handschy, F. Supon, *J. Am. Chem. Soc.* **1986**, *108*, 5211.
[10] J. P. Le Pesant, B. Mourey, M. Hareng, G. Decobert, J. C. Dubois, *Paris Display* **1984**, 217.
[11] J. W. Goodby, *Science* **1986**, *231*, 350.
[12] J. W. Goodby, T. M. Leslie, *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 175.
[13] P. Keller, *Ferroelectrics* **1984**, *58*, 3.
[14] G. Decobert, J. C. Dubois, *Mol. Cryst. Liq. Cryst.* **1984**, *114*, 237.
[15] J. C. Dubois, A. Zanoni, A. B. Beguin, *Mol. Cryst. Liq. Cryst.* **1977**, *42*, 139.
[16] J. C. Dubois, A. B. Beguin, *Mol. Cryst. Liq. Cryst.* **1978**, *47*, 193.
[17] R. Eidenschink, R. Hopf, B. S. Scheuble, A. E. Wächtler, 16 Freiburger Arbeitstagung, 1986.
[18] G. W. Gray, K. J. Harrison, *Mol. Cryst. Liq. Cryst.* **1971**, *13*, 37.
[19] G. W. Gray, D. G. McDonnell, *Mol. Cryst. Liq. Cryst.* **1976**, *37*, 189; *ibid.* **1978**, *48*, 37; *ibid.* **1979**, *53*, 147.
[20] G. W. Gray, S. M. Kelly, *Mol. Cryst. Liq. Cryst.* **1983**, *95*, 101; *ibid.* **1984**, *104*, 335.
[21] J. W. Goodby, G. W. Gray, 'Smectic Liquid Crystals', Leonard Hill, Glasgow, 1984, and ref. cit. therein.
[22] G. W. Gray, 'Advances in Liquid Crystals', Academic Press, London, 1976, Vol. 2, and ref. cit. therein.
[23] G. W. Gray, S. M. Kelly, *Mol. Cryst. Liq. Cryst.* **1981**, *75*, 109.
[24] S. M. Kelly, T. Huynh-Ba, *Helv. Chim. Acta* **1983**, *66*, 1850.
[25] S. M. Kelly, Hp. Schad, *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 239, and ref. cit. therein.
[26] S. M. Kelly, Hp. Schad, *Helv. Chim. Acta* **1985**, *68*, 813.
[27] N. Carr, G. W. Gray, *Mol. Cryst. Liq. Cryst.* **1985**, *124*, 27.
[28] S. M. Kelly, Hp. Schad, *Helv. Chim. Acta* **1985**, *68*, 1444.
[29] H. Takatsu, K. Takeuchi, H. Sato, *Japan Display* **1983**, 228.
[30] N. Carr, G. W. Gray, D. G. McDonnell, *Mol. Cryst. Liq. Cryst.* **1983**, *97*, 13.
[31] M. Schadt, M. Petrzilka, P. R. Gerber, A. Villiger, G. Trickes, *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 139.
[32] Dr. A. Boller, *F. Hoffmann-La Roche*.
[33] H.-J. Deutscher, B. Laaser, W. Dölling, H. Schubert, *J. Prakt. Chem.* **1978**, *320*, 191.
[34] T. Szezucinski, R. Dabrowski, *Mol. Cryst. Liq. Cryst.* **1982**, *88*, 55.
[35] R. Rich, A. Villiger, E. Widmer, DOS 3201 721, 1982.