67. Ferroelectric Liquid Crystals

Part 9[1])

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

by **Stephen M. Kelly**

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

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About 65 diverse phenyl benzoates incorporating a *trans*-1,4-disubstituted cyclohexane ring *and* at least one lateral substituent have been synthesised. The dependence of the liquid-crystal transition temperatures of these materials on various lateral substituents (F, Cl, CN, and Br) in different positions of the esters has been investigated systematically. The influence of up to four F-atoms in various positions of a standard ester has been thoroughly studied and the optimum combination for a broad smectic C mesomorphic range established. In consequence, three homologous series incorporating the 4-alkoxy-2,3-difluorobenzoic-acid moiety were prepared. An additional C=C bond was introduced into the alkyl chain attached to the cyclohexane ring of some of these esters and the resulting modifications of the transition temperatures determined. Three ester series incorporating a lateral substituent *and* the optically active (+)-(*S*)-(1-methylheptyl)oxy substituent have also been synthesised, and similar effects have been observed. These materials can be used as important components of commercial chiral smectic C mixtures for electro-optic display device applications.

Introduction. – The synthesis, liquid-crystal transition temperatures [1–3], and some other physical properties [4] of a variety of substituted phenyl benzoates incorporating a *trans*-1,4-disubstituted cyclohexane ring have been reported recently [1–4]. The effect of lateral substituents, chain length, optically active centres, and several linking units on the liquid-crystal transition temperatures of these esters has been investigated to differing degrees. It has been found that the presence of a lateral substituent on one or both of the aromatic rings of the esters can lead to a broadening of the temperature range of the smectic C mesophase [1–3] and, in the case of optically active esters, to an increase in the spontaneous polarisation [4]. The scope of these investigations has now been increased to include a larger number of ester types (*e.g.* incorporating a CH_2O linking unit), polyfluoro substitution, and the introduction of a C=C bond in the terminal alkyl chain of some of these esters. These materials have been designed as components of improved ferroelectric, chiral smectic C mixtures for commercial electro-optic display devices [4].

The required laterally substituted benzoic acids were synthesised according to modified literature methods [5] in most cases. The laterally substituted phenols were prepared as described in [2] [6]. The required optically active acids were synthesised using similar methods utilising (–)-(*R*)-2-octanol *(Fluka, puriss.)* as the chiral starting material. An

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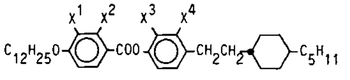
[1]) 'Ferroelectric Liquid Crystals,' Part 8: [1].

inversion of the optically active centre was observed during the alkylations *(cf. Exper. Part)*. Thus, all of the optically active esters have the same (*S*)-configuration.

Results and Discussion. – The liquid-crystal transition temperatures and some enthalpies of fusion of 14 substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(dodecyloxy)benzoates **1** are listed in *Table 1*. The transition temperatures of these laterally substituted esters are plotted against the effective size (Å) of the corresponding lateral substituent (X^1, X^2, X^3, and X^4) in *Figs. 1–4*, respectively. As can be seen from the table and the figures, the transition temperatures of the esters **1** depend not only on the nature of the lateral substituent, but also on its position. With the exception of the CN-substituted compound (X^1 = CN, X^{2-4} = H), the clearing point (N-I) of the 3-substituted 4-(dodecyloxy)benzoates (X^1 = H, F, Cl, Br, X^{2-4} = H) decreases with increasing size of the lateral substituent. The relationship is linear to a first approximation. A similar effect is observed for the smectic C-nematic transition temperatures (S_C-N) and to a lesser extent for the other smectic transition temperatures (S_A-N and S_3-S_C). The exception to these general trends is the nitrile (X^1 = CN, X^{2-4} = H) whose sole liquid-crystal modification is a smectic A phase. Similar behaviour for related compounds [6] has been rationalised in terms of the relatively large dipole moment (4.0 D) of the CN function compared to the dipole moment of the other lateral substituents studied (*e.g.* 1.5 D for X^1 = Br). An interesting aspect of these results is the broader smectic C mesophase range (54°) of the F-substituted ester (X^1 = F; X^{2-4} = H) compared to that (40°) of the corresponding non-laterally substituted ester (X^{1-4} = H). As can be clearly seen from *Table 1* and *Fig. 2*, the same substituents (F and Cl) at C(2) lead to much larger decreases in the observed liquid-crystal transition temperatures compared to those of the corresponding 3-substituted esters.

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



1

X^1	X^2	X^3	X^4	C-S/N	S_3-S_C[a])	S_C-S_A/N/I[a])	S_A-N/I	N-I	ΔH
H	H	H	H	58	78	118	132	147	23.7
F	H	H	H	72	(56)	110	125	135	26.3
Cl	H	H	H	65	–	100	–	127	
CN	H	H	H	68	–	–	128	–	
Br	H	H	H	80	–	(79)	–	114	31.1
H	F	H	H	52	(44)	98	–	137	22.2
H	Cl	H	H	55	–	(37)	–	104	33.6
H	H	F	H	71	–	79	–	133	32.4
H	H	Cl	H	53	–	–	–	112	
H	H	CN	H	62	–	66	–	121	34.4
H	H	Br	H	46	–	–	–	106	30.2
H	H	H	F	59	–	96	120	133	31.7
H	H	H	Cl	57	–	–	–	125	
H	H	CN	CN	100	–	131	–	–	25.7

[a]) ( ) Represents a monotropic transition temperature.

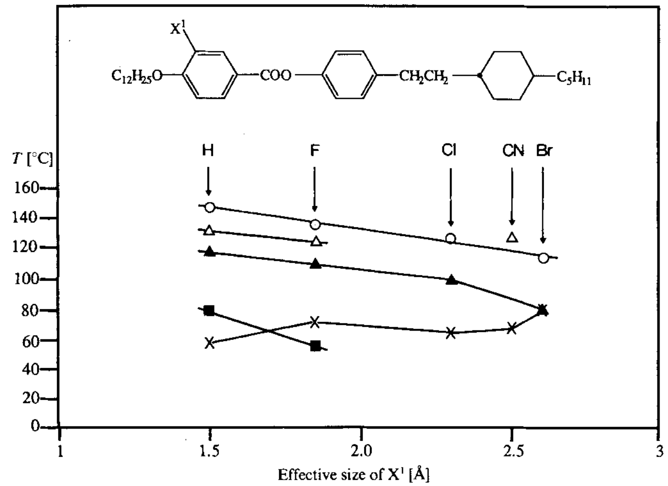


Fig. 1. *Transition temperatures* vs. *the size of the lateral substituent* X^1 (X: crystal-smectic 3/smectic C/smectic A/nematic transition; ■: smectic 3-smectic C transition; ▲: smectic C-smectic A/nematic transition; △: smectic A-nematic/isotropic transition; ○: nematic-isotropic transition)

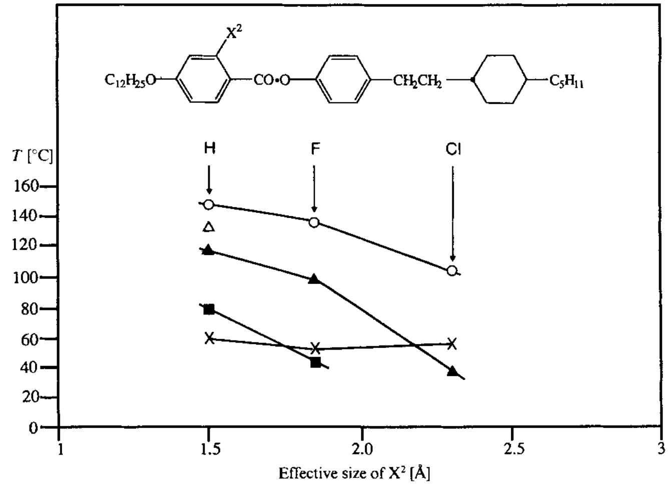


Fig. 2. *Transition temperatures* vs. *the size of the lateral substituent* X^2 (X: crystal-smectic 3/smectic C/nematic transition; ■: smectic 3-smectic C transition; ▲: smectic C-smectic A/nematic transition; △: smectic A-nematic transition; ○: nematic-isotropic transition)

Comparison of the liquid-crystal transition temperatures recorded in *Table 1* and plotted separately in *Figs. 1–4* for the four series of lateral substituents (X^{1-4}) reveals that substitution in the central phenylene ring (X^3, X^4) depresses the transition temperatures of all the observed mesophases more than substitution in the benzoic-acid part (X^1, X^2) of **1**. The clearing point (N-I), the smectic C-nematic transition temperature (S_C-N), and the melting point (C-S_3, C-S_C, C-S_A, C-N) are all lower to approximately the same

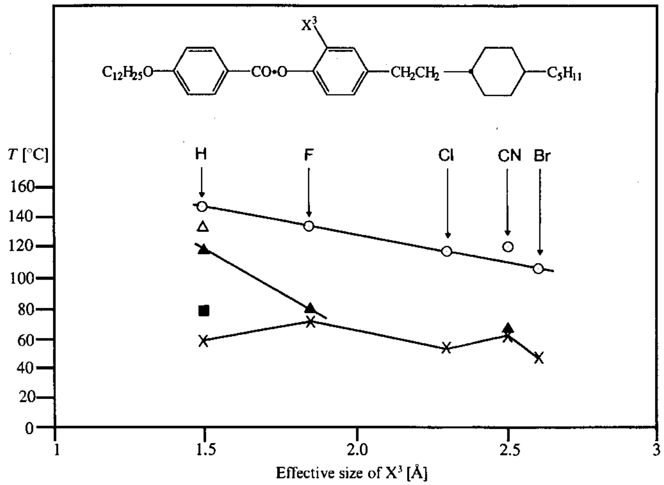


Fig. 3. *Transition temperatures* vs. *the size of the lateral substituent* X^3 (X: crystal-smectic 3/smectic C/nematic transition; ■: smectic 3-smectic C transition; ▲: smectic C-smectic A/nematic transition; △: smectic A-nematic transition; ○: nematic-isotropic transition)

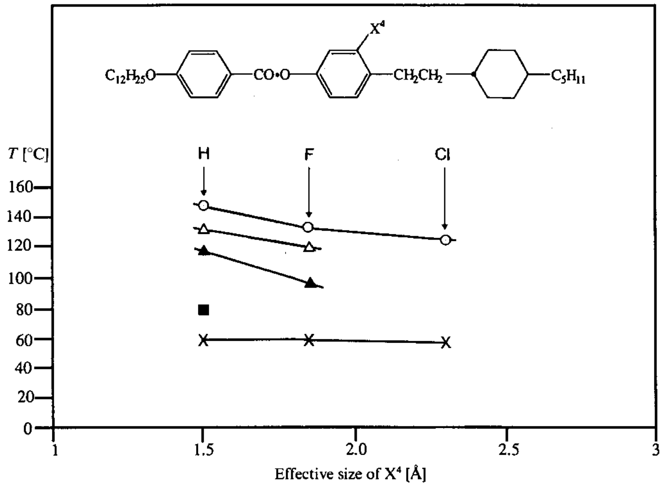
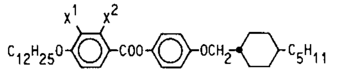


Fig. 4. *Transition temperatures* vs. *the size of the lateral substituent* X^4 (X: crystal-smectic 3/smectic C/nematic transition; ■: smectic 3-smectic C transition; ▲: smectic C-smectic A transition; △: smectic A-nematic transition; ○: nematic-isotropic transition)

extent (5°, 5°, and 7°, respectively, on average) comparing those compounds with the same phases for the same substituent. No ordered mesophase could be observed. It is interesting to note that, while the cyano-benzoate (X^1 = CN; X^{2-4} = H) only exhibits a smectic A mesophase, the corresponding nitrile (X^3 = CN, X^1 = X^2 = X^4 = H) exhibits an enantiotropic smectic C mesophase and no smectic A mesophase. The dinitrile (X^{1-2} = H; X^{3-4} = CN) possesses a smectic C-isotropic liquid transition (S_C-I) which is most unusual.

This smectic C transition occurs at a higher temperature (131°) than that (66°) of the corresponding mono-nitrile (X^3 = CN, $X^1 = X^2 = X^4$ = H) or that (118°) of the non-laterally substituted material (X^{1-4} = H). The melting point (C-S_C) is also considerably higher (+38° and +42°, respectively). These considerable differences may be attributed to the large effective dipole perpendicular to the long molecular axis of the molecule [7].

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



2

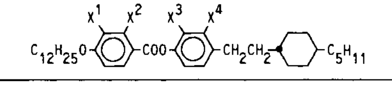
X^1	X^2	C-S/N	S_4-S_C[a])	S_C-N	N-I	ΔH
H	H	73	81	129	152	
F	H	76	(54)	123	139	13.2
Cl	H	70	–	107	133	26.1
CN	H	96	–	97	106	
Br	H	68	–	89	120	
H	F	52	–	99	138	38.5
H	Cl	58	–	(45)	113	29.7
F	F	77	–	122	142	30.0

[a]) ( ) Represents a monotropic transition temperature.

Collated in *Table 2* are the liquid-crystal transition temperatures and some enthalpies of fusion for the 4-[(*trans*-4-pentylcyclohexyl)methoxy]phenyl 4-(dodecyloxy)benzoates **2**. The esters **2** differ from **1** only in the presence of an O-atom in the non-ester linking unit instead of a CH_2 unit. This relatively small difference is reflected in marginally higher liquid-crystal transition temperatures (C-S_3, C-S_4, C-S_C, S_3-S_C, S_4-S_C, S_C-S_A, S_C-N, and N-I) for the methoxy compounds **2** compared to those of the ethyl compounds **1**. The highly sensitive nature of some liquid-crystal mesophases is demonstrated by the absence of a smectic A mesophase for the esters **2** and the different ordered smectic mesophases (S_3 and S_4, respectively) of the esters **1** and **2**. Comparison of the transition temperatures of the difluoro-substituted compound ($X^1 = X^2$ = F) with those of the corresponding non-fluoro-substituted compound ($X^1 = X^2$ = H) reveals the same relationship as that for the corresponding esters **3** with an ethylene bridge (see *Table 3*). Although the liquid-crystal transition temperatures of **1** and **2** are very similar, it has been established that the methyleneoxy-substituted esters **2** are substantially more viscous than the corresponding ethylene-substituted esters **1** [4]. Thus, further investigations concentrated on compounds with an ethylene bridge and at least one F-atom, as such compounds are shown here to have the broadest smectic C mesophase range and also reasonably low viscosities [4].

The liquid-crystal transition temperatures of the F-substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(dodecyloxy)benzoates **3** are recorded in *Table 3* along with those of the corresponding non-laterally substituted ester (X^{1-4} = H). The transition temperatures are organised in the table according to degree of F-substitution, *i.e.* from mono- to tetrafluoro-substituted esters. Analysis of the data in *Table 3* reveals several salient features. The clearing point (N-I), the smectic A-nematic transition temperature (S_A-N), and the ordered smectic mesophase-smectic C transition temperature (S_3-S_C) decrease with increasing degree of F-substitution (on average). Only the mono-fluo-

Table 3. *Transition Temperatures* [°C] *of the Compounds* **3**



3

X^1	X^2	X^3	X^4	C-S/N	S_3-S_C[a]	S_C-S_A/N	N-I	
H	H	H	H	58	78	118	132	147
F	H	H	H	72	(56)	110	125	135
H	F	H	H	52	(44)	98	–	137
H	H	F	H	71	< 25	79	–	133
H	H	H	F	59	< 25	96	120	133
F	H	F	H	48	< 25	80	–	119
H	F	F	H	44	< 25	55	–	122
F	H	H	F	62	< 25	102	115	124
H	F	H	F	40	< 25	91	104	125
F	F	H	H	64	< 25	114	–	138
H	H	F	F	60	< 25	82	–	128
F	F	F	H	64	< 25	83	–	120
F	F	H	F	66	< 25	112	–	127
F	H	F	F	58	< 25	82	–	116
H	F	F	F	48	< 25	69	–	119
F	F	F	F	71	< 25	90	–	118

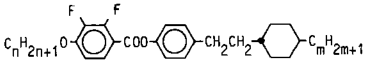
[a] ( ) Represents a monotropic transition temperature.

roesters exhibit a (monotropic) ordered mesophase (S_3, as yet not identified). The smectic C transition (S_C-S_A and S_C-N) occurs at a lower temperature for all of the F-substituted compounds compared to the non-laterally substituted ester (X^{1-4} = H). The melting point C-S_C) of the F-substituted compounds is generally higher than that (C-S_3) of the corresponding non-laterally substituted material. The most outstanding aspect of the transition temperatures collated in *Table 3* is the considerable broadness of the smectic-C mesophase range of many of the prepared compounds **3**. This is a direct consequence of the greater depression of the ordered smectic mesophase than of the smectic C mesophase caused by the presence of one or more F-atoms. A comparison of the transition temperatures of the non-fluoro-substituted compound (X^{1-4} = H) and those of a difluoro-substituted material ($X^1 = X^2$ = F, $X^3 = X^4$ = H) reveals a marginal difference in the melting and clearing points (6° and 9°, respectively) as well as in the smectic C-nematic transition temperature (4°). The difference in the transition temperatures of the ordered smectic mesophase transition is much larger ($>$ 50°).

Having established that difluoro substitution of the benzoic-acid part ($X^1 = X^2$ = F, $X^3 = X^4$ = H) of **3** has the most advantageous effect on the broadness of the smectic C mesophase range, it was decided to prepare three homologous series of the 4-[2-(*trans*-4-alkylcyclohexyl)ethyl]phenyl 4-alkoxy-2,3-difluorobenzoates **4**. The liquid-crystal transition temperatures (C-S_C, C-N, S_C-N, and N-I) and some enthalpies of fusion (ΔH) of the esters **4** are collated in *Table 4*.

The melting points (C-S_C, C-N) and clearing points (N-I) of the three homologous series of **4** are surprisingly similar (64°, 58°, and 58°; 142°, 143°, and 140° on average, respectively). However, the smectic C-nematic transition temperatures of the esters increases with increasing length of the terminal alkyl chain (*m* = 3, 5, and 7). Thus, the

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



4

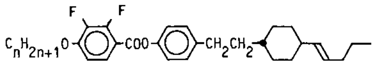
n	*m*	C-S$_C$/N	S$_C$-N[a])	N-I	*ΔH*
7	3	74	(62)	149	
8	3	73	(71)	147	26.6
9	3	60	81	142	
10	3	52	89	141	33.4
11	3	61	95	138	36.8
12	3	61	100	136	33.0
7	5	69	79	148	26.1
8	5	68	88	146	17.2
9	5	54	98	143	37.9
10	5	41	105	142	33.4
11	5	53	110	139	35.0
12	5	64	114	138	35.0
7	7	66	92	143	28.7
8	7	69	103	144	28.0
9	7	58	110	140	48.6
10	7	48	116	140	41.6
11	7	53	119	138	28.2
12	7	52	120	137	36.1

[a]) ( ) Represents a monotropic transition temperature.

mesomorphic range of the smectic C phase also increases with increasing chain length (19°, 41°, and 52°, on average, respectively). A remarkable feature of the thermodynamic data in *Table 4* is the absence of either a smectic A phase or an ordered smectic mesophase. Due to this favourable combination of liquid-crystal transition temperature, the esters **4** are especially suitable as components of ferroelectric, chiral smectic C mixtures [4]. The ability of the 4-alkoxy-2,3-difluorobenzoic-acid moiety incorporated in three-ring esters to induce an enantiotropic smectic C mesophase over a wide temperature range has also been demonstrated recently for different compounds to those presented here [8].

The liquid-crystal transition temperatures and some *ΔH* values for the 4-{2-(*trans*-4-[(*E*)-1-pentenyl]cyclohexyl)ethyl}phenyl 4-alkoxy-2,3-difluorobenzoates **5** are collated in *Table 5*. The only difference between **5** and **4** (*n* = 7–12; *m* = 5) is the presence of an

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



5

n	C-S$_C$	S$_C$-N	N-I	*ΔH*
7	72	81	156	24.4
8	74	92	155	25.2
9	54	101	151	33.2
10	49	109	149	21.4
11	53	115	146	29.1
12	61	119	145	32.8

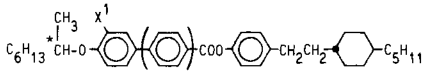
additional C=C bond in a *trans*-position in the terminal alkyl chain. The resulting differences in the thermodynamic data (C-S_C, S_C-N, and N-I) are a general increase (3°, 4°, and 7°, on average, respectively) in all three transition temperatures. This induces an almost negligible increase in the smectic C mesomorphic temperature range (1°, on average). These results are generally consistent with those found for other esters [9] although in those cases only smectic B and nematic mesophases were observed.

The introduction of C=C bond in the 4-(4-*trans*-pentylcyclohexyl)phenyl 2,3-difluoro-4-(dodecyloxy)benzoate (C-S_C, 67°; S_C-N, 116°; N-I, 153°) to produce the 4-(4-*trans*-[(*E*)-3-pentenyl]cyclohexyl)phenyl 2,3-difluoro-4-(dodecyloxy)benzoate(C-S_C, 66°; S_C-N, 113°; N-I, 163°) affects the liquid-crystal transition temperatures to a more significant degree than for the esters **3** and **4**. Whereas both the melting point (C-S_C) and the smectic C-nematic transition temperature (S_C-N) are marginally lower (1° and 3°, respectively), the clearing point (N-I) is clearly higher (10°) for the ester containing the additional C=C bond in the 3-position of the terminal alkyl chain. This correlates with the results for other esters with respect to the nematic-isotropic transition temperature, but *not* for the smectic-nematic transition temperature [9], where a significant broadening of the nematic phase was observed as well as a large depression in the smectic B transition temperatures.

Thus, it has been shown that a C=C bond with *trans*-substitution (*E*) in the 1-position leads to a minimal increase in the smectic C mesophase range, a corresponding substitution in the 3-position gives rise to a marginal narrowing of the range of the smectic C mesophase. It has already been shown that similar substitution in the 4-position of a wide variety of phenyl benzoates [10] and phenylpyrimidines [11] induces significant decreases in all of the liquid-crystal transition temperatures, while, at the same time, increasing the smectic C mesophase range in some cases. Thus, the smectic C mesophase appears to be *more* stable to alkenyl substitution than the smectic B mesophase [9].

The liquid-crystal transition temperatures and some ΔH values for the substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-[(*S*)-(1-methylheptyl)oxy]benzoates **6** (*n* = 0) are recorded in *Table 6*. The optically active esters **6** are characterised by low melting points (C-S_A and C-Ch), moderate clearing points (S_A-I and Ch-I), and the absence of a chiral smectic C mesophase or other ordered mesophases. It is noteworthy that the nitrile (X^1 = CN) only exhibits an enantiotropic smectic A phase like the corre-

Table 6. *Transition Temperatures* [°C] *and Enthalpies of Fusion* [KJ·mol^{-1}] *for the Compounds* **6**



6

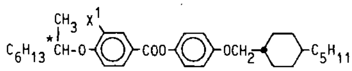
X^1	*n*	C-S_E/S_A/Ch	S_E-*S_C/S_A	*S_C-Ch	S_A-Ch/I	Ch-I	ΔH
H	0	28	–	–	–	78	25.4
F	0	27	–	–	–	69	
Cl	0	–2	–	–	–	48	
CN	0	37	–	–	52	–	7.6
Br	0	–42	–	–	–	40	
H	1	75	110	134	–	195	26.4
Cl	1	60	86	–	147	169	21.0
CN	1	63	83	–	157	–	
Br	1	58	79	–	126	156	

sponding achiral ester **1** ($X^1 = CN$, $X^{2-4} = H$; see *Table 1*). Another interesting characteristic of the nitrile **6** is the exceptionally low enthalpy of fusion. Two examples ($X^1 = Cl$ and Br) of **6** exhibit an enantiotropic chiral nematic phase at and above room temperature. This is not a common phenomenon in pure substances [10–12].

Also recorded in *Table 6* are the liquid-crystal transition temperatures and some ΔH values of the 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4′-[(*S*)-(1-methylheptyl)oxy]-biphenyl-4-carboxylates **6** ($n = 1$). The introduction of a third 1,4-disubstituted phenylene ring to produce the esters **6** ($n = 1$) results in an increase in the absolute values of the observed transition temperatures and in the number of mesophases observed. The melting point (C-S_E, C-S_A, C-Ch), the smectic A transition temperature (S_A-Ch and S_A-I), and the clearing point (S_A-I and Ch-I) of the esters **6** ($n = 1$) are all much higher (+59°, +105°, and +115°, on average, comparing only data for the same mesophases for the same lateral substituents) than those of the esters **6** ($n = 0$). The esters **6** ($n = 1$) also exhibit an enantiotropic smectic C phase ($X^1 = H$) and an enantiotropic smectic E phase ($X^1 = H$, Cl, CN, and Br). The chiral smectic C mesophase of the nitrile **6** ($n = 1$) exhibits ferroelectric properties.

The liquid-crystal transition temperatures and some ΔH values of the laterally substituted 4-[(*trans*-4-pentylcyclohexyl)methoxy]phenyl 4-[(*S*)-(1-methylheptyl)oxy]benzoates **7** are listed in *Table 7*. The liquid-crystal polymorphism of **7** is very similar to that of the corresponding esters **6** ($n = 1$) with a CH_2 unit instead of the O-atom in the non-ester linking unit. The absolute values of the melting point (C-S_A and C-Ch), the smectic-isotropic transition temperature (S_A-I), and the clearing point (S_A-I and Ch-I) are greater (+34°, +5°, +14°, on average, respectively) for the esters **7** than the corresponding values of the esters **6** ($n = 0$). This is consistent with previous results obtained for the analogous non-optically active esters **1** and **2** (see *Tables 1* and *2*).

Table 7. *Transition Temperatures* [°C] *and Enthalpies of Fusion* [KJ · mol^{-1}] *for the Compounds* **7**



7

X^1	C-S_A/Ch	S_A-I	Ch-I	ΔH
H	54	–	94	21.0
F	46	–	77	31.5
Cl	34	–	61	
CN	50	57	–	12.2
Br	12	–	51	

The optically active esters **6** and **7** can be used in admixture with non-optically active substances (*e.g.* the esters **1**–**5**), which exhibit a smectic C mesophase, to create ferroelectric, chiral smectic C mixtures for commercial electro-optic display devices [4].

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Experimental Part

(Mr. *B. Müller* and Mr. *U. Wyss* are thanked for technical assistance.)

General. The liquid-crystal transition temp. of the compounds prepared recorded in *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 gas, cooled by liquid N_2, to pass through the stage at a controlled rate. The liquid-crystal transition temperatures 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. 4 cm × 8 cm precoated TLC plates, SiO_2 *SIL G/UV*$_{254}$, layer thickness 0.25 mm (*Macheray-Nagel,* Düren, FRG) were utilised.

Column-chromatography (CC) 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 *MS9* (*AEZ,* Manchester) spectrometer. DMPA = 4-(Dimethylamino)pyridine, DCC = *N,N'*-dicyclohexylcarbodiimid.

*2-Bromo-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(Dodecyloxy)benzoate* (**1**; X^1,X^2,X^4 = H, X^3 = Br). A soln. of 4-(dodecyloxy)benzoic acid (15.6 g, 0.051 mol), 2-bromo-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol [2] (18.0 g, 0.051 mol), DCC (12.6 g, 0.061 mol), DMAP (0.1 g), and CH_2Cl_2 (250 ml) was stirred overnight at r.t. The precipitated material was filtered off and the filtrate evaporated down under reduced pressure. The solid residue was purified by CC (toluene/hexane 4:1) and subsequent crystallisation from EtOH, until constant liquid-crystal transition temp. were obtained (see *Tables 1–7* for the transition temp. and enthalpies of fusion for this ester and the other esters prepared using this general method). IR (KBr): 1740, 1604, 1510, 1253, 1221, 1165, 1063, 845. MS: 289 ($C_{19}H_{29}O_2^+$), 185, 187 ($C_7H_6BrO^+$).

*2-Cyano-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(Dodecyloxy)benzoate* (**1**; X^1,X^2,X^4 = H, X^3 = CN). A soln. of 2-bromo-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(dodecyloxy)benzoate (26 g, 0.041 mol), anh. CuCN (9.1 g, 0.101 mol), and 1-methyl-2-pyrrolidinone (200 ml) was heated at 185° for 3 h. The cooled mixture was poured onto 15% NaOH soln. and stirred for 40 min. This mixture was shaken with Et_2O (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 slightly reduced pressure and the resultant solid residue purified by CC (toluene/hexane 1:1) and subsequent crystallisation from AcOEt, until constant liquid-crystal transition temp. were obtained (see *Tables 1–7* for the transition temp. for this ester and other esters prepared using this general procedure). IR (KBr): 2225, 1731, 1606, 1513, 1261, 1222, 1170, 841. MS: 299 ($C_{20}H_{29}NO^+$), 289 ($C_{19}H_{29}O_2^+$).

1-(Dodecyloxy)-2-fluorobenzene. A mixture of 2-fluorophenol (30 g, 0.27 mol), 1-bromododecane (81 g, 0.32 mol), anh. K_2CO_3 (149 g, 1.08 mol), and $C_2H_5COCH_3$ was heated over night under gentle reflux. The raw product was poured onto H_2O (2000 ml) and shaken with CH_2Cl_2 (4 × 250 ml). The combined org. layers were washed with H_2O (1000 ml), dil. Na_2CO_3 soln. (500 ml), and again with H_2O (500 ml) before being dried ($MgSO_4$). After removal of inorg. material, the solvent was removed under reduced pressure. The raw product was purified by CC (toluene) to yield pure (98%) product (71 g, 95%). IR (film): 2925, 2854, 1589, 1507, 1250, 1119, 744. MS: 280 (M^+).

1-Bromo-4-(dodecyloxy)-3-fluorobenzene. A soln. of Br_2 (34 g, 0.244 ml) in CH_2Cl_2 (50 mol) was added dropwise to a soln. of 1-(dodecyloxy)-2-fluorobenzene (60 g, 0.244 mol) and CH_2Cl_2 (200 ml) at r.t. The resultant soln. was stirred overnight and then added to H_2O (1000 ml). The org. layer was separated off, washed with dil. Na_2CO_3 soln. (2 × 500 ml) and H_2O (2 × 500 ml), and then dried ($MgSO_4$). The drying agent was removed by filtration and the solvent by evaporation under reduced pressure. This yielded pure (99%), product (70 g, 91 %). IR (film): 2935, 1504, 1264, 1130, 802. MS: 358/360 (M^+).

4-(Dodecyloxy)-3-fluorobenzonitrile. A soln. of 1-bromo-4-(dodecyloxy)-3-fluorobenzene (50 g, 0.139 mol), anh. CuCN (19 g, 0.021 mol), and 1-methyl-2-pyrrolidinone (150 ml) was treated at 180° for 3 h. The cooled mixture was added to a mixture of $FeCl_3$ (20 g), conc. HCl (1 ml), and H_2O (200 ml) and stirred for 30 min at 60–70°. The cooled mixture was shaken with Et_2O (4 × 200 ml). The combined org. layers were washed with H_2O (500 ml), dil. Na_2CO_3 soln. (500 ml), and again with H_2O (500 ml), and consequently dried ($MgSO_4$). The filtered soln. was evaporated down under slightly reduced pressure. The raw product was purified by CC (toluene) and crystallisation (hexane) at –25° to yield pure (99.8%) product (36 g, 85%). M.p. 34–35°. IR (KBr): 2291, 1614, 1579, 1514, 1284, 1124, 990, 814, 729. MS: 305 (M^+).

4-(Dodecyloxy)-2-fluorobenzonitrile (92%) was prepared using the same procedure. IR (film): 2302, 1610, 1585, 1278, 1120, 820. MS: 305 (M^+).

4-(Dodecyloxy)-3-fluorobenzoic Acid. A soln. of 4-(dodecyloxy)-3-fluorobenzonitrile (10 g), conc. H_2SO_4 (10 ml), H_2O (10 ml), and glacial AcOH (100 ml) was treated at 100° overnight. The cooled soln. was poured onto H_2O (1000 ml). The resultant precipitate was filtered off, washed with portions of H_2O, pressed dry, and then crystallised from EtOH to yield the pure acid (7.5 g, 71%; C-I, 135°; N-I, 109°). IR (KBr): 2921, 2850, 1659, 1149, 1004. MS: 324 (M^+).

4-(Dodecyloxy)-2-fluorobenzoic acid was prepared using the same procedure (65%; C-N, 95°; N-I, 102°). IR (KBr): 3150, 3080, 2669, 2542, 1693, 1619, 1507, 1288, 854. MS: 324 (M^+).

2-Chloro-4-(dodecyloxy)benzaldehyde. A mixture of 2-chloro-4-hydroxybenzaldehyde (10.0 g, 0.064 mol), 1-bromododecane (17.5 g, 0.071 mol), anh. K_2CO_3 (35 g, 0.256 mol), and AcOEt (200 ml) was treated overnight under gentle reflux. The inorg. material was separated off by filtration and the filtrate evaporated. The residue was purified by CC (toluene). The raw product was crystallised from hexane at −25° to yield the pure aldehyde (9.5 g, 73%). M.p. 34–35°. IR (KBr): 2919, 2853, 2766, 1679, 1600, 1473, 1248, 1033, 797. MS: 324/326 (M^+).

2-Chloro-4-(dodecyloxy)benzoic Acid. Jones reagent (10 ml) was added dropwise to a soln. of 2-chloro-4-(dodecyloxy)benzaldehyde (8.5 g, 0.026 mol) and $(CH_3)_2CO$ (250 ml) cooled *via* an ice bath. A precipitate was formed almost immediately. The mixture was stirred for a further 60 min at r.t., and then poured onto H_2O (500 ml). The precipitate was filtered off, washed with portions of H_2O, pressed dry, and crystallised from hexane to yield the pure acid (4.2 g, 47%; C-I, 87°; N-I, 51°). IR (KBr): 2644, 2568, 2517, 1682, 1596, 1470, 1275, 1228, 1129, 864. MS: 340/342 (M^+).

3-Chloro-4-(dodecyloxy)benzoic Acid. A soln. of 4-(dodecyloxy)benzoic acid (10 g, 0.033 mol), *N,N'*-dichlorobenzenesulfonamide (3.7 g, 0.016 mol), glacial AcOH (150 ml), and conc. H_2SO_4 (0.5 ml) was stirred at r.t. for 2 h and then heated at 80° for further 2 h. The cooled soln. was poured onto H_2O (1000 ml) and the resultant precipitate filtered off, washed with portions of H_2O, pressed dry, and finally crystallised from EtOH to yield the pure acid (8.4 g, 76%; C-N, 99°; S_c-N, 92°; N-I, 102°; [5], C-I, 101.5°; S-N, 84°; N-I, 88°). IR (KBr): 2619, 2561, 1686, 1598, 1505, 1278, 1124, 1061, 824. MS: 340, 342 (M^+).

The following acids were prepared using the same procedure: *3-Chloro-4-{[(S)-1-methylheptyl]oxy}benzoic acid* (50%): IR (film): 2994, 2858, 1688, 1599, 1500, 1272, 1140, 1050. MS: 284, 286 (M^+).

3'-Chloro-4'-{[(S)-1-methylheptyl]oxy}-4-biphenylcarboxylic acid (60%): m.p. 147–148°. $[\alpha]_D^{20} = +0.068$ ($c = 1.0$, $CHCl_3$). IR (KBr): 2667, 2549, 1675, 1605, 1487, 1278, 1120, 1018, 814. MS: 360, 362 (M^+).

Methyl 3-Bromo-4-hydroxybenzoate. A soln. of Br_2 (55 g, 0.345 mol) in glacial AcOH (20 ml) was added to a soln. of methyl 4-hydroxybenzoate (50 g, 0.329 mol) and glacial AcOH (200 ml) at r.t. After the addition was completed, the soln. was stirred overnight and then poured onto H_2O (1000 ml). The aq. soln. was shaken with CH_2Cl_2 (3 × 200 ml). The combined org. layers were washed with H_2O (1 × 1000 ml), dil. $NaHCO_3$ soln. (2 × 500 ml), again with H_2O (1000 ml), and dried ($MgSO_4$). The drying agent was removed by filtration and the filtrate evaporated under reduced pressure. The raw product (76 g, 99%) was used in the next step without further purification.

Methyl 3-Bromo-4-(dodecyloxy)benzoate. A mixture of methyl 3-bromo-4-hydroxybenzoate (75 g, 0.325 mol), 1-bromododecane (89 g, 0.357 mol), anh. K_2CO_3 (179 g, 1.300 mol), and AcOEt (500 ml) was heated under gentle reflux for 64 h. The mixture was worked up and purified as described above to yield the pure product (126 g, 97%). IR (film): 2917, 2852, 1710, 1599, 1498, 1243, 1119, 1048. MS: 398, 400 (M^+).

Methyl 3-bromo-4-{[(S)-1-methylheptyl]oxy}benzoate (90%) was prepared using the same procedure. IR (film): 2916, 2850, 1712, 1601, 1497, 1242, 1120, 1047. MS: 342, 344 (M^+).

3-Bromo-4-(dodecyloxy)benzoic Acid. A soln. of methyl 3-bromo-4-(dodecyloxy)benzoate (50 g, 0.125 mol), anh. KOH (16 g, 0.288 mol), EtOH (300 ml), and H_2O (100 ml) was heated overnight at 75°. The cooled mixture was acidified (pH 1) with 25% HCl. The liberated acid was filtered off, washed with portions of H_2O, pressed dry, and finally crystallised from EtOH to yield the acid (42 g, 81%). M.p. 108°. IR (KBr): 2612, 1677, 1277, 1128, 1044. MS: 384, 386 (M^+).

3-Bromo-4-{[(S)-1-methylheptyl]oxy}benzoic acid (78%) was prepared using the same procedure. $[\alpha]_D^{20} = +0.154$ ($c = 1.0$, $CHCl_3$). IR (film): 2929, 2856, 2854, 2594, 1689, 1269, 1118, 1044. MS: 328, 330 (M^+).

4-(Dodecyloxy)-2,3-difluorobenzene. A mixture of 2,3-difluorobenzene (5 g, 0.0038 mol), bromododecane (24 g, 0.0096 mol), anh. K_2CO_3 (21 g, 0.0154 mol), and AcOEt (250 ml) was treated under gentle reflux overnight. The mixture was added to H_2O (1000 ml) and shaken with CH_2Cl_2 (3 × 100 ml). The combined org. layers were washed with H_2O (250 ml), dil. $NaHCO_3$ soln. (250 ml), and H_2O (250 ml), and then dried ($MgSO_4$). After removal of the drying agent, the filtrate was evaporated under slightly reduced pressure and the residue purified by CC (hexane). The pure (99.8%) product (10.5 g, 92%) was used in the next reaction without further purification. IR (film): 2926, 2854, 1625, 1515, 1260, 1080, 765.

The following compounds were prepared using the same procedure: *2,3-difluoro-4-(heptyloxy)benzene* (90%): IR (film): 2930, 2867, 1620, 1514, 1259, 1080, 766. MS: 228 (M^+).

2,3-Difluoro-4-(octyloxy)benzene (86%): IR (film): 2925, 1626, 1515, 1256, 1081, 765. MS: 242 (M^+).

2,3-Difluoro-4-(nonyloxy)benzene (97%): IR (film): 2927, 2853, 1622, 1515, 1254, 1081, 765. MS: 256 (M^+).

4-(Decyloxy)-2,3-difluorobenzene (87%): IR (film): 2926, 2854, 1627, 1514, 1254, 1170, 1080, 765. MS: 270 (M^+).

2,3-Difluoro-4-(undecyloxy)benzene (83%): IR (film): 2926, 2854, 1626, 1515, 1259, 1081, 765.

4-(Dodecyloxy)-2,3-difluoroacetophenone. A soln. of AcCl (0.6 g, 0.008 mol) and CH_2Cl_2 (25 ml) was added dropwise to a mixture of 4-(dodecyloxy)-2,3-difluorobenzene (2 g, 0.007 mol), $FeCl_3$ (0.6 g, 0.009 mol), and CH_2Cl_2 (75 ml) cooled *via* an ice/EtOH bath. The resulting mixture was allowed to re-attain r.t. and stirred overnight. The mixture was added to H_2O (500 ml) and the org. layer separated off. The aq. layer was shaken with CH_2Cl_2 (3 × 50 ml). The combined org. layers were washed with conc. Na_2CO_3 soln. (100 ml) and H_2O (2 × 250 ml), and then dried ($MgSO_4$). The filtered soln. was evaporated under reduced pressure and the residue purified by CC (toluene). Crystallisation from hexane yielded pure (99.9%) product (1.1 g, 48%). M.p. 43–44°. IR (KBr): 1688, 1616, 1466, 1281, 1051, 817. MS: 340 (M^+).

The following compounds were prepared using the same procedure: *2,3-difluoro-4-(heptyloxy)acetophenone* (47%): m.p. 37°. IR (KBr): 1688, 1618, 1519, 1282, 1197, 1082, 808. MS: 270 (M^+).

2,3-Difluoro-4-(octyloxy)acetophenone (55%): m.p. 41°. IR (KBr): 1680, 1620, 1525, 1278, 1205, 1091, 810. MS: 284 (M^+).

2,3-Difluoro-4-(nonyloxy)acetophenone (50%): m.p. 40°. IR (KBr): 2916, 2849, 1674, 1619, 1514, 1312, 1085, 820. MS: 298 (M^+).

4-(Decyloxy)-2,3-difluoroacetophenone (61%): m.p. 35–36°. IR (KBr): 2921, 2859, 1688, 1616, 1575, 816. MS: 312 (M^+).

2,3-Difluoro-4-(undecyloxy)acetophenone (69%): m.p. 44–45°. IR (KBr): 2914, 2849, 1674, 1620, 1516, 1315, 1100, 1086, 819. MS: 326 (M^+).

4-(Dodecyloxy)-2,3-difluorobenzoic Acid. A soln. of NaOH (2.0 g, 0.0499 mol), Br_2 (2.3 g, 0.0147 mol), and H_2O (10 ml) was added dropwise to a soln. of 4-(dodecyloxy)-2,3-difluoroacetophenone (1.0 g, 0.0029 mol) and dioxane (10 ml). After 2 or 3 min, a yellow precipitate was observed. The mixture was stirred at r.t. for further 30 min and then heated at 50° for another 30 min. The excess of Br_2 was destroyed with sodium-metabisulphite soln. The mixture was poured onto 25% HCl and stirred for 20 min. The resultant precipitate was filtered off, washed with portions of H_2O, pressed dry, and crystallised from EtOH to yield the acid (0.75 g, 75%; C-I, 113°; N-I, 110°). IR (KBr): 2919, 2850, 1699, 1622, 1516, 1304, 1084, 821. MS: 342 (M^+).

The following acids were prepared using the same procedure: *2,3-difluoro-4-(heptyloxy)benzoic acid* (54%): C-I, 114°; N-I, 109°. IR (KBr): 2682, 1699, 1629, 1515, 1904, 820. MS: 272 (M^+).

2,3-Difluoro-4-(octyloxy)benzoic acid (78%): C-S_C, 105°; S_C-S_A, 111°; S_A-N, 112°; N-I, 113°. IR (KBr): 2859, 2699, 1692, 1622, 1488, 1301, 1089, 820. MS: 286 (M^+).

2,3-Difluoro-4-(nonyloxy)benzoic acid (78%): C-I, 114°; N-I, 111°. IR (KBr): 2594, 2678, 1693, 1622, 1515, 1297, 820. MS: 300 (M^+).

4-(Decyloxy)-2,3-difluorobenzoic acid (80%): C-N, 110°; N-I, 113°. IR (KBr): 2681, 2587, 1692, 1622, 1485, 1420, 1309, 819. MS: 314 (M^+).

2,3-Difluoro-4-(undecyloxy)benzoic acid (92%): C-I, 116°; N-I, 112°. IR (KBr): 2645, 2620, 1692, 1622, 1515, 1300, 820, 720. MS: 328 (M^+).

*4-(Dodecyloxy)-2,3-difluorophenyl (*trans*-4-Pentylcyclohexyl)methyl Ketone.* A soln. of (*trans*-4-pentylcyclohexyl)acetyl chloride (0.022 mol; prepared from the acid with $SOCl_2$ in the usual way) and CH_2Cl_2 (50 ml) was added dropwise to a mixture of $FeCl_3$ (3.8 g, 0.024 mol), 3-(dodecyloxy)-1,2-difluorobenzene (5.5 g, 0.0184 mol), and CH_2Cl_2 (100 ml), cooled *via* an ice/EtOH bath. The resulting mixture was allowed to re-attain r.t. and stirred overnight. The mixture was poured onto 25% HCl (100 ml) and stirred for 20 min. The org. layer was separated off and the aq. layer was shaken with CH_2Cl_2 (3 × 50 ml). The combined org. layers were washed with H_2O (250 ml), dil. $NaHCO_3$ soln. (250 ml), and again with H_2O (250 ml), and then dried ($MgSO_4$). After filtration, the soln. was evaporated down to yield a solid residue. The raw product crystallised from $(CH_3)_2CO$ at –25° to yield the pure (99.5%) product (1.9 g, 21%; C-I, 65°; S_A-I 64°). IR (KBr): 1680, 1619, 1512, 1309, 1192, 1089, 809. MS: 492 (M^+).

The following ketones were prepared using the same procedure: *2-fluoro-4-methoxyphenyl (*trans*-4-pentylcyclohexyl)methyl ketone* (50%): m.p. 71–72° ([6]: 71–72°). IR (KBr): 2922, 2846, 1670, 1613, 1509, 1240, 853. MS: 168 ($C_9H_9FO_2$).

*3-Fluoro-4-methoxyphenyl (*trans*-4-pentylcyclohexyl)methyl ketone* (58%): m.p. 74–75°. IR (KBr): 2913, 2849, 1676, 1614, 1521, 1262, 1182, 1020, 809. MS: 320 (M^+).

*2,3-Difluoro-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl Dodecyl Ether.* A soln. of 2,3-difluoro-4-methoxyphenyl (*trans*-4-pentylcyclohexyl)methyl ketone (1.9 g, 0.0039 mol) and CH_2Cl_2 (50 ml) was added dropwise to a suspension of $LiAlH_4$ (0.24 g, 0.0064 mol), $AlCl_3$ (1.9 g, 0.0145 mol), and Et_2O (50 ml). An exothermic reaction was observed. The mixture was heated under gentle reflux for 2 h; H_2O (25 ml) and then 25% HCl (100 ml) were added carefully to the cooled (ice/EtOH bath) mixture. The resultant mixture was stirred, until all the inorg. salts had been dissolved and two layers had been formed. The org. layer was separated off and the aq. layer shaken with Et_2O (3 × 100 ml). The combined org. layers were washed with H_2O (500 ml), dil. Na_2CO_3 soln. (250 ml), and H_2O (250 ml), then dried ($MgSO_4$), filtered, and evaporated under slightly reduced pressure. The residue was purified by CC (toluene/hexane 4:1). Crystallisation from hexane at −25° yielded the pure (95%) product (1.7 g, 92%; C-S_A, 23°; S_A-N, 30°; N-I, 35°). IR (KBr): 1696, 1512, 1291, 1175, 1089, 798. MS: 478 (M^+).

The following ethers were prepared using the same procedure: *3-fluoro-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl methyl ether* (97%). IR (film): 2919, 2849, 1750, 1627, 1585, 1507, 1280, 1152, 1037, 833. MS: 306 (M^+).

*2-Fluoro-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl methyl ether* (87%): m.p. 32–33°. IR (KBr): 2920, 2847, 1515, 1278, 808. MS: 306 (M^+).

*2,3-Difluoro-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol.* A 1M soln. of Br_3B in CH_2Cl_2 (3.1 ml) was added dropwise to a soln. of 2,3-difluoro-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl dodecyl ether (1.5 g, 0.003 mol) and anh. CH_2Cl_2 (50 ml), cooled *via* an ice-bath. The soln. was stirred at r.t. for 1 h and then poured onto H_2O (250 ml). 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 H_2O (250 ml), dil. $NaHCO_3$ soln. (500 ml), and again with H_2O (250 ml), before being dried ($MgSO_4$), filtered, and evaporated down. The solid residue was crystallised from hexane to yield the pure (99.8%) product (1.0 g, 93%). M.p. 61–62°. IR (KBr): 3947, 1640, 1607, 1489, 1308, 1211, 1029, 810. MS: 310 (M^+).

The following phenols were prepared using the same procedure: *2-fluoro-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol* (79%): m.p. 77–78°. IR (KBr): 3406, 2919, 2846, 1609, 1520, 1284, 1112, 815. MS: 292 (M^+).

*3-Fluoro-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol* (87%): m.p. 77–78° ([6]: 77–78°). IR (KBr): 3337, 2919, 2848, 1626, 1508, 1284, 1109, 845. MS: 292 (M^+).

*2-Chloro-4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol.* H_2SO_4 (0.2 cm^3) was added to a soln. of 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol (5.0 g 0.018 mol), *N,N*-dichlorobenzenesulfonamide (2.1 g, 0.009 mol), and glacial AcOH (150 ml). The resulting soln. was stirred for a further 2 h at r.t. and then poured onto H_2O (1000 ml). The resultant precipitate was filtered off, washed with more H_2O, and pressed dry. The raw product was then purified by CC (toluene). Crystallisation from hexane at 0° yielded the pure (99.8%) phenol (2.5 g, 44%). M.p. 68–69°. IR (KBr): 3409, 1582, 1498, 1191, 1059, 820. MS: 308, 310 (M^+).

2-Fluorophenyl Acetate. A soln. of 2-fluorophenol (7.4 g, 0.080 mol), AcCl (6.5 g, 0.092 mol), pyridine (45 ml), and toluene (40 ml) was stirred for 1 h. The resultant mixture was poured onto H_2O (150 ml) and then shaken with Et_2O (2 × 100 ml). The combined org. layers were washed with 3N HCl (50 ml), H_2O (50 ml), and $NaHCO_3$ soln. (50 ml), and again with H_2O (50 ml) before being dried ($MgSO_4$). After removal of the drying agent by filtration, the solvent was removed by evaporation under reduced pressure to yield a liquid residue (7.2 g, 52%) which was used in the next reaction without further purification.

3-Fluoro-4-hydroxyacetophenone. A mixture of 2-fluorophenyl acetate (7.2 g, 0.052 mol) and $AlCl_3$ (8.6 g, 0.064 mol) was heated at 140° for 30 min. The cooled raw product was added to a mixture of ice and 3N HCl and then shaken with H_2O (3 × 50 ml). The combined org. layers were shaken with conc. Na_2CO_3 soln. (3 × 100 ml). The combined aq. layers were acidified with 25% HCl and then shaken with Et_2O (3 × 50 ml). The combined org. layers were washed with H_2O (250 ml), dil. $NaHCO_3$ soln. (50 ml), and again with H_2O (50 ml), and then dried ($MgSO_4$). The drying agent was removed by filtration and the solvent by evaporation under reduced pressure. The solid residue was crystallised from hexane/AcOEt to yield the pure (99.7%) product (3.7 g, 51%). M.p. 126–127°. IR (KBr): 3239, 1689, 1583, 1521, 1249, 1169, 1020, 848. MS: 154 (M^+).

*3-Fluoro-4-{[(*S*)-1-methylheptyl]oxy}acetophenone.* A mixture of (*S*)-1-methylheptyl 4-toluenesulfonate (2.6 g, 0.009 mol), 3-fluoro-4-hydroxyacetophenone (1.1 g, 0.007 mol), anh. K_2CO_3 (3.9 g, 0.028 mol), and AcOEt

(100 ml) was heated under reflux overnight. The mixture was worked up as described above. CC (toluene) yielded the pure (95%) product (1.6 g, 84%). $[\alpha]_D^{20} = +0.050$ (c = 1.0, $CHCl_3$). IR (film): 2931, 2857, 1689, 1608, 1512, 1270, 1141, 820. MS: 266 (M^+).

3-Fluoro-4-{[(S)-1-methylheptyl]oxy}benzoic Acid. A soln. of Br_2 (1.5 g, 0.0095 mol), NaOH (1.3 g, 0.0320 mol), and H_2O (10 ml) was added dropwise to a soln. of *3-fluoro-4-{[(S)-1-methylheptyl]oxy}acetophenone* (0.5 g, 0.0019 mol) and dioxane (10 ml) at r.t. The resultant soln. was stirred for 1 h at this temp. and then at 55° for 30 min. Sodium-metabisulphite soln. was added to neutralise excess Br_2, and 25% HCl was added to acidify the soln. (pH 3). An oily layer was observed on addition of the acid. The resultant mixture was shaken with CH_2Cl_2 (3 × 30 ml). The combined org. layers were washed with H_2O (250 ml), dil. Na_2CO_3 soln. (100 ml), and H_2O (250 ml), and finally dried ($MgSO_4$), filtered and evaporated down under reduced pressure. The liquid residue was pure (96%) acid (2.5 g, 98%). M.p. 55–57° ([13]: 57–59°). $[\alpha]_D^{20} = +0.048$ (c = 1.0, $CHCl_3$). IR (KBr): 2932, 2857, 1690, 1280, 1195. MS: 268 (M^+).

3'-Bromo-4'-hydroxybiphenyl-4-carbonitrile. A soln. of Br_2 (3.0 g, 0.020 mol) and glacial AcOH (10 ml) was added dropwise to a soln. of 4'-hydroxybiphenyl-4-carbonitrile (3.7 g, 0.019 mol) and glacial AcOH (50 ml) at r.t. The resulting soln. was stirred overnight and then poured onto H_2O (500 ml). The resulting precipitate was filtered off, washed with portions of H_2O, pressed dry, and crystallised from EtOH to yield the pure (99.7%) product (2.7 g, 52%). M.p. 201–202°. IR (KBr): 3340, 2290, 1602, 1492, 1287, 1178, 816. MS: 273, 275 (M^+).

3'-Bromo-4'-{[(S)-1-methylheptyl]oxy}biphenyl-4-carbonitrile. A mixture of (*S*)-1-methylheptyl 4-toluenesulfonate (2.4 g, 0.0082 mol), 3'-bromo-4'-hydroxybiphenyl-4-carbonitrile (2.7 g, 0.0099 mol), anh. K_2CO_3 (4.6 g, 0.0396 mol), and AcOEt (100 ml) was heated overnight under reflux. The mixture was worked up as described above and the residue purified by CC (toluene) to yield the pure product (3.7 g, 97%). IR (film): 2930, 2854, 2227, 1601, 1489, 1275, 1116, 1048, 842. MS: 385, 387 (M^+).

4'-{[(S)-1-Methylheptyl]oxy}biphenyl-4-carbonitrile (92%) was prepared using the same procedure. IR (film): 2928, 2225, 1599, 1490, 1274, 1116, 1049, 838. MS: 307 (M^+).

3'-Bromo-4'-{[(S)-1-methylheptyl]oxy}biphenyl-4-carboxylic Acid. A soln. of 3'-bromo-4'-{[(*S*)-1-methylheptyl]oxy}biphenyl-4-carbonitrile (3.5 g, 0.009 mol), anh. KOH (2.3 g, 0.036 mol), H_2O (0.4 ml, 0.018 mol), and ethylene glycol (100 ml) was heated under reflux for 2 h. The cooled soln. was poured onto 25% HCl (100 ml) and stirred for 30 min. The resultant mixture was shaken with CH_2Cl_2 (3 × 50 ml). The combined org. layers were washed with H_2O (500 ml), dil. Na_2CO_3, soln. (2 × 100 ml), and again with H_2O (250 ml), and finally dried ($MgSO_4$). After filtration to remove inorg. material, the filtrate was evaporated and the solid residue crystallised from EtOH to yield the pure (99.6%) acid (1.4 g, 38%; C-S_A, 107°; S_A-I, 141°). $[\alpha]_D^{20} = +0.121$ (c = 1.0, $CHCl_3$). IR (KBr): 2992, 2856, 2669, 2594, 1675, 1609, 1570, 1520, 1277, 1046, 814. MS: 404, 406 (M^+).

4'-{[(S)-1-Methylheptyl]oxy}biphenyl-4-carboxylic acid was prepared using the same procedure (C-S_C^*, 167°; S_C^*-Ch, 177°; Ch-I, 196°; [14]: C-S_C^*, 160°; S_C^*-Ch, 177°; Ch-I, 196°): IR (KBr): 2933, 2856, 2722, 2546, 1685, 1601, 1560, 1523, 1186, 838. MS: 326 (M^+).

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