50. Ferroelectric Liquid Crystals

Part 3[1])

Achiral Phenyl Benzoates Incorporating a *trans*-4-Pentylcyclohexyl Moiety

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(22.XII.87)

About twenty substituted phenyl benzoates incorporating a *trans*-4-pentylcyclohexyl moiety have been synthesised. The synthesis, liquid-crystal transition temperatures, and enthalpies of fusion are reported. The effect of variations in chainlength and central linkage on the liquid-crystal transition temperatures is discussed.

Introduction. – The synthesis, liquid-crystal transition temperatures, and some other physical properties of a variety of chiral, substituted phenyl benzoates incorporating a *trans*-1,4-disubstituted cyclohexane ring have been reported [1] [2]. The effect of chain length, lateral substituents, and various central linking units on the liquid crystal transition temperatures of these esters was studied systematically. These new compounds can be used to make stable mixtures exhibiting chiral smectic C and nematic mesophases for display device applications [3] [4].

An alternative approach to the preparation of such mixtures is to dope an achiral base mixture exhibiting advantageous liquid-crystal transition temperatures with a chiral substance possessing a high spontaneous polarisation [5] [6]. The advantages of this approach are the increased simplicity of mixture preparation and synthesis.

To produce suitable liquid crystals as basic components of an achiral mixture [5] [6], a variety of substituted phenyl benzoates incorporating a *trans*-1,4-disubstituted cyclohexane ring were prepared corresponding to the analogous chiral esters already reported [1] [2]. The effect of various central linking units (CH_2CH_2, OCH_2, CO–O, O–OC) on the liquid-crystal transition temperatures of the esters was investigated to establish the optimal combination of substituents. These new achiral esters can be used as major components of stable mixtures exhibiting chiral smectic C and chiral nematic mesophases as well as a smectic A mesophase over the desired temperature range for commercial display-device applications [2]. The addition of a chiral substance to these materials is sufficient to induce ferroelectric properties in the smectic C mesophase [2].

Results and Discussion. – The liquid-crystal transition temperatures and enthalpies of fusion of six homologues of the 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-alkoxybenzoates **1** are collated in *Table 1* and plotted against the number of C-atoms (n) in the terminal C-chain attached to the acid part of the esters in *Fig. 1*.

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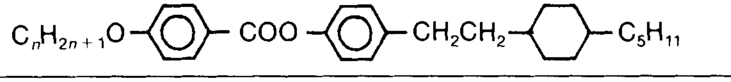
[1]) 'Ferroelectric Liquid Crystals', Part 2: [1].

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



1

C_nH_{2n+1}	C-S_4/S_c	S_4-S_c	S_3-S_c[a])	S_c-S_A/N	S_A-N	N-I	ΔH
C_7H_{15}	67	–	(51)	68	–	160	5.542
C_8H_{17}	68	–	(57)	87	–	158	7.846
C_9H_{19}	68	–	(57)	101	–	154	8.177
$C_{10}H_{21}$	61	–	(59)	110	–	153	5.949
$C_{11}H_{23}$	54	68	–	120	125	149	7.881
$C_{12}H_{25}$	58	78	–	118	132	147	5.699

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

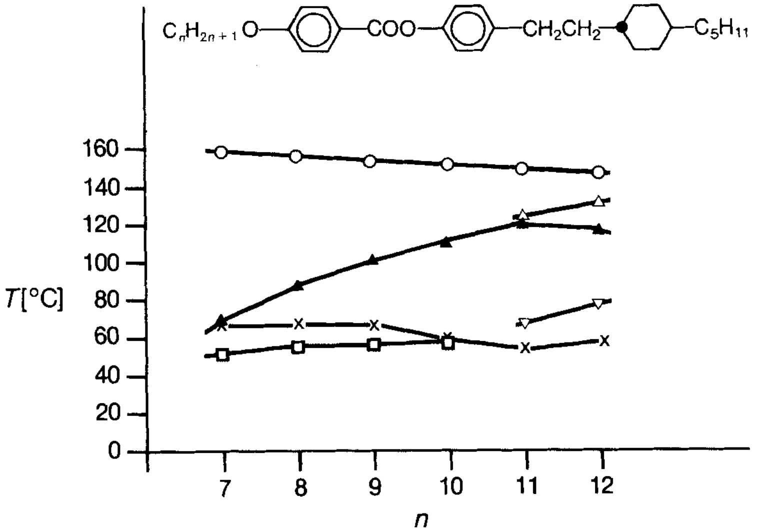
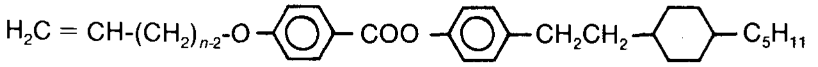


Fig. 1. *Plot of the transition temperatures* vs. *the number of* CH_2 *groups* (*n*) *in the C-chain* (C_nH_{2n+1}) *of the esters* (X, crystal-smectic 4-smectic C transition; ▽, smectic 4-smectic C transition; □, smectic 3-smectic C transition; ▲, smectic C-smectic A/nematic transition; △, smectic A-nematic transition; ○, nematic-isotropic liquid transition)

It can be seen from *Table 1* and *Fig. 1* that the clearing points (N-I) of the esters decrease proportionately as the C-chain lengthens. The melting points (C-S_4, C-S_c) are irregular, but show a general tendency to decrease with increasing alkyl-chain length. The early members of the series (*n* = 7–10) exhibit a monotropic smectic mesophase transition (S_3-S_c), while the two remaining homologues possess an enantiotropic ordered smectic mesophase (S_4) and a smectic A mesophase. All six homologues exhibit an enantiotropic smectic C mesophase transition (S_c-N, S_c-S_A) which increases with increasing C-chain before reaching a maximum (*n* = 11) and decreasing slightly. Thus, two homologues (*n* = 11, 12) of the esters **1** exhibit the desired liquid-crystal mesophases (S_c, S_A, and N) for display device applications [2–4].

The liquid-crystal transition temperatures of the esters **1** compare favorably with those of the analogous esters [8] with a Ph ring instead of the cyclohexane ring. Compar-

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



2

n	C-S_4/S_c	S_4-S_c[a])	S_3-S_c[a])	S_c-S_A/N	S_A-N	N-I	ΔH
7	69	–	–	53	–	159	8.649
8	62	–	(44)	73	–	153	7.733
9	55	(44)	–	92	–	153	6.861
10	69	(57)	–	104	110	148	9.622
11	51	69	–	101	124	148	6.991
12	57	76	–	99	127	143	

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

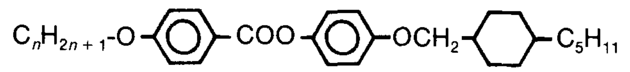
ing only those homologues with the same number of CH_2 units in the terminal C-chains, the melting points (C-S_4, C-S_c) and the transition temperatures of the ordered smectic mesophases (S_4-S_c, S_3-S_c) are lower on average (9°, 13°, and 12°, respectively) for the esters **1** than those of the corresponding fully aromatic esters [8]. The smectic-C-to-nematic transition temperature (S_c-N) is also lower, approximately to the same extent (7°). The smectic-A-to-nematic transition temperature (S_A-N) and the clearing point (N-I) are both higher (9° and 29°, respectively, on average) for the esters **1**.

In *Table 2* are to be found the liquid-crystal transition temperatures (C-S_4/S_c, S_4-S_c, S_c-S_A/N, S_A-N, N-I) of the compounds **2** corresponding to the compounds **1**, but containing an additional double bond (C=C) in the terminal C-chain attached to the acid moiety.

Comparison of the data in *Tables 1* and *2* reveals that the melting points (C-S_4/S_c) and clearing points (N-I) of the esters **1** and **2** are almost identical (63° and 155°; 61° and 152°, respectively). All the other transition temperatures (S_4-S_c, S_3-S_c, S_c-S_A/N, S_A-N) are lower, almost to the same degree (12–16°), for the alkenyl esters **2** compared with those of the analogous alkyl esters **1**. The ordered smectic phases (S_3 and S_4) appear earlier in the homologous series **2** than in **1**. Thus, the double bond in a terminal position in the alkyl chain of these mesogens does not change the liquid-crystal transition temperatures to a large extent.

The liquid-crystal transition temperatures (C-S_3/S_c, S_3-S_c, S_c-N, N-I) and some ΔH values of six homologues of the 4-[(*trans*-4-pentylcyclohexyl)methoxy]phenyl 4-alkoxy-

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



3

C_nH_{2n+1}	C-S_3/S_c	S_3-S_c[a])	S_c-N	N-I	ΔH
C_7H_{15}	80	(71)	90	163	6.677
C_8H_{17}	81	(76)	107	163	4.595
C_9H_{19}	75	(74)	110	156	6.290
$C_{10}H_{21}$	78	72	114	154	6.070
$C_{11}H_{23}$	66	76	125	154	6.895
$C_{12}H_{25}$	73	81	129	152	

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

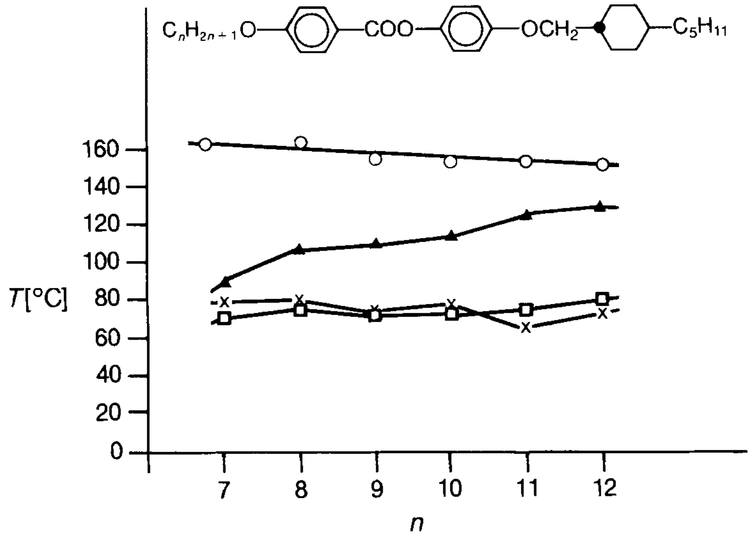


Fig. 2. *Plot of the transition temperatures* vs. *the number of CH_2 groups (n) in the C-chain* (C_nH_{2n+1}) *of the esters* (X, crystal-smectic 3-smectic C transition; □, smectic 3-smectic C transition; ▲, smectic C-nematic transition; ○, nematic-isotropic liquid transition)

benzoates **3** are listed in *Table 3* and plotted against the number of C-atoms (*n*) in the terminal C-chain attached to the acid part of the esters *(Fig. 2)*.

The trends in the liquid-crystal transition temperatures of the ethers **3** are similar to those of the corresponding ethyl compounds **1** which contain a CH_2 unit instead of an O-atom. The major differences in the thermal data are the absence of two smectic mesophases (S_4 and S_A) and the higher absolute values for the ethers **3**. The ΔH values are somewhat lower on average (-0.725 Kcal·mol^{-1}).

The thermal data (C-S_3/S_c, S_3-S_c, S_c-S_A/N, S_A-N, N-I) of the compounds **4** incorporating an additional double bond (C=C) in the therminal C-chain are recorded in *Table 4*.

Comparison of the liquid-crystal transition temperatures collected in *Tables 3* and *4* reveals that the values for the alkenyl esters **4** are consistently lower (11°, on average) than those of the corresponding alkyl esters **3**. This is a similar depression to that observed for the corresponding esters **1** and **2** (13°, on average) with a CH_2 unit instead of an O-atom in the second linkage.

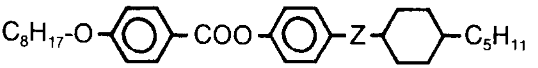
Table 4. *Transition Temperatures* [°C] *and Enthalpies of Fusion* [Kcal·mol^{-1}] *for Compounds* **4**

$H_2C=CH\text{-}(CH_2)_{n-2}\text{-}O$–⟨⟩–COO–⟨⟩–$OCH_2$–⟨⟩–$C_5H_{11}$ **4**

n	C-S_3/S_c	S_3-S_c[a])	S_c-N	N-I	ΔH
7	73	–	80	158	5.935
8	58	63	88	150	4.908
9	69	(62)	100	152	6.185
10	71	(64)	112	148	5.378
11	68	76	120	147	6.803
12	71	72	122	148	

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

Table 5. *Transition Temperatures* [°C] *for Compounds of Structure:*



Compound	Z	C-S	S_2-S_c[a])	S_c-N	S_A-N	N-I
1	CH_2CH_2	68	(57)	87	–	158
3	OCH_2	81	(73)	104	–	163
5	–	81	(65)	97	–	182
6	CO–O	87	(76)	107	–	201
7	O–OC	84	–	–	98	170

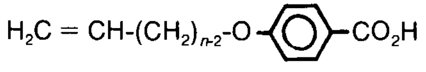
[a]) ( ) Indicates a monotropic transition temperature.

The liquid-crystal transition temperatures of five substituted phenyl benzoates **1**, **3**, and **5**–**7** containing a *trans*-pentyl cyclohexyl moiety and a central linking unit Z are listed in *Table 5*.

The most remarkable feature of the thermal data recorded in *Table 5* is their similarity. The liquid-crystal transition temperatures of the first four esters **1**, **3**, **5**, and **6** differ on only a moderate extent (maximum 25°) from their average values (C-S, 79°; S_2-S_c, (68°), S_c-N, 99°; N-I, 176°) despite large differences in the rigidity, linearity, and polarisability of the four central linkages Z. The fifth ester **7** does not exhibit an observable smectic C or ordered smectic mesophase, but does possess an additional smectic A mesophase. Despite these differences, the melting point (C-S_A) and clearing point (N-I) show minor divergences (+5° and −6°, respectively) from the average values for the first four esters **1**, **3**, **5**, and **6**. These trends are similar, although not exactly identical, to those observed for the analogous esters containing a (*S*)-6-methyloctyloxy C-chain instead of the octyloxy C-chain of the esters **1**, **3**, and **5**–**7** [1] [2].

The liquid-crystal transition temperatures of an homologous series of 4-(alkenyloxy)benzoic acids, prepared as intermediates for the final products **2** and **4**, are recorded in *Table 6*. The clearing points (N-I) of the acids show the normal pattern of alternation [9] and decrease with increasing number (*n*) of CH_2 units in the terminal C-chain. The melting points (C-S_c/N) exhibit a similar trend, while remaining irregular. The smectic C to nematic transition temperatures (S_c-N) vary in a most unusual way.

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



n	C-S_c/N	S_c-N	N-I	*n*	C-S_c/N	S_c-N	N-I
4	116	–	141	9	90	108	142
5	125	–	151	10	77	116	137
6	101	–	141	11	81	124	138
7	89	132	149	12	73	123	131
8	78	122	139				

Experimental Part

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

General. See [1].

*4-[2-(*trans*-4-Pentylcyclohexyl)ethyl]phenyl 4-(Octyloxy)benzoate* (**1**; *n* = 8). A soln. of 4-(octyloxy)benzoic acid (0.46 g, 0.0018 mol), 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenol [1] (0.5 g, 0.0018 mol), DMAP (0.04 g), DCC (0.45 g, 0.0022 mol), and CH_2Cl_2 (50 ml) was stirred at r.t. overnight and then filtered to remove precipitated material. The filtered soln. was evaporated under reduced pressure and the solid residue eluted down a silica-gel column using toluene. The ester thus obtained was crystallised from EtOH until constant transition temp. were obtained (see *Tables 1–4* for the liquid-crystal transition temp. of this ester and other esters **1**–**4** prepared using this method). IR (KBr): 3430*m*, 2916*s*, 2850*s*, 1725*s*, 1606*m*, 1511*m*, 1470*w*, 1315*w*, 1257*s*, 1202*m*, 1170*s*, 1076*m*, 847*m*. MS: 233 ($C_{15}H_{21}O_2^+$).

trans-*4-Pentylcyclohexyl 4-{{[4-(Octyloxy)phenyl]carbonyl}oxy}benzoate* (**6**) was prepared by the esterification of 4-{[4-(octyloxy)benzoyl]oxy}benzoic acid and *trans*-4-pentylcyclohexanol [7] as described above for **1** (see *Table 5* for the liquid-crystal transition temp.). IR (KBr): 1708*s*, 1604*s*, 1511*m*, 1266*s*, 1208*s*, 847*m*. MS: 353 ($C_{22}H_{25}O_4^+$).

4-{[4-(Octyloxy)benzoyl]oxy}benzoic Acid. Jones reagent (4 ml) was added dropwise to a soln. of 4-formylphenyl 4-(octyloxy)benzoate (4 g, 0.011 mol) and anh. acetone (100 ml) cooled *via* an ice-bath. A white precipitate could be observed after the addition was completed. The mixture was stirred at r.t. for a further 2 h and then added to ice (500 g) and stirred for 30 min. The white solid was filtered off, washed with H_2O, pressed dry, and crystallised from EtOH to yield pure acid (2.2 g, 53%; C-S_c, 139°; S_c-N, 164°; N-I, 221°). IR (KBr): 2853*m*, 2670*w*, 2557*w*, 1734*s*, 1687*s*, 1603*s*, 1510*m*, 1255*m*, 1158*s*, 1063*s*, 847*m*. MS: 233 ($C_{15}H_{21}O_2^+$).

4-Formylphenyl 4-(Octyloxy)benzoate. A soln. of 4-(octyloxy)benzoic acid (5.0 g, 0.020 mol), 4-hydroxybenzaldehyde (2.5 g, 0.020 mol), DMAP (0.04 g), DCC (5.0 g, 0.024 mol), and CH_2Cl_2 was stirred at r.t. overnight. The solvent was removed from the filtered soln. under slightly reduced pressure to yield raw product which was purified by column chromatography using toluene and crystallisation from hexane at 0° to yield pure aldehyde (5.5 g, 77%; C-N, 59°; N-I, 68°). IR (KBr): 2739*w*, 1736*s*, 1699*s*, 1605*s*, 1511*m*, 1269*s*, 845*m*. MS: 233 ($C_{15}H_{21}O_2^+$).

*4-{[(*trans*-4-Pentylcyclohexyl)carbonyl]oxy}phenyl 4-(Octyloxy)benzoate* (**7**) was prepared by the esterification of *trans*-4-pentylcyclohexane-1-carboxylic acid [7], and 4-hydroxyphenyl 4-(octyloxy)benzoate as described above for the esters **1**. IR (KBr): 1725*s*, 1729*s*, 1605*s*, 1506, 1257*s*, 1164*s*, 1071*m*, 847*m*. MS: 233 ($C_{15}H_{21}O_2^+$), 121 ($C_7H_5O_2^+$).

4-(10-Undecenyloxy)benzoic Acid. A soln. of methyl 4-(10-undecenyloxy)benzoate (30 g, 0.0985 mol), anh. KOH (30 g, 0.5357 mol), EtOH (400 ml), and H_2O (40 ml) was heated at 75° overnight. A white precipitate was observed, and 25% HCl (500 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%) acid (20 g, 97%; see *Table 6* for the liquid-crystal transition temp. of this acid and other acids prepared using this method).

Methyl 4-(10-Undecenyloxy)benzoate. A mixture of 10-undecencyl *p*-toluenesulfonate (40 g, 0.123 mol), methyl 4-hydroxybenzoate (16 g, 0.103 mol), anh. K_2CO_3 (57 g, 0.410 mol), and $CH_3COC_2H_5$ (200 ml) was heated under reflux overnight. The cooled mixture was added to H_2O (1000 ml), shaken with Et_2O (3 × 100 ml), and the combined org. layers were washed with H_2O (2 × 500 ml) and dried ($MgSO_4$). After removal of the solvent under reduced pressure, the residue was purified by filtration over silica gel using toluene and subsequent crystallisation from hexane to yield pure product (32 g, 85%). M.p. 35–36°.

10-Undecenyl p*-Toluenesulfonate.* A soln. of TsCl (59 g, 0.308 mol) and anh. pyridine (100 ml) was added dropwise to a soln. of 10-undecenol (50 g, 0.294 mol) cooled *via* an ice-bath so that the internal temp. did not rise above 5°. A white precipitate was observed to form during the next 8 h, while the mixture was stirred and cooled *via* the ice-bath. H_2O (500 ml) was added and the resultant soln. stirred for a further 2 h and then shaken with Et_2O (3 × 100 ml). The combined org. layers were washed with 25% HCl (2 × 250 ml), H_2O (1 × 500 ml), dil. $NaHCO_3$ (1 × 500 ml), H_2O (1 × 500 ml), and dried ($MgSO_4$). After removal of the drying agent by filtration and the solvent under partially reduced pressure, the raw product (91 g, 96%) was used immediately in the next reaction without further purification.

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