Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Four unit linking groups II. Some novel smectic C materials

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To cite this Article Kelly, S. M. , Fünfschilling, J. and Leenhouts, F.(1991) 'Four unit linking groups II. Some novel smectic C materials', Liquid Crystals, 10: 2, 243 — 260
To link to this Article: DOI: 10.1080/02678299108036429
URL: http://dx.doi.org/10.1080/02678299108036429

LIQUID CRYSTALS, 1991, VOL. 10, NO. 2, 243–260

Four unit linking groups
II. Some novel smectic C materials

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(*Received 29 August 1990; accepted 23 October 1990*)

About 40 diverse phenyl benzoate esters incorporating a *trans*-1-4-disubstituted cyclohexane ring joined to the central aromatic core by new four unit linking groups (C_4H_8, C_4H_6, C_3H_6O and C_3H_4O) have been synthesized. The effect of various lateral substituents (F, Cl, CN and Br) and especially two fluorine atoms in the 2,3-positions of the 4-*n*-alkoxybenzoate part of the esters has been investigated. Three homologous series of 5-*n*-alkyl-2-(4-phenyl)pyrimidines incorporating the same four unit linking groups have also been prepared. Many members of the ester and pyrimidine series exhibit enantiotropic smectic C mesophases at moderately elevated temperatures. Several esters and pyrimidines have been found to improve the surface alignment and temperature range of chiral smectic C mixtures for surface stabilized ferroelectric liquid crystal displays. The effect of the new four unit linking groups on the liquid crystal transition temperatures, rotational viscosity and spontaneous polarization of their host structures in a standard chiral C mixture has been studied and compared to that of analogous materials containing no central linkage and standard central linkages (—, C_2H_4, CH_2O and COO). Several lactate ester derivatives incorporating the four unit linking groups have also been prepared and been found to exhibit a moderately high spontaneous polarization.

1. Introduction

The synthesis, liquid crystal transition temperatures [1–4], and some other physical properties [5, 6] of a wide variety of substituted phenyl benzoates incorporating a *trans*-1,4-disubstituted cyclohexane ring have been reported recently [1–6]. The effect of chain length, lateral substituents, optically active centres, and several two unit linking groups as well as single bonds on the liquid crystal transition temperatures, viscosity and spontaneous polarization of these substituted phenyl benzoate esters has been investigated systematically. It was found that the presence of a lateral substituent, especially a fluorine atom, on one or both of the aromatic rings of the esters can give rise to a broadening of the smectic C mesophase range, without increasing the viscosity excessively [1–6] and, for the optically active esters, to a substantial increase in the spontaneous polarization [5, 6]. The scope of these investigations has now been increased to include a systematic study of the effect of four separate four unit linking groups in analogous structures to those mentioned on the liquid crystal transition temperatures, viscosity and spontaneous polarization of such esters. The 3-propyloxy, (*E*)-3-allyloxy, 4-butyl and (*E*)-3-butenyl central linkages (C_3H_6O, C_3H_4O, C_4H_8 and C_4H_6, respectively) were shown recently to be suitable linking units for a wide range of

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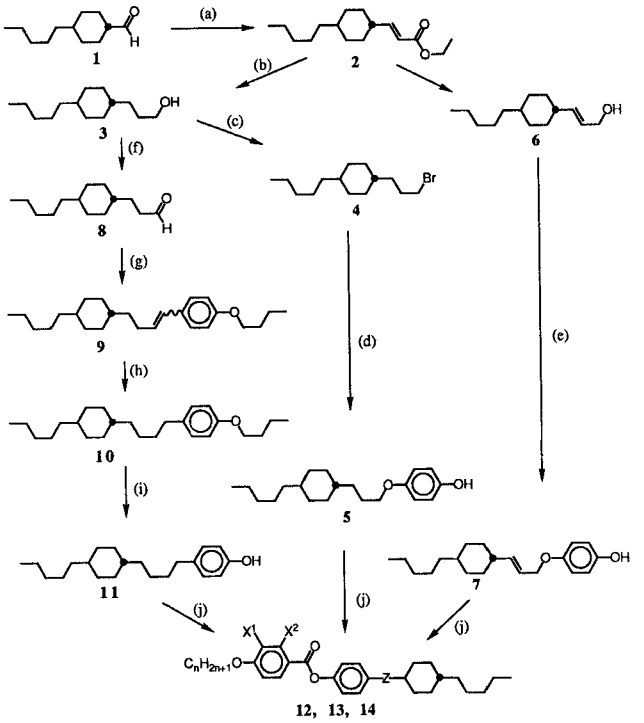
0267–8292/91 $3·00

liquid-crystalline structures [7]. A homologous series of 5-*n*-alkyl-2-phenylpyrimidines and several lactate acid ester derivatives have also been prepared containing the new linking units as these structures have also been shown to be of commercial interest for electrooptic display device applications [7–10].

2. Synthesis

The reaction sequence leading to the esters **12**, **13** and **14** is shown in scheme 1. The *trans*-acrylate ester **2** was prepared via a Wittig–Horner reaction [11] using the aldehyde **1** [12] as starting material. Reduction of the *trans*-acrylate **2** to the propanol **3** proceeded with subsequent hydrogenation of the carbon–carbon double bond using lithium–aluminium hydride. Bromination of the alcohol **3** yielded the bromide **4**, which was used in a Williamson ether synthesis with hydroxyquinone to give the phenol **5**. Esterification [13] of the phenol **5** with the required substituted 4-(*n*-alkoxy)benzoic acids [4], DCC and DMAP [13] gave the propyloxy esters **12** ($Z = C_3H_6O$).

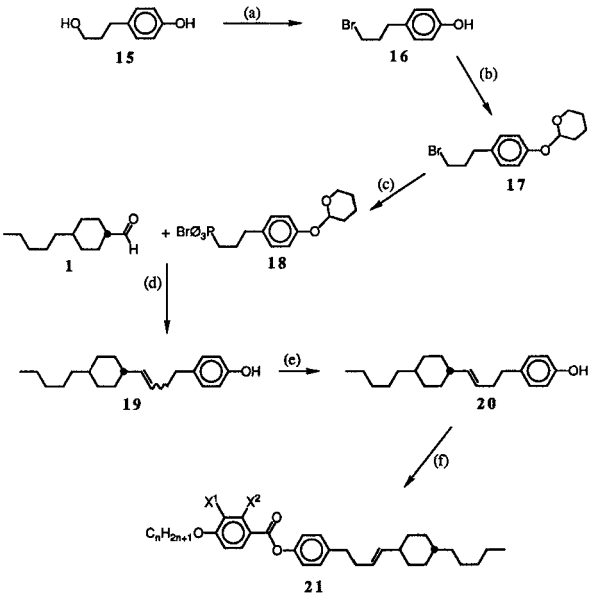


Scheme 1. (*a*) $P(OC_2H_5)_2CH_2CO_2C_2H_5$/KOH/tetrahydrofuran, (*b*) $LiAlH_4$/ether, (*c*) Br_2/TPP/acetonitrile, (*d*) K_2CO_3/HO–C_6H_4–OH/butanone, (*e*) DEAD/TPP/HO–C_6H_4–OH/tetrahydrofuran, (*f*) CrO_3/HCl/pyridine, (*g*) Wittig salt/$KOC(CH_3)_3$/tetrahydrofuran, (*h*) Pd/C/ethyl acetate, (*i*) BBr_3/dichloromethane, (*j*) DCC/DMAP/dichloromethane.

Reduction of the *trans*-acrylate **2** with diisobutylaluminium hydride [14] yielded the corresponding *trans*-allylalcohol **6**, which was used in a Mitsunobu reaction [15] with hydroxyquinone to prepare the phenol **7**. Esterification in the normal way of the phenol **7** with the required 4-(*n*-alkoxy)-2,3-difluorobenzoic acids [4] gave the desired alkoxy substituted esters **13** ($Z = C_3H_4O$).

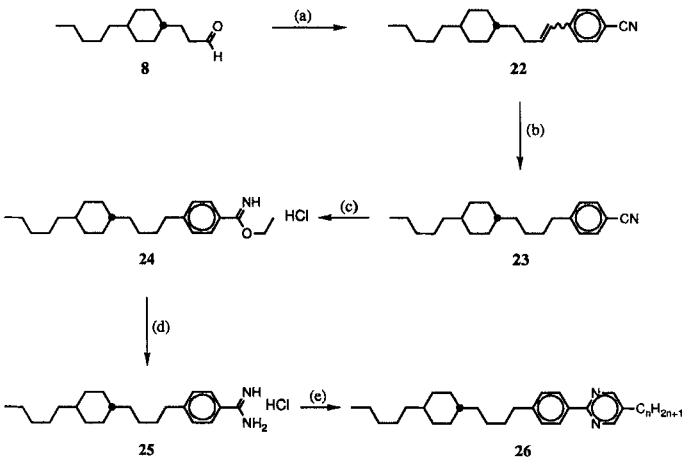
Oxidation of the alcohol **3** with pyridine chlorochromate [16] to the corresponding aldehyde **8** followed by a Wittig reaction yielded the aromatic substituted butene **9** as a mixture of *trans* and *cis* isomers (*E*/*Z*). Hydrogenation using palladium on charcoal yielded the ether **10**, which was dealkylated using borontribromide [17], to the phenol **11**, which in turn gave the desired butyl substituted esters **14** ($Z = C_4H_8$) in the usual way [13] with DCC.

The synthesis of the esters **21** incorporating a *trans* carbon–carbon double bond in the central butene linkage ($Z = C_4H_6$) is demonstrated in scheme 2. Bromination of the alcohol **15** with tetrabromomethane and triphenylphosphine [18] led to the 4-(1-bromo-3-propyl)phenol **16**, which was protected as the tetrahydropyranyl ether **17**, before being converted to the Wittig salt **18**. The subsequent Wittig reaction with the aldehyde **1** led directly to the phenol **19**, with loss of the protecting group during the reaction. The primary *cis* product **19** ($E/Z \approx 9:1$) was isomerized using benzene sulphinic acid [19] to give the pure *trans* isomer **20**, which was converted in the usual way [13] to the desired butenyl substituted esters **12**.



Scheme 2. (*a*) CBr_4/TPP/dichloromethane, (*b*) DHP/$[(CH_3)_3Si]_2SO_2$/dichloromethane, (*c*) TPP/dimethylformamide, (*d*) C_4H_9Li/*tert.*-butyl methyl ether, (*e*) $C_6H_5SO_2H$/ethanol, (*f*) DCC/DMAP/dichloromethane.

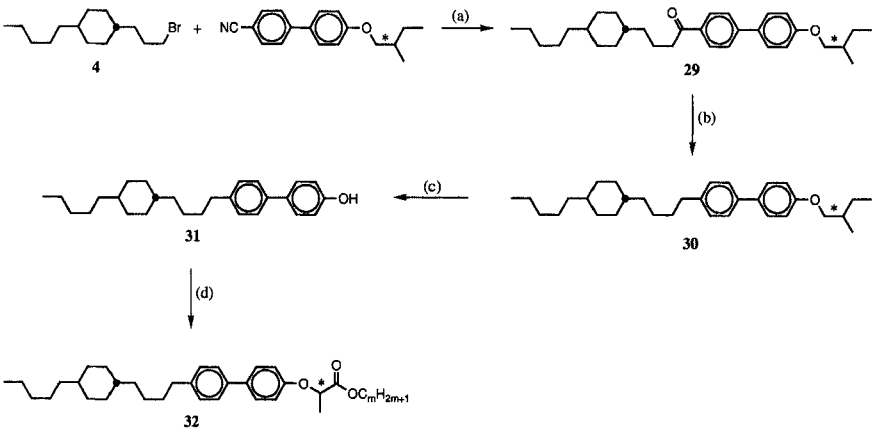
The preparation of the substituted butyl phenylpyrimidines **26** is shown in scheme 3. The nitrile **23** prepared from the aldehyde **8** via a Wittig reaction and hydrogenation of the product **22**, was converted into the amidine hydrochloride salt **25** via the imidoethyl ether **24** using first hydrogen chloride and then ammonia in the usual way [9]. Conversion of the benzamidine **25** to the desired product **26** using 2-(methoxymethylidene)dodecanal [9] completed the synthesis of this butyl substituted product. The short reaction sequences leading to the various pyrimidines **27** and **28** are described in the experimental part and require no comment.



Scheme 3. (*a*) Wittig salt/$KOC(CH_3)_3$/tetrahydrofuran, (*b*) Pd/C/ethyl acetate, (*c*) HCl/EtOH/toluene, (*d*) NH_3/EtOH, (*e*) $C_nH_{2n+1}C(CHO)CHOCH_3/NaOCH_3/CH_3OH$.

The optically active lactates **32** were prepared as depicted in scheme 4 from the corresponding phenol **31** and the required *L*-(+)-lactates in a Mitsunobu reaction [15] with inversion of the configuration at the chiral centre [20]. The phenol **31** was prepared by dealkylation using borontribromide of the corresponding ether **30**, produced by the hydrogenation of the ketone product **29** of the Grignard reaction between the nitrile [21] and the bromide **4**.

The synthesis of two further optically active chiral dopants **34** and **35** using only the Mitsunobu reaction [15, 20] is also exemplified in the experimental section.

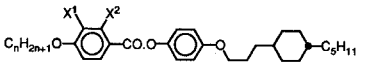


Scheme 4. (*a*) Mg/ether/HCl, (*b*) Pd/C/ethyl acetate, (*c*) BBr_3/dichloromethane, (*d*) DEAD/TPP/$HOC^*H(CH_3)CO_2C_mH_{2m+1}$/tetrahydrofuran.

3. Results

The liquid crystal transition temperatures and some enthalpies of fusion of the 4-[3-*trans*-4-(pentylcyclohexyl)propyloxy]phenyl 4-(alkoxy)benzoates **12** are collated in table 1. The melting point (T_{CS_2} and T_{CS_C}) is relatively independent of the chain length (*n*), although a slight tendency towards decreasing melting point with increasing chain

Table 1. Liquid crystal transition temperatures and enthalpies of fusion for the esters of the structure:



n	X^1	X^2	T_{CS_2/S_C}/°C	$T_{S_2S_C}$/°C	T_{S_CN}/°C	T_{NI}/°C	ΔH/kJ mol^{-1}
7	H	H	74	(67)	86	148	43·2
8	H	H	68	(67)	99	147	37·4
9	H	H	77	(68)	109	144	49·7
10	H	H	64	(70)	116	143	
11	H	H	75	(71)	121	141	38·0
12	H	H	58	75	125	140	27·0
7	F	F	79	—	94	139	43·2
8	F	F	70	—	103	138	37·0
9	F	F	73	—	110	136	45·8
10	F	F	68	—	115	135	41·0
11	F	F	68	—	118	133	47·5
12	F	F	66	—	121	133	45·9
12	F	H	69	—	120	129	22·2
12	Cl	H	60	—	105	122	40·9
12	CN	H	103	—	(97)	(100)	
12	Br	H	70	—	92	112	45·5

length may be observed. The smectic C–nematic transition temperature (T_{S_CN}) and the ordered smectic C mesophase (S_2, as yet unidentified)–smectic C transition temperature ($T_{S_2S_C}$) both increase with increasing chain length. However, the smectic C–nematic transition temperature increases more dramatically than the ordered smectic mesophase–smectic C transition temperature, which leads to a broadening of the smectic C mesophase range (20°C→50°C). The nematic–isotropic transition decreases marginally on lengthening the carbon chain, which, with the increasing smectic C–nematic transition temperature, leads to a narrowing of the nematic temperature range.

The introduction of two fluorine atoms in the 2 and 3 positions of the acid moiety of the esters **12** ($X^1 = X^2 = F$) leads on average to a small increase (+8°C) in the melting point (T_{CS_2}) and (T_{CS_C}), a minimal increase (+1°C) in the smectic C–nematic transition temperature (T_{S_CN}) and a small decrease (−8°C) in the clearing point (T_{NI}). A significant difference between the non-fluoro-substituted ($X^1 = X^2 = H$) and the 2,3-difluoro-substituted ($X^1 = X^2 = F$) esters **12** is the absence of an ordered smectic mesophase for the latter materials. Similar behaviour has been observed for related esters [3, 4].

The presence of a lone lateral substituent (X^1 = F, Cl, CN, Br; $X^2 = H$) in the 2-position of the acid part of the esters **12** results in the absence of an ordered smectic mesophase and a general decrease in the smectic C–nematic transition temperature (T_{S_CN}) and the clearing point (T_{NI}). On average the melting point (T_{CS_2}) and (T_{CS_C}) is increased substantially (+18°C) which leads to a significant decrease (−22°C) in the smectic C mesophase range. This behaviour has been rationalized in terms of steric effects dependent on the size of the lateral substituent [1–4].

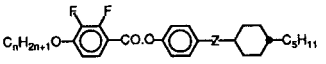
The liquid crystal transition temperature and the enthalpies of fusion of the esters **12–14** and **21** are collated in table 2. The four homologous series (n = 7–12) of the esters **12**, **13**, **14** and **21** differ only in the nature of the central linking unit ($Z = C_3H_6O$, C_3H_4O, C_4H_8, C_4H_6, respectively). The four series are characterized by the presence of only one smectic modification (S_C), which may be attributed to the dominating effect of

the 2,3-difluoro-4-(alkoxy)benzoic acid moiety [4]. Further common properties are the increasing smectic C–nematic transition temperatures (T_{ScN}) and decreasing clearing points (T_{NI}) associated with an increasing chain length ($n = 7$–12). As is often the case, definite tendencies in the melting point (T_{CSc}) are difficult to determine and evaluate quantitatively. The presence of a double bond in the central linking unit (C_4H_6) or an oxygen atom (C_3H_6O or C_3H_4O) leads on average to an increase (+7°C, +18°C, +18°C and +15°C, +14°C, +18°C, respectively) in the smectic C–nematic transition temperature and the clearing point, with respect to the transition temperatures of the corresponding butyl-esters **14** ($Z = C_4H_8$). The melting point (T_{CSc}) also increases (0°C, +6°C and +11°C), but less markedly.

The liquid crystal transition temperature and some enthalpies of fusion of the 5-*n*-alkyl-2-substituted phenylpyrimidines **26**, **27** and **28** are collated in table 3. The melting points (T_{CS_3}), (T_{CSc}) and (T_{CN}) of all three homologous series of butyl, 3-propyloxy, (*E*)-3-allyloxy derivatives (**26, 27** and **28,** respectively) are on average very similar (74°C, 79°C, and 81°C, respectively). The butyl compounds **26** exhibit on average a smectic C mesophase and clearing point (T_{NI}) at lower temperatures (77°C and 113°C, respectively) than the corresponding 3-propyloxy (100°C and 135°C, respectively) or (*E*)-3-allyloxy (100°C and 139°C, respectively) compounds.

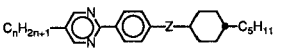
It has been found that the 5-*n*-alkyl-2-([4-*trans*-4-pentylcyclohexyl)-1-butyl] phenyl)pyrimidines **26** dissolved in small concentrations in standard chiral smectic C

Table 2. Liquid crystal transition temperatures and enthalpies of fusion for the esters of the structure:



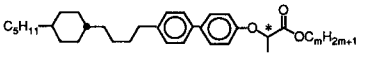
n	*Z*	T_{CSc}/°C	T_{ScN}/°C	T_{NI}/°C	ΔH/kJ mol^{-1}
7	~_/~	67	70	128	—
8	~_/~	70	82	123	30·2
9	~_/~	71	91	121	—
10	~_/~	69	96	120	29·6
11	~_/~	58	103	119	49·9
12	~_/~	56	107	118	—
7	~\=/~	55	77	140	15·3
8	~\=/~	75	88	140	27·7
9	~\=/~	77	99	137	27·3
10	~\=/~	72	106	136	25·5
11	~\=/~	60	111	134	—
12	~\=/~	51	115	133	25·4
7	~_O~	79	94	139	43·2
8	~_O~	70	103	138	37·0
9	~_O~	73	110	136	45·6
10	~_O~	68	115	135	41·0
11	~_O~	68	118	133	47·5
12	~_O~	66	121	133	45·9
7	~\=O~	73	95	144	17·6
8	~\=O~	76	106	143	18·0
9	~\=O~	74	114	141	22·3
10	~\=O~	80	119	140	24·5
11	~\=O~	77	121	137	24·0
12	~\=O~	73	124	137	—

Table 3. Liquid crystal transition temperatures and enthalpies of fusion for the pyrimidines of the structure:



n	Z	T_{CS_3/S_CN}/°C	$T_{S_3S_C}$/°C	$T_{S_CS_AN}$/°C	T_{S_AN}/°C	T_{NI}/°C	ΔH/kJ mol^{-1}
5		78	—	—	—	119	—
6		79	—	—	—	113	18·9
7		77	—	—	—	116	18·6
8		69	—	(64)	—	110	15·5
9		74	(62)	82	97	113	15·9
10		66	71	86	102	109	—
5		82	—	—	—	139	19·2
6		74	—	—	—	135	—
7		84	—	—	—	137	16·1
8		79	—	88	—	133	25·3
9		83	—	103	—	133	—
10		69	—	110	—	130	32·2
5		77	—	—	—	144	—
6		83	—	—	—	139	18·1
7		91	—	—	—	141	18·5
8		87	—	88	—	138	17·2
9		79	—	102	—	138	—
10		68	—	110	—	134	—

Table 4. Liquid crystal transition temperatures and enthalpies of fusion for the lactate esters of the structure:

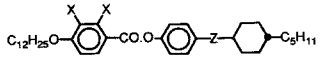


m	T_{CS_B}/°C	T_{S_BI}/°C	ΔH/kJ mol^{-1}
1	66	98	14·3
2	71	76	
3	40	78	28·2
4	59	69	

mixtures [5, 6] induce an excellent surface alignment of the smectic C director as well as depressing the melting point of the host mixture. Thus the switching properties, contrast and temperature range of the chiral smectic C mesophase are improved for surface stabilized ferroelectric liquid crystal displays [22].

In table 4 we list the liquid crystal transition temperatures and some enthalpies of fusion for the optically active lactate acid derivatives **32**. The short homologous series ($n = 1$–4) only possesses an enantiotropic smectic mesophase (S_B) which exhibits the normal pattern of alternation. No chiral mesophases could be observed. These optically active esters can be used as chiral dopants in base achiral smectic C mixtures to induce a spontaneous polarization.

Table 5. Liquid crystal transition temperatures, rotational viscosity $\gamma_{eff} = \gamma \sin^2 \theta$, S_C^* tilt angle θ, spontaneous polarization P_s and γ, the calculated rotational viscosity for a nematic-like structure with $\theta = 90°$ for the esters of the structure below for a 13 mol % mixture with a chiral smectic C base mixture.



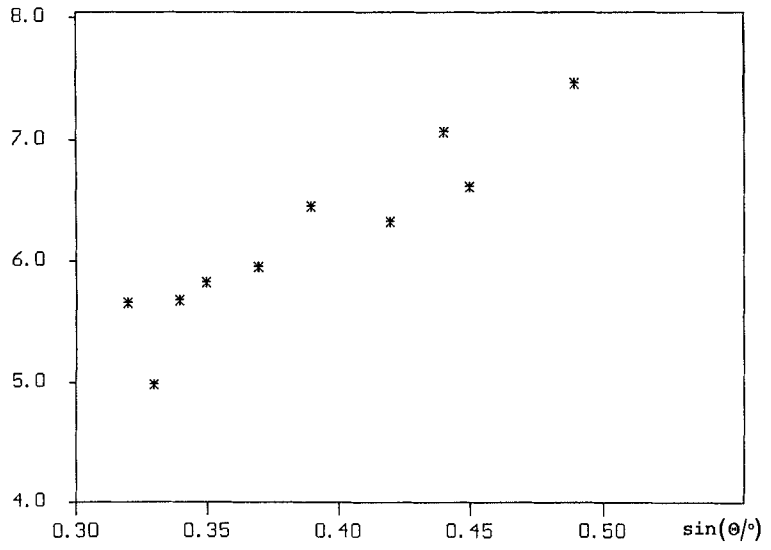
Z	X	T_{CS_A/S_C}/°C	$T_{S_AS_C}$/°C	$T_{S_CS_A/N}$/°C	T_{S_AN}/°C	T_{NI}/°C	θ/°	γ/mPa s	$\gamma \sin^2 \theta$	P_s/nC cm^{-2}
	H	58	78	118	132	147	21·5	378	50·8	5·94
	H	73	81	129	—	153			76·0	6·50
	H	72	94	121	141	160	20·3	363	43·7	5·81
	H	55	79	113	117	128				
	H	56	94	124	—	141				
	H	58	75	125	—	140				
	H	77	(76)	127	—	144				
	F	64	—	114	—	138	29·2	383	91·3	7·44
	F	77	—	122	—	143				
	F	67	—	116	—	153				
	F	56	—	107	—	118	26·9	528	108·1	6·60
	F	51	—	115	—	133				
	F	66	—	121	—	133			154·5	7·84
	F	73	—	124	—	137				

4. Discussion

The liquid crystal transition temperatures of two separate series of known esters [1–4] and the esters **12**, **13**, **14** and **21** differing only in the presence of two fluorine atoms in the 2 and 3 positions of the acid moiety and in the nature of the central linking unit (*Z*) are collated in table 5. The salient differences in the two sets of parallel data are the absence of ordered smectic mesophases or of a smectic A mesophase. The melting points differ on average marginally (+1°C), whereas both the smectic C–nematic transition temperatures and the clearing point of the difluoro-substituted esters are on average lower (−6°C and −9°C) than the non-substituted esters. The absence of an ordered smectic mesophase for the difluoro-substituted esters leads on average to a broadening of the smectic C mesophase temperature range (+11°C) as shown in the Results section. A notable characteristic of both series of esters is the remarkable similarity in the transition temperatures of the esters incorporating no central linkage (*Z* = —), a two unit and a four unit linkage (C_2H_4, CH_2O and C_4H_8; C_4H_6, C_3H_6O and C_3H_4O; respectively). All of the variation in the liquid crystal transition temperatures observed for both series (±20°C) are surprisingly small. The presence of a double bond or an additional oxygen atom in the central linking unit of the esters increases both the smectic–nematic and nematic–isotropic transition temperatures. Similar tendencies in the transition temperatures of a series of phenylpyrimidines are shown in table 6.

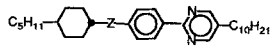
In the figure the measured values for the spontaneous polarization (P_s) of the mixtures in tables 5 and 6 are plotted versus $\sin(\Theta)$($\Theta = S_C^*$ tilt angle), displaying a linear relationship between these two quantities. The variations in P_s are thus primarily due to a variation of Θ.

In the analysis of the polarization current the quantity $\gamma_{eff} = \gamma \sin^2(\Theta)$ is measured [23], where γ is the rotational viscosity of a corresponding nematic-like structure ($\Theta = 90°$). The data in tables 5 and 6 show a large variation of the values for γ_{eff}.



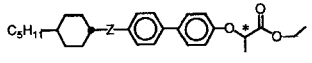
Spontaneous polarization P_s versus the sine of the S_C^* tilt angle Θ for some of the mixtures shown in tables 5 and 6.

Table 6. Liquid crystal transition temperatures, rotational viscosity $\gamma_{eff} = \gamma \sin^2 \theta$, S_C^* tilt angle θ, spontaneous polarization P_s and γ, the calculated rotational viscosity for a nematic-like structure with $\theta = 90°$ for the esters of the structure below for a 13 mol% mixture with a chiral smectic C base mixture.



Z	T_{CS_B/S_C}/°C	$T_{S_BS_C}$/°C	$T_{S_CS_A}$/°C	T_{S_AN}/°C	T_{NI}/°C	θ/°	γ/mPa s	$\gamma \sin^2 \theta$	P_s/nC cm^{-2}
	84	—	98	118	132	20·0	256	30·0	5·66
	87	—	118	—	142	23·2	250	38·8	6·44
	60	83	93	131	152	18·7	258	26·6	5·64
	64	85	104	—	161	25·8	239	45·2	7·05
	66	71	86	102	109	19·3	292	31·9	4·97
	69	—	110	—	130	25·1	284	51·1	6·31
	69	—	110	—	134				

Table 7. Liquid crystal transition temperatures, spontaneous polarization P_s and switching time τ at 25°C for some of the lactate esters of the structure below with an achiral smectic C base mixture.



Z	$T_{CS_BS_A}$/°C	T_{S_ACh}/°C	T_{S_BI}/°C	T_{ChI}/°C	ΔH/kJ mol^{-1}	P_s/nC cm^{-2}	τ/μs	$P_s\tau$/nC cm^{-2} μs
	71	—	76	—		2·8	2000	0·8
	79	80	—	81	33·2	36	740	3·2
	77	76	—	83	25·8	30	760	3·0

However, most of these variations are again due to the tilt angle Θ. After correction for Θ, we find.

(i) Z = direct bond or Z = two unit bridge yield the same viscosity, even for methoxy or ester bridges.
(ii) Fluorination has little effect on γ.
(iii) The four unit bridges yield a 20 per cent to 40 per cent higher viscosity (note that the values given are for a 13 mol % mixture, the extrapolated values for the pure compounds are correspondingly larger).
(iv) The additional ester bridge for the compounds in table 5 increases the viscosity even more than the introduction of a four unit bridge.
(v) The S_C^* tilt angle Θ is the quantity that is most sensitive to the structure of the liquid crystal used: the values for Θ in the 13 mol % mixtures vary from 18·7° to 29·2°. The apolar bridges yield for both the two-membered and the four-membered units lower tilt angles than the more polar bridges. The tilt angle seems to be related to the transverse dipole moment: in table 6 it is seen to increase from the ethane to the methoxy bridge and then to the ester bridge, further table 5 clearly shows the increase of Θ due to the fluorination of one of the rings.

5. Conclusion

It has been shown that four unit linking groups, i.e. butyl, (*E*)-3-butenyl, 3-propyloxy, (*E*)-3-allyloxy (C_4H_8, C_4H_6, C_3H_6O, C_3H_4O) can be incorporated in molecular structures to create novel liquid-crystalline materials, which exhibit enantiotropic, wide-range smectic C mesophases. The usual relationships between the liquid crystal transition temperatures of the phenyl benzoates **12**, **13**, **14** and **21** and the presence, position and nature of a variety of lateral substituents (F, Cl, Br and CN) have been established. 2,3-Difluoro-substitution of the benzoic acid moiety of the ester leads to wide-range enantiotropic smectic C mesophases at elevated temperatures. A *trans* carbon–carbon double bond or an oxygen atom in the central four unit linking groups induce both a higher smectic C–nematic and a nematic–isotropic transition temperature. Similar tendencies have been observed for analogous 5-*n*-alkyl-2-(4-substituted phenyl)pyrimidines **26**, **27** and **28**. The smectic C mesophases of the four unit linking groups exhibit significantly higher viscosity values than those of the corresponding substances incorporating a direct bond or two unit linking groups as the central linkage (—, C_2H_2, CH_2O and COO). Small amounts of the 5-*n*-alkyl-2-([4-(*trans*-4-pentylcyclohexyl)-1-butyl]phenyl)pyrimidines **26** improve the surface alignment and the temperature range of chiral smectic C mixtures for surface stabilized ferroelectric liquid crystal devices. The tilt angle of the chiral smectic C mesophase appears to be directly related to the transverse molecular dipole moment.

6. Experimental

The liquid crystal transition temperatures of the compounds prepared, given 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 of 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 to less than −20°C by allowing nitrogen gas, cooled by liquid nitrogen, 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 thin layer chromatography (TLC), gas chromatography (GC) and DTA analysis. A Perkin–Elmer 8310 gas chromatograph and GP-100 graphics printer were used. TLC plates (4 cm × 8 cm) coated with SiO_2 SIL G/UV_{254} and having a layer thickness of 0·25 mm (Macheray–Nagel, Düren, Germany) were utilized. 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 nitrogen unless water was present as solvent or reagent. All temperatures were measured externally unless otherwise stated. The ^1H 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.

The achiral matrix mixture Sc7 1007 [5, 6] used to determine the spontaneous polarization of the chiral dopants shown in table 7 is composed of four different alkoxyphenylalkylpyrimidines [10] (49·6 wt%) and three different tricyclic phenylbenzoates incorporating an ethane linked cyclohexane ring [1, 2] (50·4 wt %). The chiral smectic C base mixture [5, 6] used to determine the parameters listed in tables 5 and 6 consists of the same phenylpyrimidines (65 wt %) and phenylbenzoates (20 wt %) plus optically active dopants [24] (15 wt %).

Ethyl-(E)-[trans-4-pentylcyclohexyl]acrylate **2**. A solution of potassium carbonate (15 g, 0·1098 mol) in water (11 ml) was added dropwise to a solution of *trans*-4-pentylcyclohexane carboxyaldehyde (10 g, 0·0549 mol) and ethyl diethylphosphonoacetate (16 g, 0·0658 mol) in tetrahydrofuran (100 ml). The reaction mixture was stirred overnight at room temperature, poured into water (500 ml) and extracted with ether (4 × 50 ml). The combined organic layers were washed with sodium chloride solution (2 × 500 ml) dried with anhydrous magnesium sulphate, filtered and finally evaporated under slightly reduced pressure. The residue was purified by column chromatography on silica gel with toluene as eluent to give ethyl-(*E*)-[*trans*-4-pentylcyclohexyl]acrylate (yield 13·5 g, 98 per cent); bp 114–116°C/0·07 mm Hg. IR (film): 2922, 2851, 1722, 1651, 1305, 1268, 984 cm^{-1}. MS: 252 (M^+), 224, 206, 177, 164.

3-(trans-4-Pentylcyclohexyl)propanol **3**. A solution of ethyl-(*E*)-[*trans*-4-pentylcyclohexyl]acrylate (5·0 g, 0·0198 mol) and diethylether (15 ml) was added dropwise to a mixture of lithium–aluminium hydride (0·8 g, 0·0217 mol) and diethyl ether (15 ml) at room temperature. The reaction mixture was heated under reflux for a further 2 hours and then cooled to 0°C in an ice-bath. Water (25 ml) and 25 per cent hydrochloric acid (100 ml) were added dropwise to the cooled reaction mixture and then the organic layer was separated off. The aqueous layer was extracted with ether (3 × 50 ml). The combined organic layers were washed with water (500 ml), saturated potassium carbonate solution (2 × 100 ml), dried with anhydrous magnesium sulphate, filtered and then evaporated under slightly reduced pressure. The liquid residue was distilled under reduced pressure to give the pure alcohol (yield 4·0 g, 96 per cent); bp 124–126°C/1 mbar. IR (film): 3345, 2919, 2849, 1451, 1056 cm^{-1}. MS: 194 ($C_{14}H_{26}$), 166 ($C_{12}H_{22}$), 151 ($C_{11}H_{19}$).

3-(trans-4-Pentylcyclohexyl)-1-bromopropane **4**. A solution of bromine (15 g, 0·0942 mol) in anhydrous acetonitrile (50 ml) was added dropwise to a solution of triphenylphosphine (25 g, 0·0942 mol) and acetonitrile (100 ml) at room temperature under an atmosphere of nitrogen. The reaction mixture was stirred for 30 min. A white precipitate was observed. An emulsion of 3-(*trans*-4-pentylcyclohexyl)-1-propanol (20 g, 0·0942 mol) in acetonitrile (20 ml) was added dropwise to the reaction mixture.

The white precipitate disappeared during the addition and another white precipitate was formed after the addition was completed. The reaction mixture was stirred for a further 30 min and then the acetonitrile was distilled off. The reaction mixture was maintained at an oil-bath temperature of 120°C for a further 15 min and then allowed to cool. Water (1000 ml) was added and the resultant mixture shaken with dichloromethane (3 × 100 ml). The combined organic layers were washed with water (2 × 500 ml), dried with anhydrous magnesium sulphate, filtered and finally evaporated. The residue was distilled under reduced pressure to yield the pure bromide (yield 20·5 g, 79 per cent); bp 140–142°C/1·6 mbar. IR (film): 2919, 2849, 1449, 1238, 1201 cm^{-1}. MS: 276, 274 (M^+), 153.

4-[3-(trans-4-Pentylcyclohexyl)propyloxy]phenol **5**. A mixture of 3-(*trans*-4-pentylcyclohexyl)-1-bromopropane (10 g, 0·0364 mol), hydroxyquinone (20 g, 0·1816 mol), potassium carbonate (20 g, 0·1452 mol) and butanone (400 ml) was heated overnight. The reaction mixture was poured into water (1000 ml) and extracted with dichloromethane (3 × 100 ml). The combined organic layers were washed with water (2 × 500 ml), dried with anhydrous magnesium sulphate, filtered and evaporated. The residue was purified by column chromatography on silica gel using a 4 : 1 toluene/ethyl acetate mixture as eluent followed by recrystallization from hexane (yield 6 g, 54 per cent); mp 100–101°C. IR (KBr): 3357, 2910, 2848, 1510, 1230, 830 cm^{-1}. MS: 304 (M^+), 110.

(E)-3-(trans-4-Pentylcyclohexyl)allyl alcohol **6**. 20 per cent Diisobutylylaluminium hydride in hexane (100 ml) was added dropwise to a solution of ethyl-(*E*)-[*trans*-4-pentylcyclohexyl]acrylate (13·5 g, 0·01 mol) in dichloromethane (1000 ml) at room temperature and stirred for 60 min. 25 per cent hydrochloric acid (10 ml) was added dropwise to the reaction mixture, which was then poured into water (100 ml). The organic layer was separated off and the aqueous layer extracted with dichloromethane (2 × 100 ml). The combined organic layers were washed with concentrated potassium bicarbonate solution (500 ml), water (500 ml), dried with anhydrous magnesium sulphate, filtered and evaporated under reduced pressure. The residue was distilled under reduced pressure to give the pure product (yield 10 g, 89 per cent); bp 174–175°C/15 mm Hg. IR (film): 3333, 2921, 2850, 1665, 1446, 1378, 1008, 969 cm^{-1}. MS: 210 (M^+).

4-([(E)-3-(trans-4-Pentylcyclohexyl)allyl]oxy)phenol **7**. A solution of (*E*)-3-(*trans*-4-pentylcyclohexyl)allyl alcohol (10 g, 0·0459 mol), hydroxyquinone (26 g, 0·2363 mol), diethyl azodicarboxylate (8 g, 0·0459 mol), triphenylphosphine (12 g, 0·0459 mol) and tetrahydrofuran (500 ml) was stirred overnight at room temperature. The reaction mixture was evaporated under reduced pressure. The residue was dissolved in hot hexane (50 ml), filtered to remove insoluble material, particularly triphenylphosphine oxide, and evaporated again. The residue was purified by column chromatography on silica gel using 4 : 1 toluene/ethyl acetate mixture as eluent followed by recrystallization from hexane (yield 8 g, 55 per cent); mp 97–98°C. IR (KBr): 3289, 1637, 1588, 1511, 1299, 1017, 968 cm^{-1}. MS: 302 (M^+), 192, 110.

3-(trans-4-Pentylcyclohexyl)propionaldehyde **8**. A solution of 3-(*trans*-4-pentylcyclohexyl)propanol (86 g, 0·404 mol) in dichloromethane (180 ml) was added dropwise to a suspension of pyridine chlorochromate (154 g, 0·713 mol) and dichloromethane (1000 ml) at room temperature. The reaction mixture was stirred at this temperature for $2\frac{1}{2}$ hours and then ether (500 ml) was added. The reaction mixture was stirred for a further 15 min before decreasing the organic layer and washing the residue with ether (4 × 250 ml). The combined organic layers were washed with sodium

chloride solution (2 × 500 ml), dried with anhydrous magnesium sulphate, filtered and finally evaporated under slightly reduced pressure to give pure aldehyde (99·1 per cent) (yield 75 g, 92 per cent). MS: 210 (M^+).

1-Butoxy-4-[(E/Z)-4-(trans-4-pentylcyclohexyl)-1-butenyl]benzene **9**. Potassium *tert.*-butylate (13 g, 0·116 mol) was added in portions to a solution of 3-(*trans*-4-pentylcyclohexyl)propionaldehyde (15 g, 0·071 mol), [4-(butyloxy)phenyl]-methyl-triphenylphosphonium bromide (54 g, 0·107 mol) and *tert.*-butylmethyl ether (450 ml) at room temperature. A dark orange colour was observed. The reaction mixture was stirred at room temperature overnight, then poured into water (1000 ml) and extracted with ether (3 × 200 ml). The combined organic layers were washed with water (2 × 500 ml), dried with anhydrous magnesium sulphate, filtered and evaporated. The residue was purified by column chromatography on silica gel using a 4 : 1 toluene/hexane mixture (yield 21 g, 82 per cent). Recrystallization of a small sample of the *cis/trans*-mixture obtained gave pure *trans*-isomer. (T_{CS_B}) 46°C; ($T_{S_BS_A}$) 74°C; (T_{S_AN}) 76°C; (T_{NI}) 91°C. IR (KBr): 2920, 1606, 1245, 965 cm^{-1}. MS: 356 (M^+), 324, 189.

The alkene *4-[(E/Z)-4-(trans-4-pentylcyclohexyl)-1-butenyl]benzonitrile* **22** was prepared using the same procedure (yield 54 per cent). IR (film): 2920, 2849, 2228, 1607, 1508, 816 cm^{-1}. MS: 309 (M^+).

1-Butyloxy-4-[3-(trans-4-pentylcyclohexyl)-1-butyl]benzene **10**. A mixture of 1-butyloxy-4-[(E/Z)-4-(*trans*-4-pentylcyclohexyl)-1-butenyl]benzene (19 g, 0·053 mol), 10 per cent palladium on active charcoal (2 g) and toluene (100 ml) was hydrogenated until the absorbtion of hydrogen was completed. The inorganic material was removed by filtration and the filtrate evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using toluene as eluent followed by recrystallization from alcohol (yield 16 g, 84 per cent); (T_{CS_B}) 29°C; (T_{S_BI}) 43°C. IR (KBr): 2921, 2848, 1610, 1511, 1242, 1090, 825 cm^{-1}. MS: 358 (M^+), 302 ($C_{20}H_{32}O$).

The compound *4-[4-(trans-4-pentylcyclohexyl)-1-butyl]benzonitrile* **23** was prepared using the same procedure (yield 86 per cent); (T_{CI}) 59°C; (T_{NI}) (39°C).

4-[4-(trans-4-Pentylcyclohexyl)-1-butyl]phenol **11**. A one molar solution of borontribromide in dichloromethane (50 ml) was added dropwise to a solution of 1-butyloxy-4-[4-(*trans*-4-pentylcyclohexyl)-1-butyl]benzene (16 g, 0·045 mol) in dichloromethane (100 ml) and cooled using an ice-bath. The reaction solution was stirred at 0°C for about 2 hours and then poured carefully into an ice/water mixture (200 g). The organic layer was separated off and the aqueous layer extracted with dichloromethane (3 × 100 ml). The combined organic layers were washed with water (1000 ml), dilute potassium carbonate solution (500 ml) and once again with water (1000 ml), then dried with anhydrous magnesium sulphate, filtered and evaporated. The residue was recrystallized from hexane to give the pure phenol (yield 11 g, 81 per cent); mp 85–86°C.

4-[3-(trans-4-Pentylcyclohexyl)propyloxy]phenyl-4-(heptyloxy)benzoate **12**. A solution of 4-heptyloxybenzoic acid (1·9 g, 0·0082 mol), 4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]phenol (2·5 g, 0·0082 mol), dicyclohexylcarbodiimide (2·0 g, 0·0099 mol), 4-(dimethylamino)pyridine (0·04 g) and dichloromethane (50 ml) was stirred at room temperature overnight. After filtration of precipitated material, the solution was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using toluene as eluent followed by recrystallization from alcohol until the transition temperatures remained constant. Tables 1 and 2 give the liquid crystal transition temperatures and enthalpies of fusion for ester **12** and the other esters **13**, **14** and **21** prepared using this general procedure. IR (KBr): 2924, 2851, 1729, 1621, 1508, 1296 cm^{-1}. MS: 558 (M^+), 255, 157.

4-(3-Bromopropyl)phenyl **16**. A solution of tetrabromomethane (60 g, 0·1807 mol) in dichloromethane (100 ml) was added dropwise to a solution of 4-(3-hydroxypropyl)phenol **15** (254 g, 0·1642 mol), triphenylphosphine (47 g, 0·1897 mol) and dichloromethane (500 ml) at 0°C. The reaction mixture was stirred overnight at room temperature and then evaporated. Column chromatography of the residue on silica gel using 9 : 1 hexane/ethyl acetate as eluent gave pure bromide (yield 35 g, 99 per cent). IR (film): 3350, 1619, 1514, 1240, 1146, 824 cm^{-1}. MS: 214 (M^+), 173, 133, 107.

4-(3-Bromopropyl)phenyl tetrahydropyranyl ether **17**. A solution of 4-(3-bromopropyl)phenol (35 g, 0·1627 mol), 3,4-dihydro-2H-pyran (16·4 g, 0·1953 mol) bis(trimethylsilyl)sulphate (0·8 g, 0·0033 mol) and dichloromethane (500 ml) was stirred for 2 hours at room temperature. Pyridine was added and the reaction mixture evaporated. The residue was purified by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture as eluent to give the pure ether (38 g, 78 per cent). IR (film): 2949, 2872, 1611, 1510, 1294, 829 cm^{-1}. MS: 214 ($C_{9\,11}HO^+$), 107 ($C_7H_7O^+$), 85 ($C_5H_9O^+$).

[3-(4-[Tetrahydropyranyl)oxy]phenyl)propyl]triphenylphosphonium bromide **18**. A solution of 4-(3-bromopropyl)phenyl tetrahydropyranyl ether (38 g, 0·1271 mol), triphenylphosphine (40 g, 0·1525 mol) and N,N′-dimethylformamide (50 ml) was heated overnight at 100°C. A white precipitate was formed. The cooled reaction mixture was filtered and the white crystals washed with portions of ethyl acetate. The solid material was dried under vacuum and used without further purification (yield 40 g, 56 per cent); mp 225–226°C.

4-[(E/Z)-4-(trans-4-Pentylcyclohexyl)-3-butenyl]phenol **19**. A 1·6 molar solution of butyl–lithium in hexane (35 cm^3, 0·057 mol) was added dropwise to a mixture of [3-(4-[(tetrahydropyranyl)oxy]phenyl)propyl]triphenylphosphonium bromide (32 g, 0·057 mol) and *tert.*-butylmethyl ether (500 ml) at room temperature and was stirred for a further 30 min. A bright orange colour was observed. A solution of *trans*-1-formyl-4-pentylcyclohexane (10 g, 0·057 mol) and *tert.*-butylmethyl ether (10 ml) was added dropwise. An exothermic reaction was observed. The reaction mixture was stirred for a further 30 min then poured into water (500 ml) and finally extracted with ether (3 × 100 ml). The combined organic layers were washed with sodium chloride solution (2 × 500 ml), dried with anhydrous magnesium sulphate, filtered and evaporated under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture as eluent to give pure phenol (yield 5·0 g, 29 per cent; *cis/trans* mixture). IR (film): 3336, 1613, 1514, 1234, 826 cm^{-1}. MS: 300 (M^+), 107.

4-[(E)-4-(trans-4-Pentylcyclohexyl)-3-butenyl]phenol **20**. A solution of 4-[(*E*/*Z*)-4-(*trans*-4-pentylcyclohexyl)-3-butenyl]phenol (5·0 g, 0·0167 mol), benzenesulphinic acid [freshly prepared from the sodium salt (0·6 g, 0·0017 mol), concentrated hydrochloric acid (5 drops) and water (1 ml)] and ethanol (50 ml) was heated at an oil-bath temperature of 65°C overnight. The reaction mixture was poured into water (500 ml) and extracted with ether (3 × 50 ml). The combined organic layers were washed with sodium chloride solution (2 × 50 ml), dried with anhydrous magnesium sulphate, filtered and finally evaporated under reduced pressure. Purification of the residue by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture and crystallization from hexane gave the pure phenol (yield 2·2 g, 44 per cent); mp 89–90°C. IR (KBr): 3405, 2916, 2846, 1601, 1511, 1230, 965, 823 cm^{-1}. MS: 300 (M^+), 107.

4-[4-(trans-4-Pentylcyclohexyl)-1-butyl]phenylimidoethylether hydrochloride **24**. A solution of 4-[4-(*trans*-4-pentylcyclohexyl)-1-butyl]benzonitrile (11·6 g, 0·037 mol) in

ethanol (7·6 ml) and toluene (100 ml) was saturated with hydrogen chloride at 0°C and then stirred at room temperature for 2 days. The reaction mixture was evaporated under reduced pressure, shaken with ether (300 ml), filtered, washed with portions of ether and finally dried under vacuum (yield 6 g, 41 per cent). IR (nujol): 2925, 2850, 2797, 1633, 1605, 1565, 890 cm^{-1}. MS: 357 (M^+), 356 $C_{24}H_{38}NO$), 329 ($C_{24}H_{35}NO$).

4-[4-(trans-4-Pentylcyclohexyl)-1-butyl]benzamidine hydrochloride **25**. A saturated ethanolic ammonia solution (11·2 ml) was added to a solution of 4-[4-(*trans*-4-pentylcyclohexyl)-1-butyl]phenylimidoethyl ether (6 g, 0·015 mol) and ethanol (50 ml). The reaction mixture was stirred at room temperature for a further 2 days and then evaporated. The solid residue was taken up in ethanol (50 ml) and then added to ether (600 ml). The precipitated product was filtered off, washed with small portions of ether and then dried under vacuum (yield 5·2 g, 95 per cent). IR (nujol): 3248, 2919, 2849, 1675, 1542, 830 cm^{-1}. MS: 327 ($M^+ - H^+$).

5-Decyl-2-(4-[4-(trans-4-pentylcyclohexyl)-1-butyl]phenyl)pyrimidine **26** ($n = 10$). A 5 mol% solution of sodium methoxide in methanol (0·4 ml) was added dropwise to a mixture of 2-(methoxymethylidene)dodecanal [9] (0·0015 mol) 4-[4-(*trans*-pentylcyclohexyl)-1-butyl]benzamidine hydrochloride (0·4 g, 0·0016 mol) and methanol (10 ml) at room temperature and then stirred overnight. Concentrated hydrochloric acid was added (pH 3–4) and the inorganic material was filtered off. The filtrate was concentrated under reduced pressure, dichloromethane (150 ml) was added and the resultant solution washed with water (2 × 100 ml) and then dried with anhydrous magnesium sulphate. Column chromatography on silica gel using toluene as eluent followed by recrystallization from alcohol gave the pure product. The liquid crystal transition temperatures and the enthalpy of fusion of this compound and other homologues prepared using this general method are recorded in table 3. IR (KBr): 2922, 2848, 1539, 1491, 799 cm^{-1}. MS: 504 (M^+), 323 $C_{22}H_{31}N_2$), 310 ($C_{21}H_{30}N_2^+$).

5-Decyl-2-(4-[3-(trans-4-pentylcyclohexyl)propyloxy]phenyl)pyrimidine **27** ($n = 10$). A mixture of 4-(5-decyl-2-pyrimidinyl)phenol [9] (0·50 g, 0·0017 mol), 3-(*trans*-4-pentylcyclohexyl)-1-bromopropane **4** (0·55 g, 0·0022 mol), potassium carbonate (0·91 g, 0·0067 mol) and butanone (50 ml) was refluxed overnight. The cooled reaction mixture was poured into water (500 ml) and extracted with ether (3 × 50 ml). The combined organic layers were washed with water (2 × 500 ml) and dried with anhydrous magnesium sulphate, filtered and evaporated under slightly reduced pressure. The crude product was purified using column chromatography on silica gel with toluene as eluent and recrystallized from ethanol. Table 3 lists the liquid crystal transition temperatures of this compound and the other homologues ($n = 5$–9) prepared by this method. IR (KBr): 2922, 2849, 1610, 1589, 1513, 1254, 1165, 1026, 841 cm^{-1}. MS: 506 (M^+).

5-Pentyl-2-[(4-[(E)-3-(trans-pentylcyclohexyl)allyl]oxy)phenyl]pyrimidine **28** ($n = 10$). A solution of (*E*)-3-(*trans*-4-pentylcyclohexyl)allyl alcohol **6** (0·5 g, 0·0023 mol), 4-(5-pentyl-2-pyrimidinyl)phenol [9] (0·6 g, 0·0023 mol), diethyl azodicarboxylate (0·4 g, 0·0023 mol), triphenylphosphine (0·6 g, 0·0023 mol) and tetrahydrofuran (25 ml) was stirred at room temperature overnight. The reaction mixture was then evaporated under reduced pressure, the residue dissolved in hot hexane (50 ml), filtered to remove inorganic material, particularly triphenylphosphine oxide, and then finally evaporated again. Column chromatography on silica gel using toluene as eluent followed by crystallization from alcohol gave the pure product. The liquid crystal transition temperatures and enthalpy of fusion of the ether and other homologues ($n = 5$–9) prepared using this general procedure are collated in table 3. IR (KBr): 2922, 2850, 1607, 1583, 1542, 1513, 1247, 975, 798 cm^{-1}. MS: 504 (M^+), 312, 198, 186.

The following ethers were prepared using the same procedure:

Ethyl-(R)-2-[(4-hydroxy-4'-biphenylyl)oxy]propionate **33** (yield 9 per cent); mp 116–117°C. IR (KBr): 3469, 1812, 1722, 1502, 1226, 1136, 818 cm^{-1}. MS: 286 (M^+), 213 ($C_{14}H_{13}O_2$), 185 ($C_{12}H_{10}O_2$). $[\alpha]_D^{20} = +40°$ (*c.* 0·6 in $CHCl_3$).

Ethyl - (R) - 2 - ([4 - ([(E) - (trans - 4 - pentylcyclohexyl)ally]oxy) - 4' - biphenylyl] oxy)propionate **34** (yield 44 per cent); see table 7 for the liquid crystalline transition temperatures of this ether. IR (KBr): 2919, 2815, 1745, 1670, 1606, 1498, 1240, 1049, 971, 824 cm^{-1}. MS: 478 (M^+), 405 ($C_{28}H_{37}O_2$). $[\alpha]_D^{20} = +23·6°$ (*c.* 0·6 in $CHCl_3$).

Ethyl - (R) - 2 - [(4 - [3 - (trans - 4 - pentylcyclohexyl)propyloxy] - 4' - biphenylyl)oxy] propionate **35** (yield 44 per cent); see table 7 for the liquid-crystalline transition temperatures of this ether. IR (KBr): 2921, 2848, 1744, 1607, 1500, 1242, 1137, 1046, 1019, 804 cm^{-1}. MS: 480 (M^+), 286 ($C_{17}H_{18}O_4$).

(S)-4-(2-Methylbutyl)oxy-4'-[4-(trans-pentylcyclohexyl)-1-butanoyl]biphenyl **29**. A solution of 4-cyano-4'-[(2-methylbutyl)oxy]biphenyl [21] (10 g, 0·038 mol) in diethyl ether (100 ml) was added dropwise to a solution of Grignard reagent (prepared in the usual way from 3-(*trans*-4-pentylcyclohexyl)-1-bromopropane **4** (26 g, 0·094 mol), magnesium turnings (2·3 g, 0·094 mol) and diethyl ether (100 ml)). The reaction mixture was heated overnight under gentle reflux and then cooled to 0°C in an ice-bath. Hydrochloric acid (60 ml, 25 per cent) was added dropwise and the reaction mixture was again heated under gentle reflux for 1 hour. The cooled reaction mixture was extracted with diethyl ether (4 × 50 ml). The combined organic layers were washed with sodium chloride solution (100 ml), dilute potassium carbonate solution (2 × 50 ml) and again with water (50 ml), dried with anhydrous magnesium sulphate, filtered and evaporated under slightly reduced pressure. The residue was recrystallized from alcohol to give the pure ketone (yield 13·1 g, 75 per cent).

(S)-4-(2-Methylbutyl)oxy-4'-[4-(trans-4-pentylcyclohexyl)-1-butyl]biphenyl **30**. A mixture of (*S*)-4-(2-methylbutyl)oxy-4'-[4-(*trans*-4-pentylcyclohexyl)-1-butanoyl]biphenyl (10 g), ethyl acetate (500 ml) and 10 per cent palladium on active charcoal (2 g) was hydrogenated until no more hydrogen was taken up. The inorganic material was removed by filtration and the filtrate evaporated. Purification of the residue by recrystallization from alcohol gave the pure product (yield 9 g, 93 per cent). IR (KBr): 2921, 2842, 1607, 1500, 1252, 1041, 807 cm^{-1}. MS: 448 (M^+), 378 ($C_{27}H_{38}O$).

4-Hydroxy-4'-[4-trans-4-pentylcyclohexyl)-1-butyl]biphenyl **31**. A solution of 1 molar boron tribromide in dichloromethane (7 ml) was added to a solution of (*S*)-4-(2-methylbutyl)oxy-4'-[4-(*trans*-4-pentylcyclohexyl)-1-butyl]biphenyl (2·5 g, 0·0056 mol) and dichloromethane (100 ml) and cooled using an ice-bath. The reaction solution was stirred at 0°C for about 1 hour and then poured carefully into an ice/water mixture. The organic layer was separated off and the aqueous layer shaken with dichloromethane (50 ml). The combined organic layers were washed with 2 N anhydrous sodium carbonate solution (50 ml) and water (2 × 500 ml), dried with anhydrous magnesium sulphate, filtered and then evaporated. The residue was purified by column chromatography on silica gel using a 4 : 1 toluene/ethyl acetate mixture as eluent. Recrystallization from alcohol yielded the pure product (yield 2·0 g, 95 per cent); mp 174–175°C. IR (KBr): 3420, 2922, 2849, 1609, 1530, 1249, 814 cm^{-1}. MS: 378 (M^+), 183 ($C_{13}H_{11}O$).

Ethyl-(R)-2-[(4'-[4-(trans-4-pentylcyclohexyl)-1-butyl]-4-biphenylyl)oxy]propionate **32** (*m* = 2). A solution of 4-hydroxy-4'-[4-(*trans*-4-pentylcyclohexyl)-1-butyl]biphenyl (0·4 g, 0·0011 mol), ethyl-*L*-(−)-lactate (0·12 g, 0·0011 mol), triphenylphosphine (0·29 g, 0·0011 mol), diethyl azodicarboxylate (0·19 g, 0·0011 mol) and tetrahydrofuran (25 ml)

was stirred at room temperature overnight. The reaction mixture was evaporated under vacuum, dissolved in warm hexane (100 ml) and then filtered to remove insoluble material, in particular triphenylphosphine oxide. The filtrate was concentrated under reduced vacuum and the residue purified by column chromatography on silica gel using a 4 : 1 toluene/ethyl acetate mixture as eluent followed by recrystallization from alcohol until the transition temperatures remained constant. Table 4 lists the liquid crystal transition temperatures of this compound and the other homologues ($m = 1$–4) prepared by this method. IR (KBr): 2919, 2846, 1752, 1608, 1499, 1244, 1136, 821 cm^{-1}. MS: 492 (M^+).

The authors express their gratitude to Mr B. Müller, Mr S. Wehrli, Mr P. Winiger and Mr U. Wyss for sound technical assistance in the preparation of the compounds. Dr W. Arnold (NMR), Mr W. Meister (MS), Dr M. Grosjean (IR), Mr F. Wild and Mr B. Halm (DTA) are thanked for the measurement and interpretation of the required spectra. Mrs V. Kannookadan and Mr W. Janz are thanked for the determination of the other physical data reported.

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