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

4-(5-Alkyl-2-pyridinyl)phenyl alkanoates: Some novel smectic materials for display devices

S. M. Kelly[a]; J. Fünfschilling[a]; A. Villiger[a]
[a] Dept. RLCR, F. Hoffmann-La Roche Inc., Basel, Switzerland

To cite this Article Kelly, S. M. , Fünfschilling, J. and Villiger, A.(1993) '4-(5-Alkyl-2-pyridinyl)phenyl alkanoates: Some novel smectic materials for display devices', Liquid Crystals, 14: 3, 699 — 712
To link to this Article: DOI: 10.1080/02678299308027748
URL: http://dx.doi.org/10.1080/02678299308027748

LIQUID CRYSTALS, 1993, VOL. 14, NO. 3, 699–712

4-(5-Alkyl-2-pyridinyl)phenyl alkanoates: some novel smectic materials for display devices

by S. M. KELLY*, J. FÜNFSCHILLING and A. VILLIGER
F. Hoffmann-La Roche Inc., Dept. RLCR, 4002 Basel, Switzerland

Three homologous series of 4-(5-alkyl-2-pyridinyl)phenyl alkanoates have been prepared. The synthesis and the liquid crystal transition temperatures of these esters are reported. Many members of these three ester series exhibit enantiotropic, wide range smectic F mesophases and some narrow range smectic C mesophases. However, in admixture with a chiral smectic C base mixture, the esters often induce a substantial increase in the chiral smectic C–smectic A transition temperature and, at the same time, decrease the temperature of crystallization. Thus, the temperature range of the chiral smectic C mesophase is substantially extended at both high and low temperatures. Ordered smectic mesophases are only observed at very low temperatures, if at all. These chiral smectic C mixtures are characterized by short switching times in surface-stabilized ferroelectric liquid crystal displays (SSFLCD). These novel esters are of especial interest for short-pitch chiral smectic C mixtures for short pitch bistable ferroelectric liquid crystal displays (SBFLCD) with short response times.

1. Introduction

Many homologues of the known 4-(5-alkyl-2-pyrimidinyl)phenyl alkanoates exhibit wide range, enantiotropic smectic A and C as well as nematic mesophases [1]. This is the order of smectic mesophase transitions required for some electro-optic display device applications based on ferroelectric effects [2]. They have been shown recently to induce short response times in chiral smectic C mixtures containing them [2]. It was decided to synthesize a similar series of straight chain 4-(5-alkyl-2-pyridinyl)phenyl alkanoates (i.e. analogous substances in which one nitrogen atom (N) has been replaced by a methylene (CH_2) unit). This should lead to a substantial decrease in the temperature range of the smectic C mesophase and to the injection of highly ordered smectic mesophases at elevated temperatures, as is nearly always the case for apolar mesogens incorporating the pyridinylphenyl moiety [3–5]. These highly ordered smectic mesophases often give rise to a deterioration in the melting point/crystallization temperature in mixtures containing them, due to a high tendency to crystallization/precipitation and to the induction of highly ordered smectic mesophases at unacceptably high temperatures for commercial applications [2]. However, it was hoped that these new esters could be used in small quantities to increase the chiral smectic C–smectic A transition temperature (S_C^*–S_A) of chiral smectic C mixtures for electro-optic display devices, namely surface stabilized, distorted helix and short pitch bistable ferroelectric liquid crystal displays otherwise known as SSFLCDs, DHFLCDs and SBFLCDs respectively, based on ferroelectric effects [6–14].

---

* Author for correspondence.

0267–8292/93 $10·00 © 1993 Taylor & Francis Ltd.

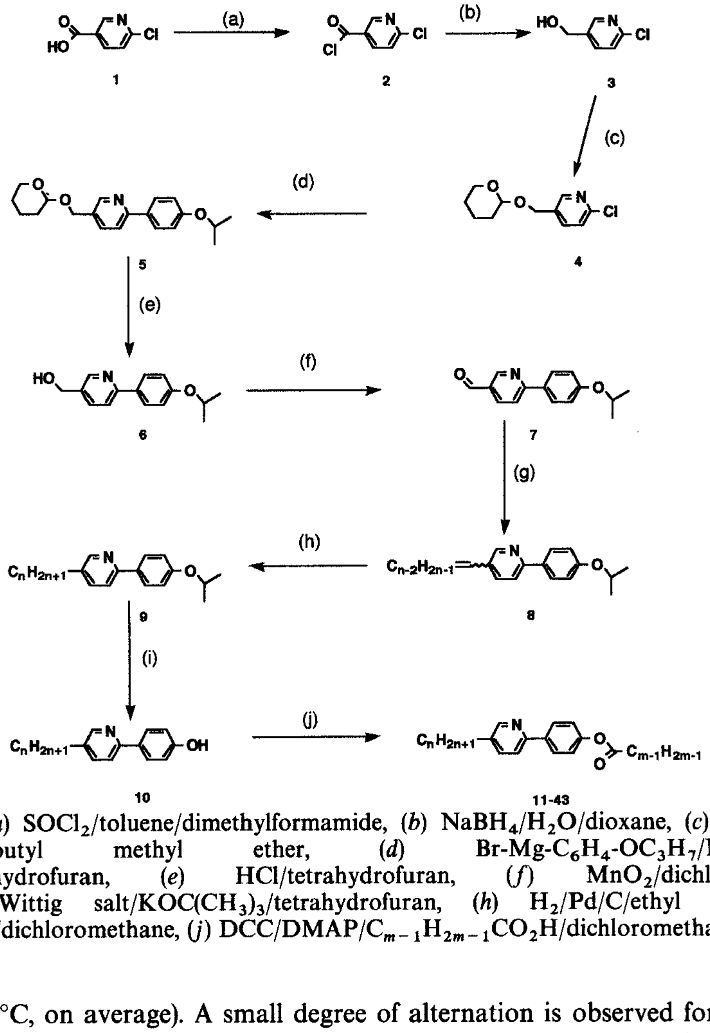
2. Synthesis

The reaction pathway used to prepare the new 4-(5-alkyl-2-pyridinyl)phenyl alkanoates **11–43** is depicted in scheme 1. The commercially available 6-chloronicotinic acid **1** is converted into the corresponding acid chloride **2** [15] in the usual way with thionyl chloride. Sodium borohydride is used to reduce the acid chloride **2** to the alcohol **3** [15] which is then protected as the tetrahydro-2-pyranyloxy derivative **4**. This is then used in a transition metal catalysed cross-coupling reaction [16] with the Grignard reagent of 1-bromo-4-isopropyloxybenzene [17] to produce the pyridinylbenzene **5**. Deprotection of **5** with 2*N* hydrochloric acid yielded the alcohol **6**, which was oxidized with mangenese oxide [18] to give the aldehyde **7**. A standard Wittig reaction with commercially available Wittig reagents yielded the alkene **8**, (as a *cis*/*trans* mixture) which was hydrogenated as usual over a palladium catalyst to give the alkyl substituted derivative **9**. Cleavage of the isopropyl group using boron tribromide produced the known phenols ($n=7$–9) [4] which could be esterified using commercially available alkanoic acids, DCC and DMAP in the usual way [19] to yield the desired esters **11–43**.

This reaction pathway involves the nickel catalysed [16] coupling of the readily accessible Grignard reagent of 4-bromophenyl isopropyl ether with 2-chloro-5-([tetrahydro-2-pyranyloxy]methyl)pyridine **4** to yield the substituted pyridinyl benzene core structure. In this case the pyridine ring is derived from a relatively cheap and readily available natural product and, thus, does not need to by synthesized during the reaction pathway. This is in contrast to the normal methods of preparation of related liquid crystals containing the pyridinylbenzene moiety described in the literature [4, 5, 20, 21]. In these particular cases the pyridine ring is formed during the reaction pathway by heating a perchlorate derivative for example, formed from a piperidine intermediate [4, 5, 21] or a cyclic lactone [20]) with an ammonium compound for example, ammonium acetate as a source of nitrogen, according to a standard procedure [22]. This is laborious and not suitable for large quantities. Since the completion of the synthetic part of this work, improved coupling reactions using boronic acids with halides or triflates have been published [23].

3. Mesomorphic properties

The liquid crystal transition temperatures and enthalpies of fusion (ΔH) of the 4-(5-heptyl-2-pyridinyl)phenyl alkanoates **11–21** are collated in table 1 and plotted against the number of the carbon atoms (m) in the acid part (including the carbonyl carbon atom) of the esters in figure 1. It is evident from the table that the esters **11–21** only exhibit smectic polymorphism and no nematic mesophase is present. It is clear that without X-ray analysis it is not possible to say with any real degree of certainty whether the smectic B mesophases observed for these esters are crystal or hexatic B, or whether the smectic F and G mesophases are not related smectic modifications [24]. Miscibility studies strongly indicate smectic F and G mesophases. A monotropic smectic B mesophase is observed at moderately low temperatures for the shortest chain lengths possible ($m=2$ and 3). The two plots of the smectic B mesophase transition temperature (S_B–I) against chain length ($m=2$–5) rise steeply for longer chain lengths and show a degree of alternation, becoming enantiotropic in the process. For longer alkyl chains ($m=6$–12) the orthogonal smectic B mesophase is replaced by the tilted smectic F mesophase. The related, but more highly ordered quasi-smectic G mesophase [23] is observed at lower temperatures, while an enanotiotropic smectic C mesophase is exhibited for the last five members of the series ($m=8$–12) over a narrow temperature



Scheme. (*a*) $SOCl_2$/toluene/dimethylformamide, (*b*) $NaBH_4/H_2O$/dioxane, (*c*) DHP/PTS/*tert.*-butyl methyl ether, (*d*) Br-Mg-C_6H_4-OC_3H_7/$NiCl_2$(dppp)/tetrahydrofuran, (*e*) HCl/tetrahydrofuran, (*f*) MnO_2/dichloromethane, (*g*) Wittig salt/$KOC(CH_3)_3$/tetrahydrofuran, (*h*) H_2/Pd/C/ethyl acetate, (*i*) BBr_3/dichloromethane, (*j*) DCC/DMAP/$C_{m-1}H_{2m-1}CO_2H$/dichloromethane.

range (⩽3°C, on average). A small degree of alternation is observed for the quasi-smectic G mesophase. The plot of the melting point (C–S_G, C–S_F, and C–S_B) of the esters **11–21** against the number of carbon atoms (*m*) in the terminal alkly chain of the acid moiety is remarkably flat, with only a moderate maximum deviation (⩽10°C) from the average (54°C). The average enthalpy of fusion (28·3 kJ mol^{-1}) for the crystal–isotropic liquid transition (C–I) is, of course, substantially higher than that for the crystal–smectic B, F and G mesophases (15·0 kJ mol^{-1}, on average) which are highly ordered smectic mesophases or plastic crystals [23].

The liquid crystal transition temperatures and enthalpies of fusion of the 4-(5-octyl-2-pyridinyl)phenyl alkanoates **22–32** are recorded in table 2 and plotted against the number of carbon atoms (*m*) in the acid moiety in figure 2. The major differences between the homologous series of the esters **11–21** and **22–32** is the absence of both a smectic G and smectic C mesophase for the esters **22–32** containing an additional methylene unit (CH_2) in the alkyl chain attached to the pyridine ring. The plots of the smectic B–isotropic liquid (S_B–I) and the smectic C–isotropic liquid (S_C–I) transition temperatures against the number of methylene units (*m*) are very similar for both series of esters. However, the transition temperatures for these mesophases are somewhat higher (⩽4–5°C) for the esters **22–32** than for the esters **11–21**. This is also true of the

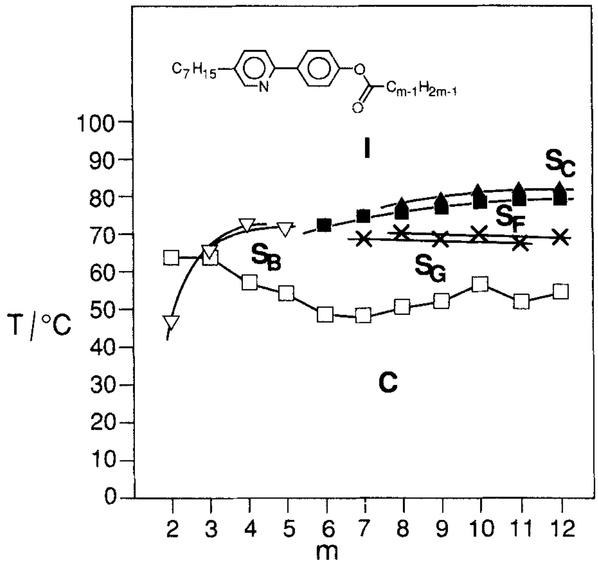
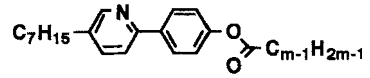


Figure 1. Plots of the transition temperatures against the number of carbon atoms (*m*) in the alkyl chain of the 4-(5-heptyl-2-pyridinyl)phenyl alkanoates **11–21** (□), crystal–smectic G/smectic F/smectic B/isotropic; X, smectic G–smectic F; ■, smectic F–smectic C/isotropic; ▽, smectic B–isotropic; ▲, smectic C–isotropic).

Table 1. The liquid crystal transition temperatures and enthalpies of fusion for the 4-(5-heptyl-2-pyridinyl)phenyl alkanoates **11–21**.



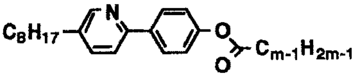
Ester	*m*	C–S/I/°C	S_G–S_F/°C	S_F–S_C/I/°C	S_B–I/°C	S_C–I/°C	Δ*H*/kJ mol^{-1}
11	2	63	—	—	(47)	—	26·7
12	3	65	—	—	(64)	—	29·9
13	4	57	—	—	71	—	14·4
14	5	48	—	—	71	—	13·5
15	6	48	—	72	—	—	11·7
16	7	48	68	74	—	—	15·8
17	8	50	68	76	—	77	15·7
18	9	52	68	78	—	79	16·6
19	10	56	69	79	—	81	14·9
20	11	52	66	79	—	81	15·0
21	12	54	68	79	—	82	17·2

( ) represents a monotropic transition temperature.

melting points, where the difference is somewhat greater (+8°C, on average). Thus the longer chain homologues (*m* = 7–12) of the octyl ester derivatives **22–32** exhibit enantiotropic, wide-range smectic F mesophases (⩽30°C, on average).

An almost identical pattern of transition temperatures is observed for the 4-(5-nonyl-2-pyridinyl)phenyl alkanoates **33–43** as is shown by reference to the data recorded in table 3 and plotted against the number of methylene units (*m*) in the acid moiety of the esters in figure 3. The melting point, the smectic B–isotropic liquid and the smectic F–isotropic liquid transition temperatures (S_B–I and S_F–I) are all higher

Table 2. The liquid crystal transition temperatures and enthalpies of fusion for 4-(5-octyl-2-pyridinyl)phenyl alkanoates **22–32**.



Ester	*m*	C–S_F/S_B/I/°C	S_F–I/°C	S_B–I/°C	Δ*H*/kJ mol^{-1}
22	2	76	—	(54)	29·2
23	3	80	—	(70)	28·7
24	4	64	—	75	17·7
25	5	65	—	75	16·6
26	6	57	—	76	14·9
27	7	57	77	—	19·8
28	8	60	80	—	20·4
29	9	61	81	—	21·0
30	10	61	83	—	22·5
31	11	42	83	—	40·4
32	12	51	83	—	19·7

( ) represents a monotropic transition temperature.

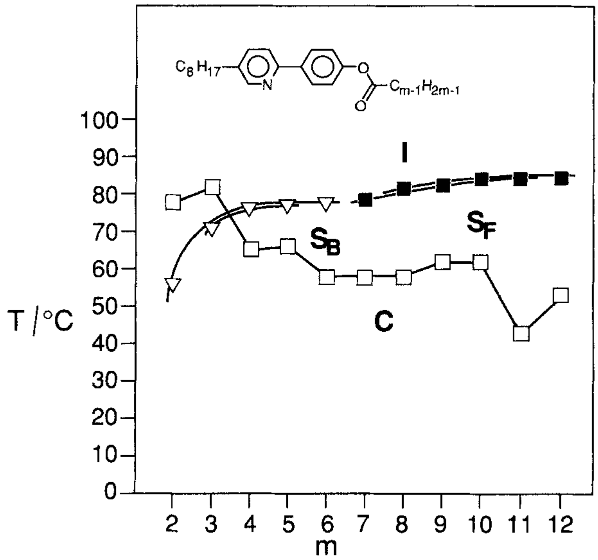
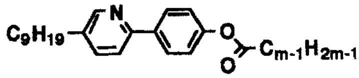


Figure 2. Plots of the transition temperatures against the number of carbon atoms (*m*) in the alkyl chain of the 4-(5-octyl-2-pyridinyl)phenyl alkanoates **22–32** (□, crystal–smectic F/smectic B/isotroipc; ■, smectic F–isotropic; ▽, smectic B–isotropic.

(⩽ + 5–6°C, on average) for the nonly esters **33–43** than for the octyl esters **22–33**, although the melting point plot is not quite so uniform.

These results contrast strongly with the enantiotropic smectic A and C mesophases often observed for the corresponding pyrimidinyl esters [1]. For these materials no ordered smectic mesophases have been reported for the analogous homologues corresponding to those reported here for the esters **11–43**.

Table 3. The liquid crystal transition temperatures and enthalpies of fusion for 4-(5-nonly-2-pyridinyl)phenyl alkanoates **33**–**43**.



Ester	*m*	C–S_B/S_F/I/°C	S_F–I/°C	S_B–I/°C	Δ*H*/kJ mol^{-1}
33	2	69	—	(57)	28·8
34	3	78	—	(74)	30·7
35	4	71	—	80	18·9
36	5	73	—	80	19·3
37	6	68	—	82	18·9
38	7	60	83	—	14·4
39	8	66	86	—	22·7
40	9	70	87	—	23·6
41	10	71	89	—	24·9
42	11	66	89	—	23·8
43	12	65	90	—	27·6

( ) represents a monotropic transition temperature.

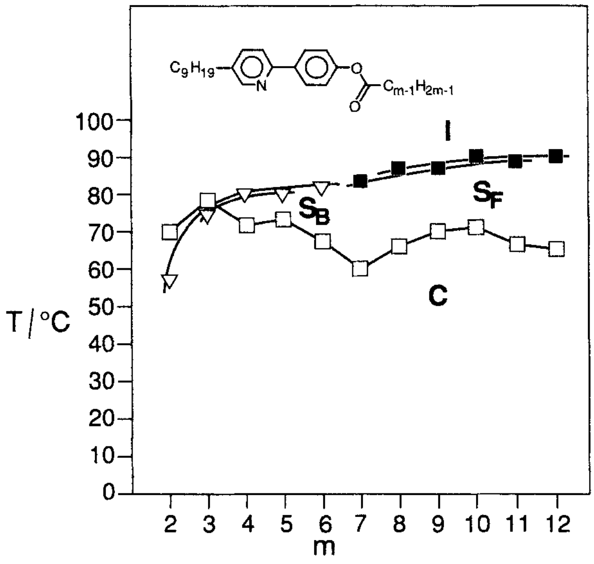


Figure 3. Plots of the transition temperatures against the number of carbon atoms (*m*) in the alkyl chain of the 4-(5-nonyl-2-pyridinyl)phenyl alkanoates **33**–**43** (□, crystal–smectic F/smectic B/isotropic; ■, smectic F–isotropic; ▽, smectic B–isotropic.

4. Physical properties

In order to investigate the suitability of the 4-(5-alkyl-2-pyridinyl)phenyl alkanoates as non-optically active components of chiral smectic C mixtures for electro-optic display device applications based on ferroelectric effects (SSFLCDs, DHFLCDs and SBFLCDs) a fixed amount (15 wt%) of selected homologues of the esters (**15**–**21**, **26**–**32** and **37**–**43**) was dissolved in a standard chiral smectic C mixture (SCO 1014; C/S_X–S_{C*} = −7·6°C, S_{C*}–S_A = 60·6°C, S_A–N* = 67·7°C and N*–I = 74·6°C; see the experimental part). The liquid crystal transition temperatures (C–S_{C^*}, S_X—S_{C^*}, S_{C^*}–S_A, S_A–N* and N*–I) the spontaneous polarization (P_s) and the observed switching time (τ) of the resulting mixtures were determined under standard conditions (τ: 10 Vpp/μ square wave, time to maximum current, at 25°C; P_s: 10 Hz, 10 Vpp/μ, triangle), see table 4. These homologues were chosen because they exhibit a tilted smectic F mesophase as well sometimes as smectic C mesophases. Thus, they were expected to be more soluble in the base chiral smectic C mixture than the shorter chain homologues, which only exhibit an orthorgonal smectic B mesophase.

The increase in the chiral smectic C–smectic A transition temperature for all three series of esters is surprising as the octyl- and nonly-substituted esters **22–32** and **33–43**, respectively, do not exhibit a smectic C mesophase. Reference to figure 4, where the chiral smectic C–smectic A transition temperatures of all three ester series are plotted against the number (*m*) of the methylene units (CH_2) in the alkyl chain of the acid part of the esters and to the data collated in table 4 reveals that the nonly substituted esters **33–43** exhibit the highest values. The series of heptyl substituted esters **15–21** exhibits a lower temperature of crystallization (−16·4°C, on average, respectively).

The switching times (τ) recorded in table 4 and plotted against the number (*m*) of methylene units (CH_2) in the alkyl chain of the acid part in figure 5 show that the switching times of the heptyl-substituted ester **15–21** are substantially longer (119 μs, on average) than for both the octyl- and nonly-substituted esters **26–32** and **37–43** (104 μs, on average for both series). This is surprising, as the value of the spontaneous

Table 4. The liquid crystal transition temperatures, spontaneous polarizations and response times for the chiral smectic C mixture SCO 1014 and a series of mixtures consisting of 15 wt% of the esters **15–21**, **26–32**, and **37–43** and 85 wt% and the mixture SCO 1014.

Ester	C/S_X–S_{C^*}/°C	S_{C^*}–S_A/°C	S_A–N*/°C	N*–I/°C	Ps/nC cm^{-2}	τ/μs
SCO 1014	−7·6	60·6	67·7	74·6	20·5	110
15	−17	59	63	71	17·1	106
16	−19	60	64	71	18·4	105
17	−17	62	65	72	18·4	98
18	−18	63	67	72	18·6	118
19	−13	64	66	72	18·2	145
20	−15	63	66	72	19·3	145
21		63	67	72	18·2	119
26	−8	60	64	71	17·4	95
27	−7	61	65	71	17·4	95
28		61	66	72	18·7	105
29	−10	63	66	72	18·8	105
30	−8	63	66	72	18·4	110
31	−8	62	66	72	18·8	105
32	−8	63	67	72	17·0	110
37	−8	61	66	71	18·1	96
38	−8	62	67	71	18·5	95
39	−9	63	67	71	17·6	100
40	−9	63	68	72	16·9	99
41	−7	64	68	72	17·5	112
42	−10	63	68	72	17·4	110
43	−5	64	69	73	17·8	114

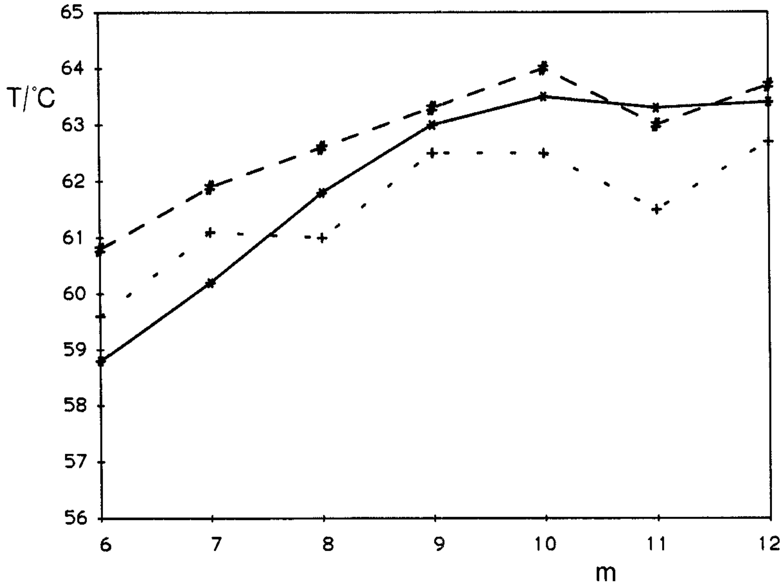


Figure 4. Plot of the chiral smectic C–smectic A transition temperature (S_{C^*}–S_A) against the number of carbon atoms (*m*) in the alkyl chain of the heptyl-, octyl- and nonly-substituted 4-(5-alkyl-2-pyridinyl)phenyl alkanoates **15–21**, **26–32**, and **37–43**, respectively (*, $n=7$; +, $n=8$; #, $n=9$).

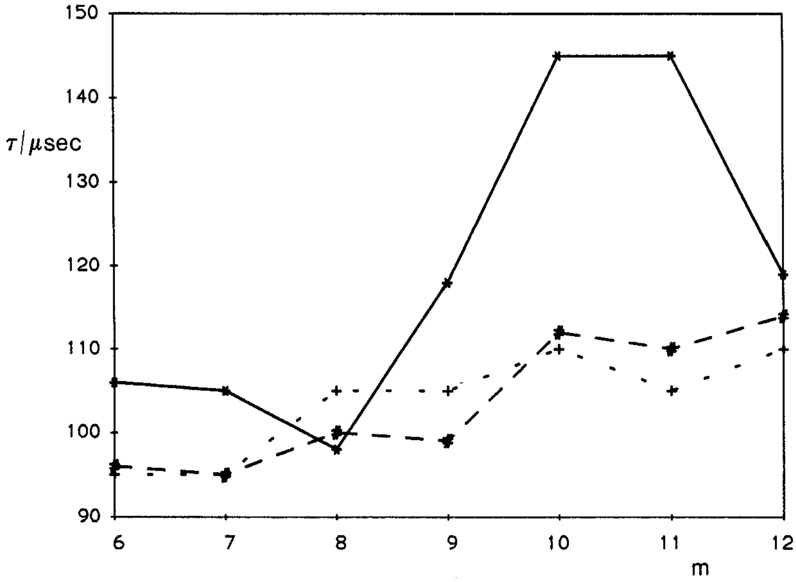


Figure 5. Plot of the switching times (τ) against the number of carbon atoms (*m*) in the alkyl chain of the heptyl-, octyl- and nonly-substituted 4-(5-alkyl-2-pyridinyl)phenyl alkanoates **15–21**, **26–32**, and **37–43**, respectively (*, $n=7$; +, $n=8$; #, $n=9$).

polarization (P_s) is almost identical (18·3, 18·1 and 17·7 nC cm^{-1}, on average, respectively) for the heptyl-, octyl- and nonyl-substituted esters, thus indicating that the tilt angle (θ) is the same for all three series [25, 26]. It is most unusual that the homologues with longer chain lengths exhibit lower viscosities than those of their shorter chain analogues.

A combination of the data depicted in figures 4 and 5 produces figure 6, where it is apparent that the nonyl-substituted esters **37–43** exhibit the most advantageous combination of a high chiral smectic C–smectic A transition temperatures and short switching times.

The ability of selected homologues of the 4-(5-alkyl-2-pyridinyl)phenyl esters **11–43** to increase the temperature range of the smectic C mesophase can be further demonstrated by reference to the data collated in table 5 for two similar mixtures containing either a homologue of the pyridinylphenyl esters **11–43** or the structurally related 4-(5-alkyl-2-pyrimidinyl)phenyl esters [1]. The base mixture consists of a chiral dopant bis(*S*)-1-methylheptyl *p*-terphenyl-4,4″-dicarboxylate [2, 27]) and two non-optically active components 2-[4-(hexyloxy)phenyl-5-nonylpyrimidine (28 wt%) and 2-[4-(nonyloxy)phenyl]-5-nonylpyrimidine, (29 wt%). The mixture 1 consists of the base mixture (61·0 wt%) and two pyridinylphenyl esters **27** and **28** (16·5 wt% and 22·5 wt%, respectively). Mixture 2 contains the base mixture (60·5 wt%) and two pyrimidinylphenyl esters [1]: 4-(5-nonyl-2-pyrimidinyl)phenyl nonanoate (21·5 wt%) and 4-(5-nonyl-2-pyrimidinyl)phenyl decanoate (18·0 wt%), respectively. In contrast to the pyridinylphenyl alkanoates, the 4-(5-alkyl-2-pyrimidinyl)phenyl alkanoates generally exhibit enantiotropic wide range smectic C mesophases [1] and have already been shown to be useful components of commercial chiral smectic C mixtures [2]. However, it can be seen from table 5 that mixture 1 containing the pyridinylphenyl alkanoates

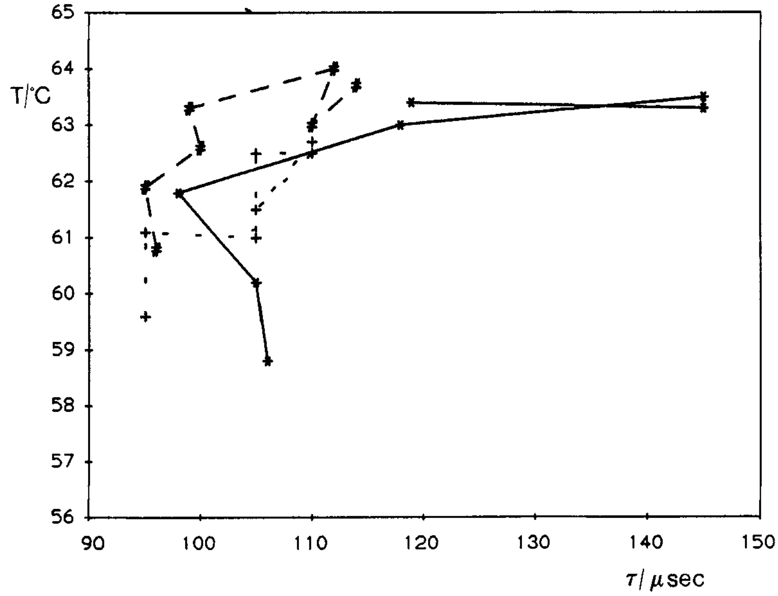


Figure 6. Plot of the chiral smectic C–smectic A transition temperature (S_{C^*}–S_A) against the switching times (τ) of the heptyl-, octyl- and nonyl-substituted 4-(5-alkyl-2-pyridinyl)phenyl alkanoates **15–21**, **26–32**, and **37–43**, respectively (*, $n=7$; +, $n=8$; #, $n=9$).

Table 5. A comparison of the liquid crystal transition temperatures and the switching times for mixture 1 containing 16·5 wt% and 22·5 wt% of the pyridinylphenyl alkanoates **17** and **18** and mixture 2 incorporating two related pyrimidinylphenyl alkanoates (21·5 wt% and 18·0 wt%) in the chiral smectic C mixture described in the text.

Mixture	C/S_X–S_{C*}/°C	S_{C*}–S_A/°C	S_A–I/°C	S_{C*}–I/°C	$\tau/\mu s$
1	$\leqslant -9$	—	—	66	42
2	>0	58	61	—	42

exhibits a chiral smectic C mesophase over a larger temperature range (75°C) than the corresponding mixture 2 incorporating the analogous pyrimidinylphenyl alkanoates (58°C); the melting point is significantly lower (−9°C) and the smectic C transition temperature is substantially higher (+8°C). Whereas mixture 2 exhibits a smectic A mesophase above the chiral smectic C mesophase, mixture 1 exhibits a direct transition from the chiral smectic C mesophase to the isotropic liquid. This turned out to be advantageous for good alignment in SBFLCD cells. The switching times of the mixtures are identical.

5. Experimental

The liquid crystal transition temperatures of the compounds prepared and recorded in tables 1–3 were determined by optical microscopy using a Leitz Otholux 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 (−50°C) by allowing N_2 gas, cooled by liquid N_2, to pass through the stage at a controlled rate. The liquid crystal transition temperatures 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 differential thermal analysis (DTA). 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 (Machery–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 N_2 unless water was present as a reagent or solvent. 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 chiral smectic C mixture SCO 1014 consists of 4-[*trans*-4-([(*R*)-2-fluorohexanoyl]oxy)cyclohexyl]phenyl 2,3,-difluoro-4-octyloxybenzoate ester (16 wt%), 2-(4-hexyloxy]phenyl)-5-nonylpyrimidine (24 wt%), 2-[4-nonyloxyphenyl]-5-nonylpyrimidine (24 wt%), 2-[4-nonyloxyphenyl]-5-heptylpyrimidine (12 wt%), 2-[4-hexyloxyphenyl]-5-octylpyrimidine (12 wt%) and 2-[4-decyloxyphenyl]-5-octylpyrimidine (12 wt%).

The determination of the physical properties of the chiral mixtures containing the new esters was carried out as previously described [2, 24, 25].

5.1. *3-Chloro-6-nicotinic acid chloride* (**2**)

A mixture of 3-chloro-6-nicotinic acid (31·4 g 0·22 mol), thionyl chloride (35·8 g, 0·30 mol), toluene (250 ml) and *N*,*N*′-dimethylformamide (1 ml) was heated under gentle reflux for 2 h. The cooled reaction mixture was evaporated down, toluene (50 ml) was added and the resultant mixture evaporated down again. This procedure was repeated once more. The resultant residue was distilled under reduced pressure to give the acid chloride (yield 31·4 g, 90 per cent); bp 110–114°C/11 cm Hg.

5.2. *2-Chloro-5-(hydroxymethyl)pyridine* (**3**)

A solution of 3-chloro-6-nicotinic acid chloride **2** (31·4 g, 0·178 mol) in dioxane (20 ml) was added dropwise to a solution of sodium borohydride (27·2 g) and water (20 ml) and stirred for 2 h. The reaction mixture was saturated with sodium chloride (5 g) and then extracted with *tert*-butyl methyl ether (4 × 50 ml). The combined organic layers were washed with brine (4 × 50 ml), dried ($MgSO_4$), filtered and then evaporated down to yield the alcohol (25·2 g, 99 per cent), which contained 4·6 per cent of an impurity, but was used in the next reaction without further purification.

5.3. *2-Chloro-5-(tetrahydro-2-pyranyloxy)methyl)pyridine* (**4**)

A mixture of 2-chloro-5-(hydroxymethyl)pyridine **3** (25·2 g, 0·176 mol), 3,4-dihydro-2H-pyran (36·8 g, 0·439 mol), 4-toluene-sulphonic acid (7·0 g) and *tert*-butyl methyl ether (200 ml) was heated at 55°C for 2 h. Triethylamine (10 ml) was added to the cooled reaction mixture, which was diluted with hexane (50 ml), washed with saturated sodium bicarbonate solution (2 × 10 ml), dried ($MgSO_4$), filtered and the residue distilled over anhydrous potassium carbonate (0·5 g) to give the ether (yield 39·3 g, 98 per cent) with a purity of 96·2 per cent); bp 108–115°C/0·1 mm Hg. MS: 227 (M^+).

5.4. *4-(5-[(tetrahydro-2-pyranyloxy)methyl]-2-pyridinyl)phenyl isopropyl ether* (**5**)

A solution of Grignard reagent (prepared in the usual way from 4-bromophenyl isopropyl ether (50 g, 0·233 mol), magnesium turnings (6·1 g, 0·256 mol) and tetrahydrofuran (250 ml)) was added dropwise to a mixture of 2-chloro-5-((tetrahydro-2-pyranyloxy)methyl)pyridine **4** (37·5 g, 0·165 mol), 1,3-bis(diphenylphosphino)propanenickel-(II)-chloride (1·8 g, 0·0035 mol) and tetrahydrofuran (400 ml) at 0°C. The reaction mixture was stirred for 3 h at 0°C and then overnight at room temperature. The reaction mixture was made alkaline (pH 8) with sodium bicarbonate solution and diluted with diethyl ether. The organic layer was separated off and the aqueous layer extracted with diethyl ether (3 × 50 ml). The combined organic layers were washed with brine (3 × 500 ml), dried ($MgSO_4$), filtered and evaporated down. The residue was purified over silica gel using a 4 : 1 hexane/ethyl acetate mixture as eluent to give the ether (yield 44·8 g, 82 per cent) which contained 6 per cent of an impurity. MS. 327 (M^+).

5.5. *4-(5-Hydroxymethyl-2-pyridinyl)phenyl isopropyl ether* (**6**)

A solution of 4-(5-[(tetrahydro-2-pyranyloxy)methyl]-2-pyridinyl)phenyl isopropyl ether **5** (44·8 g, 0·027 mol), 2*N* hydrochloric acid (100 ml) and tetrahydrofuran (750 ml) was heated at 60°C for 6 h. Diethylether (500 ml) was added to the cooled reaction mixture and the aqueous layer separated. The organic layer was washed with brine (2 × 50 ml) and saturated sodium bicarbonate solution (3 × 75 ml), dried

($MgSO_4$), filtered and evaporated down. The residue was crystallized from *tert.*-butyl methyl ether to give the alcohol (25 g, 76 per cent) with a purity of 98·8 per cent. MS. 243 (M^+).

5.6. *4-(5-Formyl-2-pyridinyl)phenyl isopropyl ether* (**7**)

Activated mangenese (IV) oxide (34·0 g, 0·391 mol) was added to a solution of 4-(5-hydroxymethyl-2-pyridinyl)phenyl isopropyl ether **6** (25 g, 0·102 mol) and dichloromethane (150 ml). The resultant mixture was heated for 4·5 h under gentle reflux and then evaporated down. The residue was purified by column chromatography on silica gel with dichloromethane as eluent and crystallization from *tert.*-butyl methyl ether to give the aldehyde (yield 20 g, 81 per cent); mp, 90·5–91°C. MS: 241 (M^+).

5.7. *4-[(E/Z)-5-hept-1-en-1-yl-2-pyridinyl]phenyl isopropyl ether* (**8**) ($n = 7$)

Potassium *tert.*-butoxide (14·0 g, 0·124 mol) was added in portions to a solution of 4-(5-formyl-2-pyridinyl)phenyl isopropyl ether **7** (20 g, 0·083 mol), hexylphosphonium bromide (55 g, 0·124 mol) and tetrahydrofuran (200 ml) at 0°C. A dark orange colour was observed during and after the addition. The reaction mixture was stirred at room temperature overnight, then poured into water (1000 ml) and the product extracted into ethyl acetate (3 x 200 ml). The combined organic layers were washed with water (2 x 500 ml), dried ($MgSO_4$), filtered and then evaporated down. The residue was taken up in warm hexane (1000 ml), stirred, filtered to remove precipitated material (PPh_3O), evaporated down again and the residue purified by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture as eluent (flash) to give a yellow oil (yield 26 g, 98 per cent). IR (Film): 2927, 1607, 1475, 1246, 954, 833. MS: 309 (M^+), 267 ($C_{18}H_{21}NO$).

The compound *4-[(E/Z)-5-oct-1-en-1-yl-2-pyridinyl]phenyl isopropyl ether* **8** ($n = 8$) was prepared using the same procedure (yield 98 per cent). IR (Film): 2926, 1607, 1511, 1245, 945, 834. MS: 323 (M^+), 281 ($C_{19}H_{23}NO$).

The compound *4-[(E/Z)-5-non-1-en-1-yl-2-pyridinyl]phenyl isopropyl ether* **8** ($n = 9$) was prepared using the same procedure (yield 90 per cent). IR (Film): 2926, 1587, 1511, 1246, 839. MS: 337 (M^+), 295 ($C_{20}H_{25}NO$).

5.8. *4-(5-Heptyl-2-pyridinyl)phenyl isopropyl ether* (**9**) ($n = 7$)

A mixture of 4-[(*E*/*Z*)-5-hept-1-en-1-yl-2-pyridinyl]phenyl isopropyl ether **8** ($n = 7$) (25 g, 0·081 mol), 10 per cent palladium on active charcoal (1·5 g) and ethyl acetate (250 ml) was hydrogenated until the absorption of hydrogen was completed. The inorganic material was removed by filtration and the solvent removed by evaporation under reduced pressure. The residue was purified by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture as eluent followed by recrystallization from hexane (yield 25 g, quantitative). IR (Film): 2928, 1606, 1513, 1247, 1065, 843, 807. MS: 311 (M^+) 269 ($C_{18}H_{23}NO$), 194 ($C_{12}H_{20}NO$).

The compound *4-(5-octyl-2-pyridinyl)phenyl isopropyl ether* (**9**) ($n = 8$) was prepared using the same procedure (yield 99 per cent). IR (Film): 2921, 2851, 1605, 1512, 1248, 820. MS: 325 (M^+), 283 ($C_{19}H_{25}NO$), 194 ($C_{12}H_{20}NO$).

The compound *4-(5-nonly-2-pyridinyl)phenyl isopropyl ether* (**9**) ($n = 9$) was prepared using the same procedure (yield 97 per cent). IR (Film): 2920, 2851, 1602, 1512, 1248. 828. MS: 339 (M^+), 297 ($C_{20}H_{27}NO$), 194 ($C_{12}H_{20}NO$).

5.9. *4-(5-Heptyl-2-pyridinyl)phenol* (**10**) (*n* = 7)

A one molar solution of boron tribromide (97 ml) was added dropwise to a solution 4-(5-heptyl-2-pyridinyl)phenyl isopropyl ether **9** (*n* = 7) (25 g, 0·080 mol) in dichloromethane (200 ml) and cooled using an ice bath. The reaction was stirred overnight at room temperature and then poured on to an ice/water mixture (400 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 (500 ml), dilute potassium carbonate (200 ml) and once again with water (500 ml), then dried ($MgSO_4$), filtered and evaporated. The residue was purified by column chromatography (flash) on silica gel using a 97 : 3 dichloromethane/methanol mixture as eluent followed by recrystallization from ethyl acetate to give the phenol (yield 11·0 g, 51 per cent) mp 105–106°C (Lit. 105–106°C [4]). IR (KBr): 2925, 2670, 2599, 1609, 1519, 827. MS: 269 (M^+), 194 ($C_{12}H_{20}NO$).

The compound *4-(5-octyl-2-pyridinyl)phenol* (**10**) (*n* = 8) was prepared using the same procedure (yield 83 per cent). mp 93–95°C. (Lit. 93–95°C [4]). IR (KBr): 3219, 2921, 2851, 2599, 1607, 1515, 1290, 1020, 840. MS: 283 (M^+), 194 ($C_{12}H_{20}NO$).

The compound *4-(5-nonly-2-pyridinyl)phenol* (**10**) (*n* = 9) was prepared using the same procedure (yield 82 per cent). mp 87–88°C. (Lit. 85–87·5°C [4]). IR (KBr): 3188, 2922, 2772, 1605, 1515, 1289, 1020, 839. MS: 297 (M^+), 194 ($C_{12}H_{20}NO$).

5.10. *4-(5-Heptyl-2-pyridinyl)phenyl acetate* (**11**) (*n* = 7; *m* = 2)

A solution of 4-(heptyl-2-pyridinyl)phenol **10** (*n* = 7) (0·25 g, 0·0009 mol), acetic acid (0·06 g, 0·0009 mol), *N*,*N*,-dicyclohexylcarbodiimide (0·23 g, 0·0011 mol), 4-(dimethylamino)pyridine (0·04 g) and dichloromethane (25 ml) was stirred at room temperature overnight. After filtration to remove precipitated material, the filtrate was evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using a 7 : 3 hexane/ethyl acetate mixture as eluent followed by recrystallization from ethanol until the liquid crystal transition temperatures were constant. The liquid crystal transition temperatures and enthalpies of fusion of this ester and other esters **12–43** prepared using this general procedure are given in tables 1–3 and plotted against the number of carbon atoms in the acid part of the ester in the figures 1–3. IR (Nujol): 2955, 2924, 2852, 1754, 1594, 1470, 1202, 839. MS: 311 (M^+), 269 ($C_{18}H_{23}NO$), 194 ($C_{12}H_{20}NO$).

The authors express their gratitude to Mr C. Haby, Mr R. Schenk, Mr C. Pfleger, Mr H. R. Saladin and Mr W. Jans for technical assistance in the preparation of the compounds and the determination of their physical data. 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.

References

[1] Zaschke, H., 1975, *J. prakt. Chem.*, **9**, 1173.
[2] Fünfschilling, J., and Kelly, S. M., 1991, *Proc. 20th Freiburger Arbeitstagung Flüssigkristalle.*
[3] Maedicke, A., Demus, D., Titov, V. V., Pavluchenko, A. I., and Kovshev, E. I., 1983, *Cryst. Res. Tech.*, **18**, K45.
[4] Inoue, H., Inukai, T., Ohno, K., Saito, S., and Miyazawa, K., 1987, EPA 0 239 403.
[5] Burrow, M. P., Gray, G. W., Lacey, D. L., and Toyne, K. J., 1988, *Liq. Crystals*, **3**, 1643.
[6] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.

[7] CLARK, N. A., HANSCHY, M. A., and LAGERWALL, S. T., 1983, *Molec. Crystals liq. Crystals*, **94**, 213.

[8] BERESNEV, L. A., CHIGRINOV, V. G., DERGACHEV, D. I., POSHIDAEV, E. P., FÜNFSCHILLING, J., and SCHADT, M., 1989, *Liq. Crystals*, **5**, 1171.

[9] FÜNFSCHILLING, J., and SCHADT, M., 1989, *J. appl. Phys.*, **66**, 3877.

[10] FÜNFSCHILLING, J., and SCHADT, M., 1990, *Proc. S.I.D.*, **31**, 119.

[11] FÜNFSCHILLING, J., and SCHADT, M., 1990, *S.I.D. 90 Digest*, 106.

[12] FÜNFSCHILLING, J., and SCHADT, M., 1991, *Jap. J. appl. Phys.*, **30**, 741.

[13] SCHADT, M., *Liq. Crystals* (in the press).

[14] FÜNFSCHILLING, J., 1992, *Proc. 21st Freiburger Arbeitstagung Flüssigkristalle.*

[15] ZIEGLER, F. E., and SWEENY, J. G., 1969, *J. org. Chem.*, **34**, 3545.

[16] NEGISHI, E., 1982, *Accts. chem. Res.*, **15**, 340 and references contained therein.

[17] VILLIGER, A. (private communication).

[18] EVANS, R. M., 1959, *Q. Rev. chem. Soc.*, **13**, 61.

[19] NEISES, B., and STEGLICH, W., 1978, *Angew. Chem.*, **90**, 556.

[20] KARAMYSHEVA, L. A., KOVSHEV, E. I., PAVLUCHENKO, A. I., ROITMAN, K. V., TITOV, V. V., TORGOVA, S. I., and GREBENKIN, M. F., 1981, *Molec. Crystals liq. Crystals*, **67**, 241.

[21] GREBENKIN, M. F., PETROV, V. F., BELYEV, V. V., PAVLUCHENKO, A. I., SMIRNOVA, N. I., KOVSHEV, E. I., TITOV, V. V., and IVASCHENKO, A. V., 1985, *Molec. Crystals liq. Crystals*, **129**, 245.

[22] SCHROTH, W., and FISCHER, G. W., 1969, *Ber. Chem.*, **102**, 584.

[23] GRAY, G. W., HIRD, M., and TOYNE, K., 1991, *Molec. Crystals liq. Crystals*, **204**, 91 and references contained therein.

[24] GOODBY, J. W., 1983, *Molec. Crystals liq. Crystals Lett.*, **92**, 171.

[25] LEENHOUTS, F., KELLY, S. M., and VILLIGER, A., 1990, *Displays*, 41.

[26] LEENHOUTS, F., FÜNFSCHILLING, J., BUCHECKER, R., and KELLY, S. M., 1989, *Liq. Crystals*, **5**, 179.

[27] RABINOVITCH, A. Z., LOSEVA, M. V., CHERNOVA, N. I., POZHIDAEV, E. P., PETRASHEVICH, O. S., and NARKEEVICH, J. S., 1989, *Liq. Crystals*, **6**, 533.