

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Ferroelectric liquid crystals IV. Chiral alkenyloxyphenyl benzoates

S. M. Kelly^a; R. Buchecker^a; M. Schadt^a

^a Central Research Units, F. Hoffmann-La Roche, Basle, Switzerland

To cite this Article Kelly, S. M. , Buchecker, R. and Schadt, M.(1988) 'Ferroelectric liquid crystals IV. Chiral alkenyloxyphenyl benzoates', *Liquid Crystals*, 3: 8, 1115 – 1123

To link to this Article: DOI: 10.1080/02678298808086566

URL: <http://dx.doi.org/10.1080/02678298808086566>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Ferroelectric liquid crystals

IV. Chiral alkenyloxyphenyl benzoates

by S. M. KELLY, R. BUCHECKER and M. SCHADT

Central Research Units, F. Hoffmann-La Roche, CH-4002 Basle, Switzerland

(Received 21 December 1987; accepted 6 February 1988)

Over forty 4-alkoxyphenyl 4-alkoxybenzoates incorporating an olefinic double bond in one carbon chain and an optically active centre in the second (methyl branched) chain have been prepared. The effect of chain length and the position of the chiral centre on the liquid crystal transition temperatures of the esters has been investigated systematically. Apart from one important exception the double bond was maintained in a terminal position of the carbon chain. Several of the new esters exhibit an enantiotropic chiral smectic C mesophase at and just above room temperature.

1. Introduction

A wide variety of substituted phenyl benzoates incorporating an optically active centre in one of the terminal alkyl/alkoxy, dialkyl or dialkoxy carbon chains were synthesized a number of years ago in the search for chiral nematic materials, mostly for thermochromic applications [1-4]. Several esters also exhibited a smectic A mesophase [3] as well as the desired chiral nematic mesophase. There is only one reported case of smectic polymorphism, although the second smectic phase was not identified (now known to be a chiral smectic C phase (S_C^*) [5, 6]).

Much more recently a large number of chiral 4-alkoxyphenyl 4-alkoxybenzoates [5-11] have been prepared in the desire to produce chiral smectic C materials. A number of homologous series exhibit enantiotropic, chiral smectic C mesophases over a relatively wide temperature range, somewhat above room temperature [6-11]. The presence of two alkoxy chains (i.e., two oxygen atoms) is advantageous for the presence of smectic C mesophases as opposed to other smectic modifications [12].

The presence of a double bond ($C=C$) in the terminal carbon chain of nematic liquid crystals has been shown to have quite remarkable effects on their liquid crystal transition temperatures and other physical properties [13-18]. It was decided therefore to introduce a double bond into six homologous series of chiral 4-alkoxyphenyl 4-alkoxybenzoates to determine the effect on the liquid crystal transition temperatures of a primarily smectic class of materials. The olefinic bond was incorporated in each case in a terminal position of the carbon chain to minimize the length of the reaction pathways and to allow valid comparisons to be made for very similar homologous series. The chiral carbon chains were limited to 2-methylbutoxy, 4-methylhexyloxy and 6-methyloctyloxy. The configuration at the chiral centre is in each case (S). These limited variations in the terminal carbon chains allow the effect of alkoxy chain length and position of the optically active centre to be investigated systematically.

A similar modification of the phenyl benzoate system by incorporation of a *trans*-1,4-disubstituted cyclohexane ring and various linking groups has been reported in detail elsewhere [19-21].

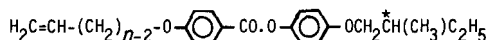
The required optically active acids and phenols were synthesized as previously described using (S)-2-methylbutanol as the chiral starting material [20]. The integrity of the optically active centre was maintained throughout the syntheses and thus each reaction intermediate and end product has the same configuration and optical purity. The desired 4-(alkenyloxy)benzoic acids were also synthesised as reported previously [21]. The required 4-(alkenyloxy)phenols were prepared by mono alkylation of 4-hydroquinone as described in the experimental section. Either the corresponding 1-bromoalkenes were used in the alkylation reaction (when commercially available) or 1-tosylalkenes prepared from the analogous alcohols.

2. Results

The liquid crystal transition temperatures (C-S_A, C-I, S_C^{*}-S_A, S_A-I, Ch-I) and enthalpies of fusion (ΔH) of the 4-[(S)-2-methylbutoxy]phenyl 4-(alkenyloxy)benzoates (*I*) are collated in table 1. The melting points (C-S_A, C-I) of the esters (*I*) fall from high values for short alkenyloxy chains, reach a minimum ($n = 9$) and then rise again. The only observable enantiotropic liquid crystal mesophase is a smectic A phase which increases with lengthening chain length. Monotropic chiral smectic C and chiral nematic (Ch) mesophases could also be observed. The enthalpies of fusion are moderately high.

An important feature of the data listed in table 1 is the complete absence of ordered smectic mesophases. This is in contrast to the corresponding esters without an olefinic double bond in the terminal alkoxy chain [3-11]. For these esters a monotropic ordered mesophase (S_H) is observed just below or above room temperature for most of the same homologues studied.

Table 1. Transition temperatures (°C) and enthalpies of fusion for the 4-[(S)-2-methylbutoxy]phenyl 4-(alkenyloxy)benzoates (*I*).

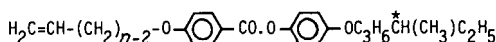


<i>n</i>	C-S _A /I	S _C [*] -S _A	S _A -I	Ch-I	$\Delta H/\text{kJ mol}^{-1}$
6	62	-	-	(40)	27.5
7	56	-	(55)	-	28.4
8	44	(26)	49	-	25.3
9	36	-	58	-	25.3
10	39	(36)	55	-	26.9
11	48	(33)	60	-	32.9
12	45	(38)	58	-	27.1

() represents a monotropic transition temperature.

Listed in table 2 are the liquid crystal transition temperatures (C-S_C^{*}, C-S_A, C-I, S_B-S_C^{*}, S_C^{*}-S_A, S_A-Ch, S_A-I, Ch-I) and the enthalpies of fusion (ΔH) of the 4-[(S)-4-methylhexyloxy]phenyl 4-(alkenyloxy) benzoates (*II*). The melting points (C-S_C^{*}, C-S_A, C-I) of the esters *II* decrease sharply with increasing chain length until a minimum is reached ($n = 10$). The enantiotropic chiral nematic mesophase observed for short chain lengths ($n = 6, 7, 8$) is replaced by a smectic A mesophase for longer chain lengths ($n = 8-11$). A pattern of alternation is observed for these two phases [12]. A chiral smectic C mesophase is only apparant for longer chain lengths ($n = 8-11$). However the chiral smectic C to smectic A transition temperature

Table 2. Transition temperatures (°C) and enthalpies of fusion for the 4-[(S)-4-methylhexyloxy]phenyl 4-(alkenyloxy)benzoates (II).



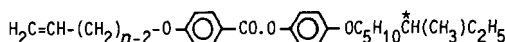
<i>n</i>	C-S _C [*] /S _A /I	S _B -S _C [*]	S _C [*] -S _A	S _A -Ch/I	Ch-I	Δ <i>H</i> /kJ mol ⁻¹
6	63	-	-	-	(58)	27.0
7	64	-	-	65	69	23.9
8	48	-	(44)	61	63	30.4
9	41	-	(39)	68	-	24.1
10	29	-	54	65	-	28.9
11	40	(31)	56	70	-	39.8
12	50	(35)	61	69	-	35.4

() represents a monotropic transition temperature.

increases greatly with increasing chain length. A monotropic smectic B mesophase could be found for the longest chain studied.

The liquid crystal transition temperatures (C-S_C^{*}, C-S_A, S_B-S_C^{*}, S_C^{*}-S_A, S_C^{*}-Ch, S_A-Ch, S_A-I, Ch-I) and enthalpies of fusion (Δ*H*) of the 4-[(S)-6-methyloctyloxy]phenyl 4-(alkenyloxy)benzoates (III) are recorded in table 3. Quite unusually the melting point (C-S_C^{*}, C-S_A) of the esters III increases generally with increasing size of the terminal chain. Otherwise the general trends observed for the other transition temperatures (S_B-S_C^{*}, S_C^{*}-S_A, S_C^{*}-Ch, S_A-Ch, S_A-I, Ch-I) are almost exactly the same as those determined for the analogous esters II with two methylene units less in the chiral alkoxy chain (see table 2). The enthalpies of fusion (Δ*H*) are, in general, rather high (34 kJ mol⁻¹, on average).

Table 3. Transition temperatures (°C) and enthalpies of fusion for the 4-[(S)-6-methyloctyloxy]phenyl 4-(alkenyloxy)benzoates (III).



<i>n</i>	C-S _C [*] /S _A	S _B -S _C [*]	S _C [*] -S _A /Ch	S _A -Ch/I	Ch-I	Δ <i>H</i> /kJ mol ⁻¹
6	45	-	51	-	65	18.6
7	42	-	(41)	74	75	31.5
8	54	-	56	71	71	34.0
9	52	-	(43)	78	-	31.6
10	63	(37)	67	75	-	43.2
11	53	(46)	69	78	-	41.7
12	52	(44)	71	75	-	34.9

() represents a monotropic transition temperature.

Collated in table 4 are the liquid crystal transition temperatures (C-I and Ch-I) and enthalpies of fusion (Δ*H*) of the 4-(alkenyloxy)phenyl 4-[(S)-2-methylbutoxy]benzoates (IV). The only liquid crystal mesophases that were observed were monotropic chiral nematic phases. These transition temperatures (Ch-I) show the normal pattern of alternation [12]. No particular trend could be determined for the melting points (C-I). The enthalpies of fusion are moderately high. This contrasts with the constitutional isomers I which exhibit smectic polymorphism at elevated temperatures for two ring systems (see table 1). This demonstrates once again that apparently small changes in the chemical structure of mesomorphic systems (in this case the reversal

Table 4. Transition temperatures (°C) and enthalpies of fusion for the 4-(alkenyloxy)phenyl 4-[(S)-2-methylbutoxy]benzoates (IV).

$$\text{C}_2\text{H}_5\overset{\ast}{\text{C}}\text{H}(\text{CH}_3)\text{CH}_2\text{-O}-\text{C}_6\text{H}_4\text{-CO}_2\text{-O}-\text{C}_6\text{H}_4\text{-O}-(\text{CH}_2)_{m-2}\text{-CH=CH}_2$$

<i>m</i>	C-I	Ch-I	ΔH kJ mol ⁻¹
4	48	–	22.9
5	55	–	25.7
6	51	(31)	26.0
7	52	(44)	25.8
8	51	(38)	25.1
9	51	(45)	27.7
10	40	(38)	–
11	46	(45)	37.7

() represents a monotropic transition temperature.

of an ester linkage) can result in large changes in the observed liquid crystal transition temperatures. Similar effects have also been observed for the analogous esters not containing the terminal double bond [8, 9].

The liquid crystal transition temperatures (C-S_C^{*}, C-Ch, C-I, S_C^{*}-Ch, Ch-I) and enthalpies of fusion (ΔH) of the 4-(alkenyloxy)phenyl 4-[(S)-4-methylhexyloxy]benzoates (V) are listed in table 5. The melting points (C-S_C^{*}, C-Ch, C-I) decrease substantially with increasing chain length to reach a minimum (*m* = 9) below room temperature before increasing again. The clearing point (Ch-I) and chiral smectic C transition temperature both reach a maximum for the same homologue (*m* = 9) after rising from low values for short chain lengths. Thus an enantiotropic chiral smectic C mesophase is observed for this homologue at room temperature over a relatively wide temperature range (20°C ↔ 41°C). No ordered smectic mesophase could be observed for this or any other homologue of the series of esters V prepared. The enthalpy of fusion is also remarkably low for this member (*m* = 9) of the series. The corresponding saturated ester (without an olefinic double bond) possesses a higher melting point (32°C), clearing point (57°) and chiral smectic C-chiral nematic transition temperature (45.5°C) [9]. However the temperature range of the chiral smectic C mesophase is significantly narrower (13.5°). Thus the presence of the olefinic double bond in the terminal alkoxy chain has led to a *broadening* of the chiral smectic C temperature range.

Table 5. Transition temperatures (°C) and enthalpies of fusion for the 4-(alkenyloxy)phenyl 4-[(S)-4-methylhexyloxy]benzoates (V).

$$\text{C}_2\text{H}_5\overset{\ast}{\text{C}}\text{H}(\text{CH}_3)\text{C}_3\text{H}_6\text{-O}-\text{C}_6\text{H}_4\text{-CO}_2\text{-O}-\text{C}_6\text{H}_4\text{-O}-(\text{CH}_2)_{m-2}\text{-CH=CH}_2$$

<i>m</i>	C-S _C [*] /Ch/I	S _C [*] -Ch	Ch-I	$\Delta H/\text{kJ mol}^{-1}$
4	58	–	(39)	37.9
5	41	(34)	58	24.2
6	38	(35)	50	20.7
7	33	37	61	16.5
8	30	40	56	11.7
9	20	41	63	8.1
10	25	40	56	9.8
11	34	42	61	27.5

() represents a monotropic transition temperature.

Displacement of the olefinic double bond of one homologue ($m = 8$) of the esters *V* to a more central position in the terminal, achiral carbon chain to yield 4-(5-(*Z*)-octenyloxy)phenyl 4-[(*S*)-4-methylhexyloxy]benzoate results in interesting changes in the liquid crystal transition temperatures. The melting point ($C-S_C^*$) and clearing point ($Ch-I$) both decrease (-8°C and -10°C , respectively). The chiral smectic *C* to chiral nematic transition temperature (S_C^*-Ch) increases to a marginal extent ($+1^\circ\text{C}$). Thus a chiral smectic *C* mesophase is observed at and above room temperature ($C-S_C^* = 22^\circ\text{C}$; S_C^*-Ch , 41°C ; $Ch-I$, 46°C). This demonstrates the stability of the chiral smectic *C* mesophase to changes in the position of the double bond. A systematic variation of the position and configuration (*Z* and *E*) of the olefinic double bond ($C=C$), whilst maintaining all other parameters constant, is required to investigate these effects consistently.

The liquid crystal transition temperatures ($C-S_C^*$, $C-Ch$, S_C^*-Ch , $Ch-I$) of the 4-(alkenyloxy)phenyl 4-[(*S*)-6-methyloctyloxy]benzoates (*VI*) are recorded in table 6, as are the enthalpies of fusion (ΔH). The melting points ($C-S_C^*$ and $C-Ch$) show a consistent minimum for intermediate chain lengths ($m = 6-9$) rising for both shorter ($m = 4, 5$) and longer ($m = 10, 11$) chains. The clearing points ($Ch-I$) possess a high degree of alternation and are still rising for the longest chain lengths investigated ($m = 11$). The chiral smectic *C* to chiral nematic mesophase transition temperatures (S_C^*-Ch) also exhibit a degree of alternation and are also still increasing for the longest alkenyloxy chains studied. No other smectic mesophases could be found. Thus the esters *VI* exhibit enantiotropic chiral smectic *C* mesophases over a wide temperature range.

Table 6. Transition temperatures ($^\circ\text{C}$) and enthalpies of fusion for the 4-(alkenyloxy)phenyl 4-[(*S*)-6-methyloctyloxy]benzoates (*VI*).

$$\text{C}_2\text{H}_5\overset{*}{\text{C}}\text{H}(\text{CH}_3)\text{C}_5\text{H}_{10}-\text{O}-\text{C}_6\text{H}_4-\text{CO}-\text{O}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_{m-2}-\text{CH}=\text{CH}_2$$

m	$C-S_C^*/Ch$	S_C^*-Ch	$Ch-I$	$\Delta H/\text{kJ mol}^{-1}$
4	43	(41)	52	26.8
5	48	54	66	20.0
6	39	51	60	24.0
7	38	56	69	21.3
8	38	57	65	24.0
9	38	61	70	27.0
10	45	60	67	21.8
11	45	63	70	35.3

() represents a monotropic transition temperature.

3. Discussion

Comparison of the data collated in tables 1-3 reveals the effect of increasing the length of the chiral chain consecutively by two methylene units while simultaneously moving the chiral centre away from the central core of the molecule to the same extent. Quite surprisingly the average melting points (48°C , 48°C and 52°C) of the three homologous series of the 4-alkoxyphenyl 4-(alkenyloxy)benzoates (*I*, *II* and *III*) are remarkably similar. All the other liquid crystal transition temperatures increase significantly with increasing chain length as is usually observed for branched chain mesogens [22-25]. This results in the appearance of strongly enantiotropic chiral smectic *C*, smectic *A* and chiral nematic mesophases for the esters *III*.

The average liquid crystal transition temperatures of the analogous 4-(alkenyloxy)-phenyl 4-alkoxybenzoates (*IV–VI*) exhibit similar trends to those of the corresponding constitutional isomers *I–III*. However, there are significant differences. The esters *IV–VI* do not exhibit either a smectic A phase or any ordered smectic phases (e.g., S_B). The average melting points (35°C) of the esters *V* are significantly closer to room temperature than those (49°C and 42°C), respectively) of the esters *IV* and *VI*. The combination of these two factors leads to the appearance of wide-range, chiral smectic C phases at, or just above, room temperature for several homologues of the esters *V* as shown in table 5.

Valid comparisons between the liquid crystal transition temperatures of the alkenyloxy-substituted esters *I–VI* and those of the corresponding alkoxy-substituted esters [6–11] (i.e., without an olefinic double bond) are difficult to make. Data for the 4-[(S)-6-methyloctyloxy]phenyl 4-alkoxybenzoates are not found in the literature. Transition temperatures for the five homologous series [6–11] corresponding to the esters *I*, *II* and *IV–VI* have only been reported for a limited number of homologues. However, it is found, in general, that the liquid crystal transition temperatures of the alkenyloxy substituted esters are somewhat lower than those of the analogous alkoxy substituted esters. The temperature range of the chiral smectic C mesophase is sometimes broader and closer to room temperature for the esters *I–VI*. This can be used to advantage in the preparation of commercial ferroelectric mixtures for electro-optic display devices [26].

4. Conclusions

The introduction of an olefinic double bond into the terminal carbon chain of the optically active 4-alkoxyphenyl 4-alkoxybenzoates gives rise to a general lowering of the liquid crystal transition temperatures. Thus several esters exhibit, enantiotropic chiral smectic C mesophases at and above room temperature. This is of advantage for display device applications. The same types of liquid crystal mesophases and trends in their transition temperatures are observed as those exhibit by the corresponding saturated esters (without a double bond in the terminal carbon-chain). The presence of the double bond can lead to a broadening of the chiral smectic C temperature range.

5. Experimental

The liquid crystal transition temperatures of the compounds recorded in tables 1–6 were determined by optical microscopy using a Leitz Ortholux II POL-BK microscope in conjunction with a Mettler FP 82 heating stage and FP 80 control unit. All the monotropic liquid crystal phases could be observed using a microscope and no virtual values (extrapolated) had to be determined. When necessary the Mettler stage could be cooled ($< -20^\circ\text{C}$) 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 (T.L.C.), gas chromatography (G.C.) and D.T. analysis. A Perkin Elmer 8310 gas chromatograph and GP-100 graphics printer were used. 4 cm \times 8 cm precoated T.L.C. plates, SiO₂ SIL G/UV₂₅₄, layer thickness 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 $^1\text{H-N.M.R.}$ 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.

4-[(S)-2-Methylbutoxy]phenyl 4-(5-hexenyloxy)benzoate. A solution of 4-(5-hexenyloxy)benzoic acid [21] (0.20 g, 0.0009 mol), 4-[(S)-2-methylbutoxy]phenol [20] (0.16 g, 0.0009 mol), N,N-dicyclohexylcarbodiimide (0.22 g, 0.0010 mol) 4-(dimethyl)-aminopyridine (0.04 g) and anhydrous dichloromethane (25 cm³) was stirred at room temperature overnight and then filtered to remove precipitated material. The filtered solution was evaporated under reduced pressure and the solid residue obtained purified using column chromatography on silica-gel using toluene as eluent. The crude ester was then crystallised from ethanol until constant liquid crystal transition temperatures were obtained (see tables 1–6 for the transition temperatures and enthalpies of fusion for this ester and the other esters prepared using this general method). I.R. (KBr): 3040, 1730, 1640, 1610, 1515, 1250, 1170, 1080, 910, 850. M.S.: 382 (M⁺)

4-(4-Pentenyloxy)phenol. A mixture of 1-bromo-4-pentene (25 g, 0.168 mol), hydroquinone (93 g, 0.838 mol), anhydrous potassium carbonate (93 g, 0.671 mol) and anhydrous butanone (300 cm³) was heated under reflux for 48 hr. The cooled mixture was added to water (1000 cm³) and shaken with diethyl ether (3 × 100 cm³). The combined organic layers were washed with water (2 × 500 cm³) and dried (MgSO₄). After removal of the solvent under reduced pressure, the crude product was purified by chromatography on silica-gel using 4:1 toluene/ethyl acetate as eluent. Crystallization from hexane at 0° yielded pure (98 per cent) phenol (15 g, 50 per cent), m.p., 49–50°C. I.R. (KBr): 3400, 1648, 1600, 1510, 1240, 980, 900, 820. M.S.: 178 (M⁺).

The following phenols were prepared using the same procedure:

4-(5-Hexenyloxy)phenol (66 per cent), m.p., 44–45°C. I.R. (KBr): 3400, 1640, 1600, 1520, 1240, 1005, 960, 830. M.S.: 192 (M⁺).

4-(6-Heptenyloxy)phenol (55 per cent), m.p., 31–32°C. I.R. (KBr): 3380, 1510, 1244, 1105, 911, 828. M.S.: 206 (M⁺).

4-(7-Octenyloxy)phenol (35 per cent), m.p., 42–43°C. I.R. (KBr): 3410, 1640, 1520, 1250, 1110, 1040, 920, 830. M.S.: 220 (M⁺).

4-(8-Nonenyloxy)phenol (44 per cent), m.p., 50–51°C. I.R. (KBr): 2930, 1680, 1605, 1510, 1260, 1170, 1060, 890, 810. M.S.: 262 (M⁺).

4-(9-Decenyloxy)phenol (52 per cent), m.p., 54–55°C. I.R. (KBr): 3420, 1650, 1520, 1250, 1110, 1040, 830. M.S.: 248 (M⁺).

4-(10-Undecenyloxy)phenol (51 per cent), m.p., 64–65°C. I.R. (KBr): 3430, 2930, 1515, 1416, 1240, 1000, 830. M.S.: 262 (M⁺).

4-[(Z)-5-Octenyloxy]phenol (53 per cent), I.R. (Film): 3390, 1700, 1510, 1450, 1230, 1040, 830. M.S.: 220 (M⁺).

10-Undecenyl tosylate. A solution of *p*-toluene sulphonyl chloride (59 g, 0.308 mol) and anhydrous pyridine (100 ml) was added dropwise to a solution of 10-undecenol (50 g, 0.294 mol) cooled *via* an ice bath so that the internal temperature did not rise above 5°C. A white precipitate was observed to form during the next 8 hr, while the reaction mixture was stirred and cooled *via* the ice-bath. Water (500 ml) was added and the resultant solution stirred for a further 2 hours and then shaken with diethyl ether (3 × 100 ml). The combined organic layers were washed with 25 per cent HCl (2 × 250 ml), water (1 × 500 ml), dilute NaHCO₃ (1 × 500 ml), water (1 × 500 ml)

and dried (MgSO_4). After removal of the drying agent by filtration and the solvent under partially reduced pressure, the crude product (91 g, 96 per cent) was used immediately in the next reaction without further purification.

The following tosylates were prepared using the same procedure:

6-Heptenyl tosylate (91 per cent).

9-Decenyl tosylate (93 per cent).

(Z)-5-Octenyl tosylate (93 per cent).

6-Heptenol. A solution of 6-heptenoic acid (19 g, 0.147 mol) and anhydrous diethyl ether (100 cm^3) was added dropwise to a mixture of lithium aluminium hydride (10 g, 0.264 mol) and anhydrous diethyl ether (100 cm^3). A strongly exothermic reaction could be observed. The reaction mixture was heated under gentle reflux for 6 hr. After decomposition of the complex and excess of hydride in the normal way [20] the organic layer was separated off and the aqueous layer shaken with diethyl ether ($2 \times 250 \text{ cm}^3$). The combined organic layers were washed with salt solution ($2 \times 500 \text{ cm}^3$) and dried (MgSO_4). The filtered solution was evaporated under vacuum to yield pure (97 per cent) alcohol (16.5 g, 98 per cent) which was used in the next reaction without further purification.

1-Bromononene. A solution of Grignard reagent (0.149 mol; prepared in the usual way from 0.149 mol magnesium and 0.140 mol 1-bromopentene) and anhydrous tetrahydrofuran (50 cm^3) was added dropwise to a solution of 1,4-dibromobutane (29 g, 0.134 mol), 1 M dilithiumtetrachlorocuprate (8 cm^3) and anhydrous tetrahydrofuran (100 cm^3) cooled *via* an ice/methanol bath. After completion of the addition the reaction mixture was maintained at this temperature for 1 hr and then allowed to reach room temperature. Water (250 cm^3) was added and the organic layer was separated off. The aqueous layer was shaken with diethyl ether ($2 \times 200 \text{ cm}^3$) and the combined organic layers washed with salt solution ($2 \times 500 \text{ cm}^3$) and dried (MgSO_4). The filtered solution was evaporated under vacuum and the liquid residue distilled under reduced pressure (b.p., 180–181°C/18 mm Hg) to yield pure (99 per cent) product (15 g, 76 per cent). I.R. (Film): 3077, 1640, 1460, 1310, 990, 910. M.S.: 204, 206 (M^+).

The authors thank the following colleagues for the measurement and interpretation of the various spectra: Dr. W. Arnold (N.M.R.), Mr. W. Meister (M.S.), Dr. M. Grosjean (I.R.), Mr. F. Wild and Mr. B. Hal'n (D.T.A.) and Mrs. J. Kohler (optical rotation). Mr. S. Wehrli and Mr. U. Wyss are thanked for competent technical assistance in the preparation of the compounds described.

References

- [1] KLANDERMANN, B., and CRISWELL, T. R., 1975, *J. Am. chem. Soc.*, **97**, 1585.
- [2] Hsu, Y. Y., and DOLPHIN, D., 1977, *Molec. Crystals liq. Crystals*, **42**, 319.
- [3] GRAY, G. W., and McDONNELL, D. G., 1978, *Molec. Crystals liq. Crystals*, **48**, 37.
- [4] LOSEVA, M. V., OSTROVSKIY, B. I., RABINOVICH, A. S., SONIN, A. S., STRUKOV, B. A., and CHERNOVA, N. I., 1978, *Prisma Zh. eksp. Teor. Fiz.*, **28**, 404.
- [5] OSTROVSKIY, B. I., RABINOVICH, A. S., SONIN, A. S., SORKIN, E. L., STRUKOV, B. A., and TARASKIN, S. A., 1980, *Ferroelectrics*, **24**, 309.
- [6] KELLER, P., 1984, *Ferroelectrics*, **58**, 3.
- [7] GOODBY, J. W., 1983, *Ferroelectrics*, **49**, 275.
- [8] GOODBY, J. W., and LESLIE, T. M., 1984, *Molec. Crystals liq. Crystals*, **110**, 175.
- [9] GOODBY, J. W., and LESLIE, T. M., 1984, *Liquid Crystals Ordered Fluids*, **4**, 1.
- [10] DECOBERT, G., and DUBOIS, J. C., 1984, *Molec. Crystals liq. Crystals*, **114**, 237.

- [11] LE PESANT, J. P., MOUREY, B., HARENG, M., DECOBERT, G., and DUBOIS, J. C., *Display '84 (Paris)*, p.217.
- [12] GRAY, G. W., and GOODY, J. W., 1984, *Smectic Liquid Crystals* (Leonard Hill), Glasgow), Chap. 3. p. 45..
- [13] SCHADT, M., and PETRZILKA, M., 1984, *Display '84 (Paris)*, p. 53.
- [14] SCHADT, M., PETRZILKA, M., GERBER, P. R., and VILLIGER, A., 1985, *Molec. Crystals liq. Crystals*, **122**, 241.
- [15] PETRZILKA, M., 1985, *Molec. Crystals liq. Crystals*, **131**, 109.
- [16] PETRZILKA, M., and GERMAN, Ä., 1985, *Molec. Crystals liq. Crystals*, **131**, 327.
- [17] SCHADT, M., BUCHECKER, R., VILLIGER, A., LEENHOUTS, F., FROMM, J., 1986, *I.E.E.E. Trans. Electron Devices*, **33**, 1187.
- [18] PETRZILKA, M., BUCHECKER, R., SCHMIEDERER, S., SCHADT, M., and GERMANN, A., 1987, *Molec. Crystals liq. Crystals*, **148**, 123.
- [19] KELLY, S. M., BUCHECKER, R., FROMM, J., and SCHADT, M., 1987, *Ferroelectrics* (in the press).
- [20] KELLY, S. M., and BUCHECKER, R., 1988, *Helv. chim. Acta*, **71**, 451.
- [21] KELLY, S. M., and BUCHECKER, R., 1988, *Helv. chim. Acta*, **71**, 461.
- [22] GRAY, G. W., and HARRISON, K. J., 1971, *Molec. Crystals liq. Crystals*, **13**, 37.
- [23] (a) GRAY, G. W., and McDONNELL, D. G., 1976, *Molec. Crystals liq. Crystals*, **37**, 189.
(b) GRAY, G. W., and McDONNELL, D. G., 1978, *Molec. Crystals liq. Crystals*, **48**, 37.
(c) GRAY, G. W., and McDONNELL, D. G., 1979, *Molec. Crystals liq. Crystals*, **53**, 147.
- [24] (a) GRAY, G. W., and KELLY, S. M., 1983, *Molec. Crystals liq. Crystals*, **95**, 101. (b) GRAY, G. W., and KELLY, S. M., 1984, *Molec. Crystals liq. Crystals*, **104**, 335.
- [25] COATES, D., 1987, *Liq. Crystals*, **2**, 63.
- [26] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.