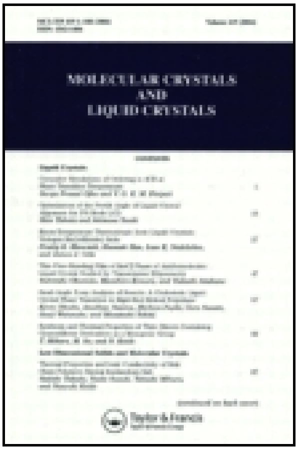

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Synthesis and Physical Evaluation of Novel Ferroelectric Materials with High Spontaneous Polarization

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Version of record first published: 13 Dec 2006.

To cite this article: M. F. Bone, M. J. Bradshaw, L. K. M. Chan, D. Coates, J. Constant, P. A. Gemmell, G. W. Gray, D. Lacey & K. J. Toyne (1988): Synthesis and Physical Evaluation of Novel Ferroelectric Materials with High Spontaneous Polarization, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 164:1, 117-134

To link to this article: http://dx.doi.org/10.1080/00268948808072117

Mol. Cryst. Liq. Cryst., 1988, Vol. 164, pp. 117–134
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Printed in the United States of America

Synthesis and Physical Evaluation of Novel Ferroelectric Materials with High Spontaneous Polarization

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(*Received: January 18, 1988*)

A large number of ferroelectric dopants incorporating a chiral lactate unit, $—O\overset{*}{C}H(CH_3)CO_2—$, have been synthesized and extrapolated values of Ps as high as 160 nC cm^{-2} have been found, although many of these compounds did not show any liquid crystal behavior. Terphenyls and laterally fluoro-substituted terphenyls incorporating the chiral lactate unit have also been synthesized, and in one case, a ferroelectric host material with an S_C^* phase and a Ps value of 124 nC cm^{-2} was obtained.

Compounds containing two chiral units (one of which was a chiral lactate unit) were also synthesized in which the two chiral units were either directly linked or separated by a phenyl ring; the latter compounds gave very high Ps values (199 nC cm^{-2}).

The effect of molecular structure on Ps, tilt angle and phase behavior is discussed for both the mono-lactates and the di-chiral compounds.

An outline (with references) of the experimental procedures used to prepare these compounds is also given.

INTRODUCTION

Since the introduction of the twisted nematic display device in the late 1960s, and the discovery of the cyanobiphenyls[1] in 1972–1973, there have been rapid advances in low voltage nematic and cholesteric displays, e.g., supertwist birefringent (SBE) displays, dyed phase change displays etc. Although these types of device have fulfilled

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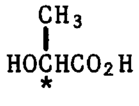
many requirements for display applications, today's needs for high density information displays and displays working at video frame-rates, comparable to those provided by cathode ray tube displays, are very difficult to achieve with current liquid crystal technology. Fast scan multiplexed twisted nematic devices have been manufactured but the visual qualities of these display devices deteriorate rapidly with increasing levels of multiplexing due to their lack of bistability and relatively slow response times.

An alternative to the use of nematic or cholesteric liquid crystals in display devices is provided by the more ordered, lamellar smectic liquid crystals. It has been shown by W. A. Crossland *et al.*[2,3] at S.T.C. (Harlow) that a device based on smectic A liquid crystals is intrinsically bistable and the electro-optic effect gives good viewing characteristics and a large number of pixels per display (in excess of 300,000 pixels for an A4 size display) can be readily multiplex addressed without degradation of performance.

Although an A4 sized device, based on the above technology, can be addressed in 840 msec., there is still a need for much faster electro-optic effects in order to achieve video frame rates permitting their use in television or in fast light shutters etc.

Recently great interest has been shown in a new type of device using ferroelectric liquid crystals.[4] Such devices may be capable of achieving submicrosecond switching, and with their intrinsic bistability, ferroelectric liquid crystals may be ideally suited for large area matrix display devices capable of operating at very fast frame rates, thus giving the required combination of high density information and fast switching speeds.

Through work in collaboration with our partners in an Alvey research program, we have developed a new organic chiral system which, with appropriate substituents, is capable of producing ferroelectric materials with very high spontaneous polarization (Ps value). These new chiral compounds are derivatives of optically active lactic acid (I).

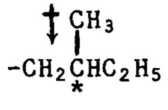


$$\mathrm{HO}\overset{\mathrm{CH_3}}{\underset{*}{\mathrm{C}}}\mathrm{HCO_2H}$$

(I)

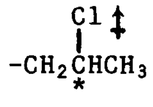
To produce materials with high spontaneous polarization, it is important to couple the motions of a lateral dipole with the chiral center.

The greater the steric interaction between the chiral group and a neighboring polar group, then the stronger is the coupling of the permanent dipole to the monoclinic environment, and the larger will be the Ps value. In many ferroelectric materials this coupling of the lateral dipole to the chiral center has been achieved by placing the lateral dipole on the chiral center itself [e.g., as in the units (II) and (III)].



$-CH_2\underset{*}{\overset{CH_3}{C}}HC_2H_5$

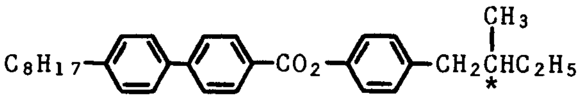
(II)



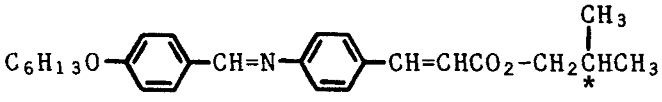
$-CH_2\underset{*}{\overset{Cl}{C}}HCH_3$

(III)

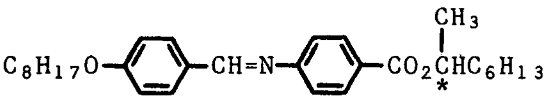
Usually, for ease of synthesis, these chiral moieties have been positioned at the end of rod-shaped molecules as shown in the following compounds.



(Lit.[5])

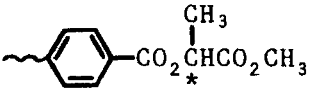


HOBACPC



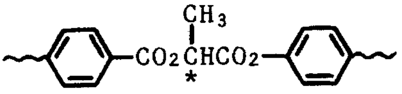
(Lit[6])

In the case of lactic acid (I), because it has two readily modified functional groups, i.e., —CO_2H and —OH, the chiral center can be positioned anywhere within a molecular structure [e.g., see structures (IV) and (V)]. This makes the lactic acid moiety far more versatile than most other chiral moieties used to generate ferroelectricity in smectic mesophases.



$\sim C_6H_4-CO_2\overset{CH_3}{\underset{*}{C}}HCO_2CH_3$

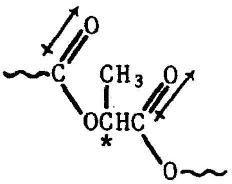
(IV)



$\sim C_6H_4-CO_2\overset{CH_3}{\underset{*}{C}}HCO_2-C_6H_4\sim$

(V)

Using the lactic acid moiety (I) to make di-esters as in structures (IV) and (V), produces compounds in which the chiral carbon atom is flanked by two lateral dipoles, e.g.



Because of the proximity of the methyl group on the central chiral carbon atom to the two flanking, lateral, carbonyl dipoles and the consequent steric hindrance, it was envisaged that such an arrangement may produce materials with relatively high Ps values.

RESULTS AND DISCUSSION

This section can be conveniently divided into two parts:

1. mono-lactates;
2. compounds with two chiral centers.

1. Mono-Lactates

Many compounds containing one lactate unit [see structures (VI), (VII) and (VIII)] have been prepared and the associated transition temperatures (°C) and physical data are given in Tables I and II.

In the mono-lactates of structure (VI), where $x = 1$ (VIa–c), a 10 mol % mixture of these compounds in RCE8† failed to exhibit an

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†See footnote to Table I.

S_C^* phase. This large depression in the S_C thermal stability of RCE8 ($T_{S_C-S_A}$ for RCE8 = 85.6°C) rendered these compounds very unsatisfactory as ferroelectric dopants and so our investigations turned to compounds of structure (VI), where $x = 2$ (VId–s). In the case of compound (VId), this also depressed the S_C phase of RCE8, but when the substituent *Y* in structure (VI) was changed from a hydrogen atom to an alkyl group [compounds (VIe, f, and g)], large Ps values (67–75 nC cm^{-2}) were obtained. Compounds (VIe) and (VIf) were the only two compounds in this series to show liquid crystal behavior. This emphasizes the fact that the structure of the lactate linking unit (with an odd number of atoms) is not ideally suited to liquid crystal behavior. The values in the column designated by S_C^*–$S_A{}^a$ show however that these four dopants do not significantly affect the S_C–S_A transition of a host material like RCE8, an important factor when considering a compound as a ferroelectric dopant.

The high Ps values of dopants (VIe–g) encouraged further work on this system with the object of producing compounds with significantly higher Ps values by using suitable substituents *Y* in structure (VI). Our initial attempts in this area [compounds (VIh, i, and j)] (using phenylalkyl groups) failed; indeed compound (VIj) gave a very low Ps value (20 nC cm^{-2}) in comparison with the compounds mentioned previously.

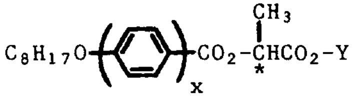
In compounds (VIk to o), the lactate moiety is now flanked by two π-systems (biphenylylcarboxy on the left and phenyl on the right); the two ester linkages produce two large carbonyl dipoles on either side of the chiral carbon atom. This structural change produced dopants (VIk and m) with very high Ps values, e.g., for (VIk) Ps = 160 nC cm^{-2}. The depression in the host S_C–S_A transition given by these dopants is relatively small; compound (VIm) shows the greater depression (11.6°C) (it also has the smaller Ps value). At that time, these compounds had the largest Ps values ever reported, but recently compounds with Ps values around 210 nC cm^{-2} have been mentioned in the literature.[8]

Different ring systems were subsequently tried as substituent *Y* in structure (VI) to see if they would improve the Ps value of 160 nC cm^{-2} given by compound (VIk). Although two of these dopants had Ps values exceeding 100 nC cm^{-2} (VIq and s) and gave very small depressions of the S_C–S_A transition, none of these compounds had a Ps value greater than 160 nC cm^{-2} (VIk). Also, two of these dopants had the disadvantage of high melting points, exceeding 100°C (VIp and r).

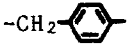
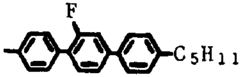
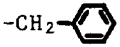
In the case of compound (VIp), as well as having a very high melting

TABLE I.

The transition temperatures and physical data for mono-lactates of structures (VI) and (VII)



(VI)

Compound No	x	Y	C-S_A,I (°C)	S_A-I (°C)	Ps[b] (nC cm^{-2})	Tilt Angle[c] (°)	S_C^*-S_A[a] (°C)
(VIa)	1		29.0	No S_C^* phase in 10 mol % of compound in RCE8.			
(VIb)	1		95.0				
(VIc)	1		106.0				
(VId)	2	-H	126.0				
(VIe)	2	$-CH_3$	57.0	(49.2)	67	16.0	76
(VIf)	2	$-C_2H_5$	39.5	42.0	74	17.0	
(VIg)	2	$-C_4H_9$	51.0		75	13.5	79
(VIh)	2		62.5		51	14.5	74

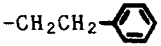
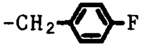
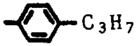
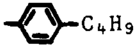
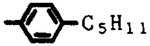
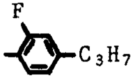
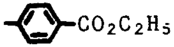
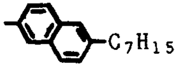
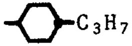
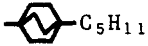
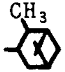
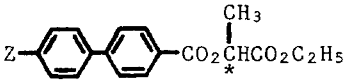
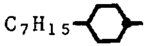
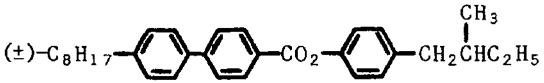
(VIi)	2		47.0	79	14.5	72
(VIj)	2		67.0	20	13.5	71
(VIk)	2		78.0	160	15.0	79
(VIl)	2		79.0	-	-	-
(VIm)	2		78.0	149	14.0	74
(VIn)	2		63.5	108	15.5	79
(VIo)	2		106.0	-	-	-
(VIp)	2		114.0	80	9.0	58
(VIq)	2		85.5	101	16.0	76
(VIr)	2		116.0	96	14.0	69
(VIs)	2		44.0	120	15.0	77

TABLE I (*Continued*)

Compound No	X	Y	C-S_A,I (°C)	Ps^b (nC cm^{-2})	Tilt Angle[c] (°)	S_C^*-S_A[a] (°C)
				(VII)		

Compound No	Z	C-S_A,I (°C)	S_B-S_A (°C)	S_A-Ch (°C)	Ch-BP (°C)	BP-I (°C)	Ps^b (nC cm^{-2})
(VIIa)		25.0					66
(VIIb)		83.0	(58.5)	117.5	119.1	120.0	

[a] This transition temperature refers to a 10 mol % solution of the compound in RCE8 (structure given below). The $T_{S_C-S_A}$ value for RCE8 is 85.6°C.



RCE8

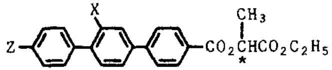
[b] This value is obtained by measuring the Ps value at 10°C below the $T_{S_C^*-S_A}$ of a 10 mol % mixture of the compound in RCE8, and then extrapolating to 100% of the compound. The handedness of Ps was negative, according to the convention adopted by Lagerwall and Dahl.[7]

[c] The tilt angle is measured on a 10 mol % mixture of the compound in RCE8. The Ps value and tilt angle for the optically active form of RCE8 (i.e., CE8) at 76°C are 3.2 nC cm^{-2} and 15° respectively. Both RCE8 and CE8 were obtained from BDH Limited, Poole, Dorset, BH12 4NN, England.

( ) Monotropic transition

TABLE II.

Transition temperatures and physical data for mono-lactates incorporating the *p*-terphenyl moiety (VIII)



(VIII)

Compound No	Z	X	$C-S_1, S_E, S_B, S_C^*, S_A$ (°C)	S_1-S_2 (°C)	$S_2-S_C^*$ (°C)	S_E-S_B, S_A (°C)	S_B-S_A (°C)	$S_C^*-S_A$ (°C)	S_A-I (°C)	Ps^b ($nC\ cm^{-2}$)	Tilt Angle[c] (°)	$S_C^*-S_A^a$ (°C)
(VIIIa)	C_5H_{11}	H	130.0			(129.0)	147.0		180.0			
(VIIIb)	C_9H_{19}	H	68.0	68.5	99.0			120.0	150.5			
(VIIIc)	C_4H_9O	H	185.0			186.5			225.0			
(VIIId)	$C_8H_{17}O$	F	40.0						116.0	104	13.5	81
(VIIIe)	$C_8H_{17}O$	H	127.0					158.5	180.2	99 (124)†	15.0 (24.0)†	90

( ) Monotropic transition.

[a,b,c] See footnote to Table I.

†From the S_C^* phase of compound (VIIIe) measured at $T_{S_C^*-S_A} - 10°$.

S_1 and S_2 . . . These smectic phases have not yet been positively identified.

point (114°C), the compound also depressed the S_C–S_A transition by 27.6°C, the largest depression we have encountered for lactates for which a Ps value could be measured. It is also interesting to note that for this compound the tilt angle was very small (9°), whereas all the other dopants in this series gave tilt angles around the value obtained for the host material, RCE8, i.e., 15° (only a small variation would be expected since the tilt angle is measured on a 10 mol % mixture of the dopant in RCE8). The small tilt angle obtained using compound (VIp) and the very large depression of the temperature of the S_C–S_A transition brought about by compounds (VIb) and (VIc), suggests that multiple ring systems used in Y in structure (VI) are not conducive to the properties of a good ferroelectric dopant.

Compounds of structure (VII) (Table I) and (VIII) (Table II) were prepared in an attempt to obtain ferroelectric materials exhibiting S_C^* phases, i.e., host materials, incorporating the lactate moiety. In the case of compounds of structure (VII), no tilted smectic phase was produced, although compound (VIIa) gave a moderate Ps value of 66 nC cm^{-2} in RCE8.

In our work on terphenyls and fluoroterphenyls,[9] we found many systems which exhibited S_C phases. Therefore, by combining the terphenyl or fluoroterphenyl moiety with the lactate moiety (I), it was hoped to produce suitable host materials with high Ps values. Two compounds of this type (VIIId) and (VIIIe) (Table II) had high Ps values (around 100 nC cm^{-2}), and although the compound incorporating the lateral fluoro-substituent (VIIId) gave the lowest melting point, only compound (VIIIe) [and compound (VIIIb)] gave a S_C^* phase. Because compound (VIIIe) exhibited a S_C^* phase it was possible for this compound to compare an extrapolated Ps value obtained for a solution in RCE8 with the value (given in brackets) measured directly using the S_C^* phase. It can be clearly seen that the extrapolated value (99 nC cm^{-2} at 80°C) is much lower than the Ps value obtained on the pure material (124 nC cm^{-2} at 148.5°C), indicating that temperature is not the prime factor and that the linear extrapolation from a 10 mol % mixture of the compound in RCE8 does not give an accurate Ps value. However, results from the extrapolation technique are still useful as they enable comparisons of the Ps values of dopants of varying structures to be made, provided that the measurements are carried out in the same host material. It can also be seen from the tilt angle results given for compound (VIIIe) on the pure material and on the mixture of compound (VIIIe) in RCE8 that when the dopant is added to RCE8 as a 10 mol % mixture, the tilt angle obtained is very close to that of pure RCE8 [the exception is compound (VIp)].

The structure of the lactate moiety (I), as already noted, is not conducive to the rod-like shape necessary for liquid crystal behavior, because the diester linkage involves five atoms which would not be expected to give linearity of the attached groups. To try and alleviate this situation, compounds of structure (IX) were prepared; in these, the phenyl ring nearest to the lactate moiety is 1,3-disubstituted so that its angular nature may correct the non-linearity of the lactate unit. The results for these compounds are given in Table III. In this particular series (IX), the compounds of interest are (IXb) and (IXc). In the case of the mono-lactate (IXb), its structure is sufficiently linear for the compound to exhibit liquid crystal behavior (including a S_C^* phase), although both the transitions were monotropic. However, the Ps value for compound (IXb) was very low (16 nC cm^{-2}), probably due to the fact that the dipole moments of the carbonyl units of the *three* ester groups are in partial opposition.

Incorporating a second lactate moiety (a di-lactate), as in the case of compound (IXc), has produced a compound which exhibits no liquid crystal behavior but has a very high Ps value (135 nC cm^{-2}). Thus, it seems that for compounds of structure (IX), either the structure of the molecule becomes more linear and thus supports liquid crystal behavior, but Ps is low [as in the case of (IXb)], or the structure of the molecule is not of the rod-like shape necessary for liquid crystal behavior [compound (IXc)], but produces a compound with a very high Ps value. In short, by rearranging the structure of compounds (IX), one produces either a host type material (IXb) or a high Ps dopant (IXc).

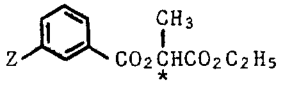
The results for compound (IXd) illustrate that too many 'bends' in the molecule are unfavorable. This molecule has two lactate moieties and two 1,3-disubstituted phenyl rings in its structure, resulting in a compound which does not exhibit liquid crystal behavior; indeed, when added to RCE8 (10 mol % mixture), no S_C^* phase was observed and consequently a Ps value could not be measured.

2. Compounds with Two Chiral Centers

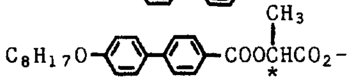
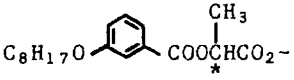
From the results obtained on compound (IXc) (Table III), it became clear that di-lactates, or, in general, compounds with two chiral centers may produce high Ps dopants. In producing compounds with two chiral centers, the two chiral moieties could either be positioned close

TABLE III.

Transition temperatures and physical data for compounds of structure (IX)



(IX)

Compound No	Z	C–I (°C)	S_C^*–S_A (°C)	S_A–I (°C)	Ps[b] (nC cm^{-2})	Tilt Angle[c] (°)
(IXa)		20.0				
(IXb)		72.0	(49.0)	(63.5)	16	13.5
(IXc)		58.5			135	14.0
(IXd)		20.0			No smectic phase in 10 mol % mixture in RCE8	

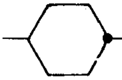
( ) Monotropic transition.

[b,c] See footnotes to Table I.

together or more widely separated by a molecular unit. To investigate the effect of directly or indirectly joining together two chiral moieties, compounds of structure (X) were synthesized; of these compounds (Xa) and (Xb) are di-lactates (two chiral lactate moieties) and compounds (Xc) and (Xd) incorporate the lactate and 2-octyl units as the chiral moieties. The results for these compounds are given in Table IV. It is clear from these results that the highest Ps values were obtained when the two chiral moieties are separated by a phenyl ring; the Ps values of 199 (Xa) and 172 (Xc) are almost double the Ps values obtained for compounds where the two chiral moieties are joined together directly.

It is interesting to note the following two points.

(a) The replacement of the terminal $—C_2H_5$ group in compound (VIf) by a C_3H_7 group [compound (VIk)] (see Table I) increased the Ps value from 74 to 160 nC cm^{-2}. Thus the very large Ps value of 199 nC cm^{-2} obtained for compound (Xa) could be largely due to the presence of the phenyl ring which helps to align the two carbonyl units flanking the chiral center; if this is the case, then the additional $—CO_2\overset{*}{C}H(CH_3)CO_2C_2H_5$ group at the end of molecule (Xa) is responsible for increasing the Ps value by only a modest amount (39 nC cm^{-2}).

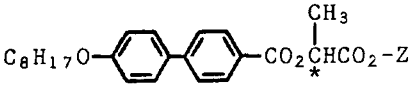
(b) Again, if we take compound (VIf) from Table I as our parent compound and replace the terminal $—C_2H_5$ group by either C_3H_7 [compound (VIq)] or $—\overset{*}{C}H(CH_3)CO_2C_2H_5$ (Xb), the Ps values for these two compounds are very similar, i.e., 101 and 105 nC cm^{-2} respectively. Thus it seems that the incorporation of the additional carbonyl group by replacing the $—C_2H_5$ group in compound (VIf) to give compound (Xb), has only marginally improved the Ps value. This again strongly suggests that the first two dipoles flanking the first chiral carbon in structure (X) are mainly responsible for the high Ps values obtained for compounds (Xa) and (Xc).

CONCLUSION

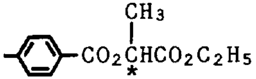
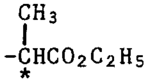
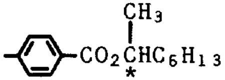
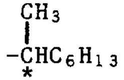
A large family of dopants incorporating the chiral lactate moiety (I) with high spontaneous polarization has been synthesized. In com-

TABLE IV.

Transition temperatures and physical data for compounds of structure (X)



(X)

Compound No	Z	C-I (°C)	S_A-I (°C)	Ps[b] (nC cm^{-2})	Tilt Angle[c] (°)	S_C^*-S_A[a] (°C)
(Xa)		96.0		199	16.0	70
(Xb)	 $-\underset{*}{\overset{CH_3}{C}}HCO_2C_2H_5$	47.0		105	15.0	76
(Xc)		65.0		172	13.5	69
(Xd)	 $-\underset{*}{\overset{CH_3}{C}}HC_6H_{13}$	42.0	(21.0)	73	13.5	-

( ) Monotropic transition.

[a,b,c] See footnote to Table I.

pounds containing one chiral lactate group, the highest Ps value obtained was 160 nC cm^{-2}. When two chiral units were present, the highest Ps value (199 nC cm^{-2}) was obtained for compounds where the two chiral centers are separated by a phenyl ring. Very few of these dopants exhibited liquid crystal behavior which reflects the non-linear structure of the lactate moiety (I).

EXPERIMENTAL

The lactate esters presented in this paper were prepared by the reaction pathway outlined in Scheme 1. The synthetic scheme is of a general nature and although the scheme shows the preparation of a lactate ester by using 4′-octoxybiphenyl-4-yl carboxylic acid and 4-propylphenol, many different carboxylic acids, phenols and alcohols can be esterified with lactic acid or substituted lactic acid (XI) to give lactate esters of structures (VI) to (X).

In the preparation of compounds containing two chiral centers the appropriate phenols were prepared by the reaction pathway outlined in Scheme 2. These phenols were then esterified with the acid (XI) shown in Scheme 1.

In both schemes, the literature references to the general synthetic methods are given.

PHYSICAL MEASUREMENTS

All final products were shown to be pure by various standard techniques (t.l.c., g.l.c., and h.p.l.c.). Confirmation of the structures of these products (and, where necessary, for any of the intermediates) was obtained by ^{1}H nmr spectroscopy (Jeol J.N.M. P.M. × 60 spectrometer), infra-red spectroscopy (Perkin-Elmer 457 grating spectrometer) and mass spectrometry (A.E.I. MS902 mass spectrometer).

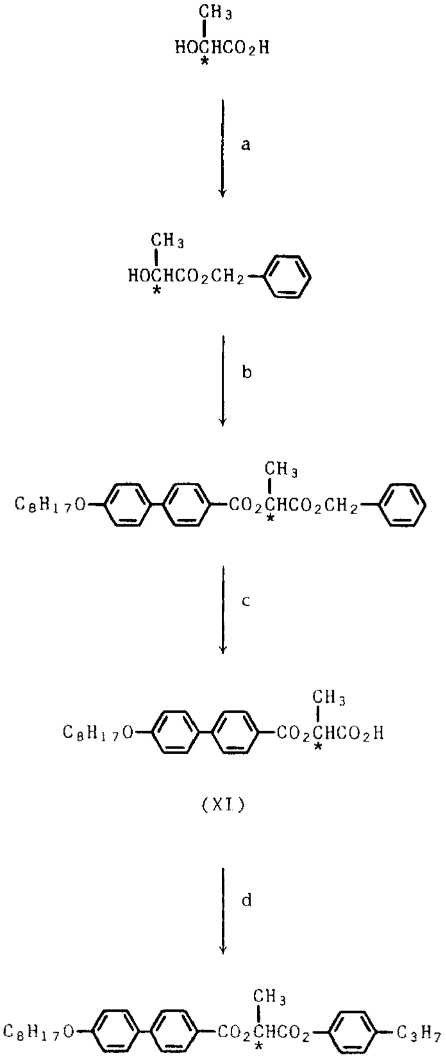
The transition temperatures were measured using a Mettler FP5 hot stage and control unit, in conjunction with an Olympus BH-2 polarizing microscope.

The spontaneous polarization (Ps values) were measured on a Diamont Bridge as described by H. Diamont *et al.*[15]

Acknowledgments

This paper is published by permission of the Director H.M.S.O. and the authors thank the U.K. Ministry of Defence for a research grant (P.A.G. and L.K.M.C.). The authors

SCHEME 1



(XI)

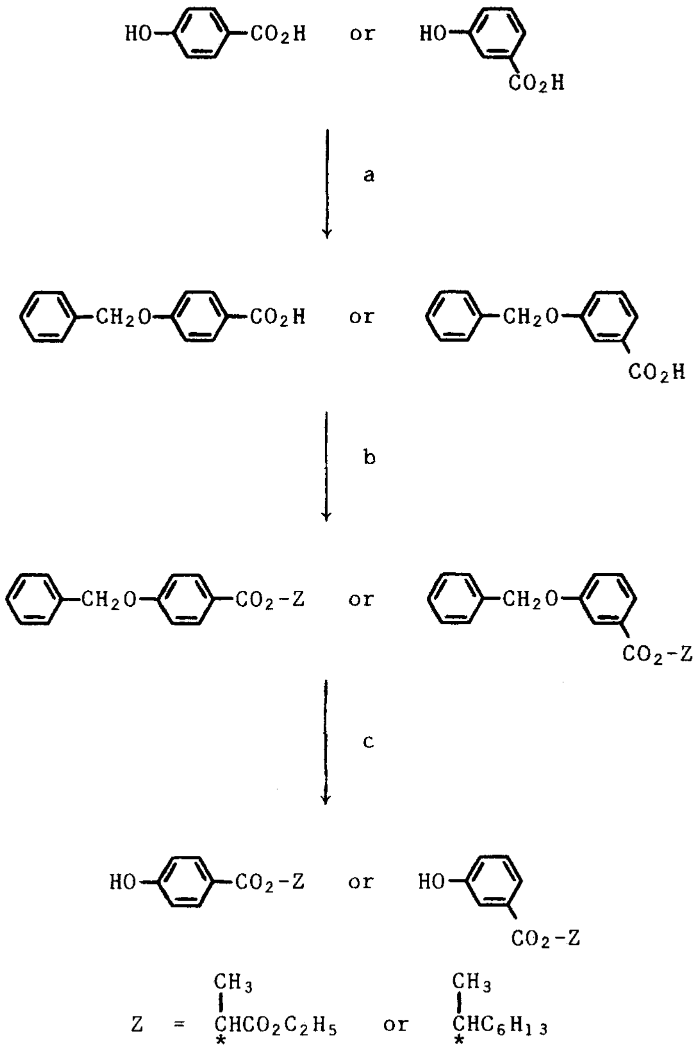
a .. (i) 20% Cs_2CO_3,CH_3OH,pH 7.0; (ii) —CH_2Br,DMF.[10]

b .. $C_8H_{17}O$——COCl,$(C_2H_5)_3N$,CH_2Cl_2.[11]

c .. 5% Pd-C,ethyl acetate,H_2.[12]

d .. N,N-dicyclohexylcarbodiimide (DCC),CH_2Cl_2,
4-(N-pyrrololidino)pyridine (N-PPY),C_3H_7—OH.[13]

SCHEME 2



a .. $-CH_2Br$,NaOH,EtOH,water.[14]

b .. similar to Step (b) in Scheme 1.[11]

c .. similar to Step (c) in Scheme 1.[12]

also thank B.D.H. Limited, Poole, Dorset for supplying a substantial number of phenols and carboxylic acids, and E. Merck, Darmstadt, F.R.G., for supplying a sample of *trans*-4-*n*-propylcyclohexanol.

The synthetic work was carried out by the Liquid Crystal Group at the University of Hull as part of a larger research program sponsored by the S.E.R.C./D.T.I. This program, entitled "Large Panel Storage Display Based on Ferroelectric Liquid Crystals," is a J.O.E.R.S./Alvey Display Programme in collaboration with S.T.C. Technology Limited (Harlow), B.D.H. Limited (Poole), R.S.R.E. (Malvern), and Thorn–E.M.I. (Hayes).

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