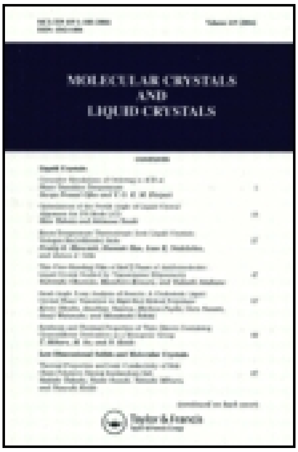

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Synthesis and Mesomorphic Properties of Some Aromatic Esters Containing 2-Butyl, 2-Octyl and 2-Methylbutyl Moieties in the Terminal Chains

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Synthesis and Mesomorphic Properties of Some Aromatic Esters Containing 2-Butyl, 2-Octyl and 2-Methylbutyl Moieties in the Terminal Chains†

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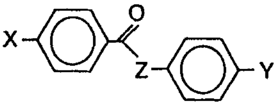
A variety of esters/thioesters (Z=O/S) with terminal chains containing sterically hindered branched chains containing $\overset{*}{\mathrm{C}}\mathrm{H(Me)Et}$,

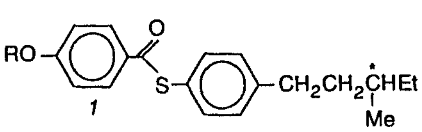


$\overset{*}{\mathrm{C}}\mathrm{H(Me)C_6H_{13}}$ and $\mathrm{CH_2CH_2\overset{*}{C}H(Me)Et}$ in either the X or Y chain attached to the benzene ring through an ether oxygen atom, $\mathrm{(CH_2)_nCO_2}$— or $\mathrm{(CH_2)_nOCO}$— with n = 0–2 and the other chain being R, RO, RCO, $\mathrm{RCO_2}$, or ROCO were synthesized as possible new ferroelectric liquid crystals or dopants in mixtures of branched chain phenylbenzoates and phenylthiobenzoates. The main goal was to incorporate substituents that favor larger spontaneous polarization than observed for the thioesters with Z = S and Y = $\mathrm{CH_2CH_2\overset{*}{C}H(Me)Et}$ and determine if these compounds would have the desired N, S_A and S_C properties. The best properties were observed in the esters with Y = $\mathrm{OCO\overset{*}{C}H(Me)Et}$. Some cyclohexane diesters and lateral substituted esters containing these branched chains were also prepared. Two branched chain esters/thioesters with X = CN were synthesized as potential cholesteric blue phase materials. These compounds were prepared using slightly modified procedures reported earlier. Comparisons in mesomorphic properties are discussed.

Keywords: liquid crystals, phenylbenzoates, phenylthiobenzoates, ferroelectrics, mesophases, chiral compounds

INTRODUCTION

The observance of smectic C* phases in the branched chain (BC) thioesters *1*



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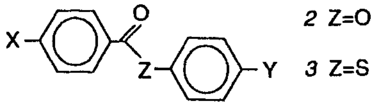
but with low spontaneous polarization (P_s) values[1,2] encouraged us to explore other modifications of branched chain esters *2* and thioesters *3*

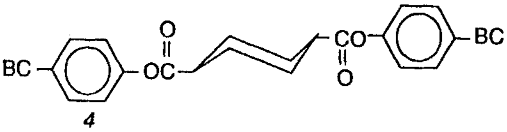


Since it is difficult to find all the properties needed for a good ferroelectric liquid crystal (FLC) material in a single compound, a better alternative seemed to be to design several esters/thioesters with different sets of a few of these properties and then use these in a variety of mixtures. The esters *2* are usually miscible with the thioesters *3* making mixture studies feasible.

Among the most desirable properties for good FLCs are a broad temperature range smectic C phase at or near room temperature; transition temperatures below 100°; a phase sequence of smectic C, smectic A and nematic; a high P_s value and a low viscosity. At the time this work was started, compounds with an α-branched chain on a benzene ring had been shown to have large P_s values. These included biphenyl-phenyl esters containing chains with $\overset{*}{C}H(Me)Et$ and $\overset{*}{C}H(Me)C_6H_{13}$ moieties attached to the benzene ring through either an ether oxygen atom or an ester group to provide chiral chains with restricted rotation.[3,4] Later the Boulder Model was formulated and used to predict which compounds would have the largest P_s values based on the direction of a dipole incorporated into the chiral chain leading to the discovery of good FLC properties in the esters *2* with $O\overset{*}{C}H(OEt)Me$.[5]

At the same time, our studies on the mesomorphic properties in the esters *2* and thioesters *3* with either X or Y having carbonyl-containing chains had shown that when either X or Y = COR enhanced smectic A phases occur at higher transition temperatures.[6,7] When Y = CO_2R, a smectic A phase is preferred without an increase in transition temperatures,[8] whereas when either X or Y = OCOR, combinations of nematic and smectics A, C and B phases, with the smectic C phase often enhanced, are seen.[9,10] The addition of spacer groups into these chains generally give lower transition temperatures and poorer mesomorphic properties.[9,11] Finally, it has become well established that a branched chain often lowers transition temperatures and enhances smectic C properties in these esters/thioesters.[1,12,13]

With the hope that these trends could be successfully balanced in structural modifications in the esters *2* and thioesters *3*, a variety of these compounds with chains containing the CH(Me)Et, $CH(Me)C_6H_{13}$ and $CH_2CH(Me)Et$ moieties were synthesized and their mesomorphic properties studied to determine if these compounds would have the desired N, S_A and S_C phases. Some of these were prepared as racemates to determine first if their mesomorphic properties were interesting enough to warrant preparing the more expensive optical isomers; others were synthesized as optical isomers for possible use as dopants. A few previously-reported esters *2* with X = $CO_2CH_2\overset{*}{C}H(Me)Et$ were prepared as another component to use in mixture studies. Two cyclohexane diesters *4* (BC = branched chain)



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and a few laterally-substituted phenylbenzoates and phenylthiobenzoates were also synthesized.

With a variety of chiral intermediates available from this work, two compounds were prepared with X = CN to study their potential cholesteric blue phase properties which are of theoretical interest. All the esters/thioesters prepared are listed in Tables I–IV. Additional esters with Y = COR′ (R′ = branched chain) and $CH_2CH(Me)R''$ will be reported in another paper[14] and mesomorphic properties for esters/thioesters *2* and *3* with X = $Me\overset{*}{C}H(OEt)O$ have already been reported.[15]

SYNTHESIS

The branched chain intermediates were synthesized using methods previously described. Some modifications to the known procedures for the synthesis of the acid and phenol with X or Y = $\overset{*}{C}H(Me)C_6H_{13}$ or their racemates[3] were made as described in the experimental section. Branched chain alkyl and alkoxy thiols were available from our earlier work.[1,13] Phenols with Y = $(CH_2)_nCO_2R'$ and $(CH_2)_nOCOR'$ (R′ = branched chain) were prepared using the methods previously reported for the straight chain analogs.[8,10,11] Most of these were liquids at room temperature and were purified by flash chromatography on silica gel. Since both optical isomers of 2-octanol are available, intermediates prepared using a S_N2 alkylation reaction causing inversion of configuration were done using the R(−) isomer giving esters with the S configuration, whereas intermediates prepared by esterification of the alcohol were done using the S(−) isomer. In this manner all the esters/thioesters were of the same absolute configuration so they could be used in mixtures without cancelling the chirality.

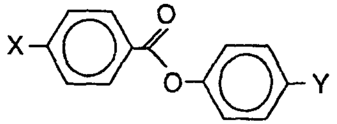
The esters/thioesters were prepared using the carbodiimide method[10] and were purified by recrystallization and/or flash chromatography until they showed only one spot by TLC and sharp clearing and melting temperatures. Structures were confirmed by IR and NMR. NMR spectra were the same as those previously reported for the analogous straight chain compounds except in the aliphatic region which agreed with data for previously published branched chain compounds. Optical rotations for those optically active compounds for which enough material was available are given in Tables V and VI. More details of these procedures are described in the experimental section.

MESOMORPHIC PROPERTIES

Mesomorphic properties of these esters/thioesters were determined by hot-stage polarizing microscopy as described in the experimental section. Transition temperatures (°C) are given in Tables I–IV. Data for a few known compounds used for comparison are also given. No mesophases were observed when X = $C_6H_{13}CH(Me)O$ in the esters *2* and only in the thioesters *3* when Y = OR where only monotropic nematic phases were seen. Mesomorphic properties improved in the esters *2* when Y = $C_6H_{13}CH(Me)O$ but only monotropic smectic A phases

TABLE I

Transition temperatures (°C) for



X[a]	Y	K[b]	B	C	A	N	I
$C_6H_{13}CH(Me)O$	C_7H_{15}	liquid to < −20°					
$C_6H_{13}\overset{*}{C}H(Me)O$	OC_7H_{15}	~ −6.0					33.6–34.3
$C_6H_{13}\overset{*}{C}H(Me)O$	$OC_{10}H_{21}$						40.5[c]
$C_6H_{13}\overset{*}{C}H(Me)O$	COC_9H_{19}	53.3					62.9–65.0
$C_6H_{13}\overset{*}{C}H(Me)O$	$CO_2C_9H_{19}$	31.4					38.0–40.3[d]
$C_6H_{13}\overset{*}{C}H(Me)O$	$OCOC_9H_{19}$	35.2					42.4–44.1
C_8H_{17}	$O\overset{*}{C}H(Me)C_6H_{13}$	−8.7					21.1–22.4
$C_8H_{17}O$	$O\overset{*}{C}H(Me)C_6H_{13}$	−10.2(K$_1$)[e]			(16.0–19.3)		22.0–22.7(K$_2$) 27.3–27.8(K$_1$)
$C_{10}H_{21}O$	$O\overset{*}{C}H(Me)C_6H_{13}$	−1.8			(26.5–27.0)		35.9–36.8
$C_9H_{19}CO$	$O\overset{*}{C}H(Me)C_6H_{13}$	64.3					67.7–68.7
$C_9H_{19}CO_2$	$O\overset{*}{C}H(Me)C_6H_{13}$	18.5(K$_2$)[f]			(22.8–23.4)		29.8–30.8(K$_1$) 25.4–27.8(K$_2$)
$C_8H_{17}O$	$O\overset{*}{C}H(Me)Et$			(37)[g]	39.5	54	67[h]
$C_{10}H_{21}O$	$O\overset{*}{C}H(Me)Et$			44	47	65	67[h]
$C_{10}H_{21}O$	$CO_2\overset{*}{C}H(Me)C_6H_{13}$	8.7			(22.3–22.7)		32.7–33.5
$C_{12}H_{25}O$	$CO_2\overset{*}{C}H(Me)C_6H_{13}$			22.5	(24.8)		44.0[i]
C_4H_9O	$CO_2CH_2\overset{*}{C}H(Me)Et$	53.2			(52.8–53.2)[s]		64.0–66.9
$C_8H_{17}O$	$CO_2CH_2\overset{*}{C}H(Me)Et$	8.3		(29.8–30.1)	32.9–33.5		57.4–58.8[j]
$C_{10}H_{21}O$	$CH_2CO_2\overset{*}{C}H(Me)Et$	42.1			49.5–50.4		59.6–60.1[k]
$C_{10}H_{21}O$	$CH_2CO_2\overset{*}{C}H(Me)C_6H_{13}$	17.2					33.8–34.5

$C_{10}H_{21}O$	$(CH_2)_2CO_2\overset{*}{C}H(Me)C_6H_{13}$	0.1			$(2.1-4.5)^l$		$17.7-18.7(K_2)^m$ $21.5-23.1(K_1)$
$C_{10}H_{21}O$	$(CH_2)_2CO_2CH(Me)C_6H_{13}$	−16.2			$(0.5-2.3)^n$		$25.8-28.5^o$
C_8H_7O	$(CH_2)_2CO_2CH_2\overset{*}{C}H(Me)Et$	liquid to < −20°					
$C_{10}H_{21}O$	$(CH_2)_2CO_2CH_2\overset{*}{C}H(Me)Et$	28.0^p	$(-7.7\text{ to }-9.3)^p$		$(17.24)^p$		18.68^p
$C_8H_{17}O$	$O_2C\overset{*}{C}H(Me)Et$	25.7		31.0–31.4	46.0	52.5	53.2–53.3
$C_{10}H_{21}O$	$OCOCH(Me)Et$	19.8	(24.8–25.0)	37.5–38.7	49.9	—	57.1–58.1
$C_{10}H_{21}O$	$OCO\overset{*}{C}H(Me)Et$	14.2	(25.1)	$39.1-39.6(K_1)^m$ $35.6-36.2(K_2)$	50.1–50.2	—	57.9–58.1
$C_9H_{19}CO$	$OCO\overset{*}{C}H(Me)Et$	78.0			$83.0-84.5(K_1)^q$	—	91.7–92.4
NC	$O\overset{*}{C}H(Me)C_6H_{13}$	liquid to −17°			^{r}		2.0–4.7

[a] *indicates an optically active carbon atom. Optical rotations are given in Table VI.

[b] K = crystallization temperature, B = smectic B, C = smectic C, A = smectic A, N = nematic and I = isotropic liquid.

[c] Reported in Reference 16.

[d] The presence of at least two crystal forms with different melting temperatures was apparent when the broad melting temperatures were observed, unless the crystallized sample was allowed *to set for a long time at room temperature.*

[e] Two interchangeable crystal forms ($K_2 \xrightarrow{6.4-8.7°} K_1$) having different melting temperatures were observed.

[f] Two interchangeable crystal forms ($K_2 \xrightarrow{20.1-21.7°} K_1$) having different melting temperatures were observed.

[g] An enantiotropic smectic C phase was reported in Reference 17.

[h] Data from Reference 18.

[i] Data from Reference 3.

[j] Data agree to previous results in Reference 19.

[k] Earlier data showed a monotropic S_C^* phase at 35° in Reference 19. Our high crystallization temperature prevented observance of this phase.

[l] Confirmed by DSC T = 2.58, ΔH = 0.34 kJ/mol

[m] Two crystal forms with two different melting temperatures were observed. DSC showed melting from cooled melt at 16.96, ΔH = 22.58 kJ/mole.

[n] Confirmed by DSC T = 0.60, ΔH = 1.35 k, 1 mole.

[o] DSC shows primary melting at 18.15°, ΔH = 19.54 kJ/mole, secondary peak at 24.86°, ΔH = 0.56 kJ/mole.

[p] This material melts below room temperature. Sharp accurate transition temperatures could not be obtained from microscopy studies. These data were obtained from DSC scans. ΔH values (kJ/m) were as follows: 27.50 (K-I), 1.36 (A-I), 1.03 (A-B) and 3.51 (B-K). The broadness of the melting peak made it impossible to determine whether the smectic phase is enantiotropic or monotropic.

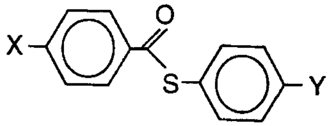
[q] Two interconvertible crystal forms were observed. The melt gave K_2 which on reheating changed to K_1 at 80.7–82.6. K_1 melted to the S_A phase.

[r] This material has a smectic A phase which did not crystallize on cooling to −17°. The value in the I column is for S_A to I.

[s] The smectic A phase was seen while the melt crystallized and was not always observed.

TABLE II

Transition temperatures (°C) for



X[a]	Y	K[b]	C	A	N*	BPI	I
$C_6H_{13}CH(Me)O$	C_5H_{11}	9.4					29.6–35.1[c]
$C_6H_{13}CH(Me)O$	C_7H_{15}	−6.1					34.1–34.9
$C_6H_{13}\overset{*}{C}H(Me)O$	C_7H_{15}	6.7					35.6–37.2
$C_6H_{13}CH(Me)O$	$C_{12}H_{25}$	~12[d]					33.9–34.9
$C_6H_{13}\overset{*}{C}H(Me)O$	OC_8H_{17}	<−20			[e]		−0.8 to 1.7
$C_6H_{13}\overset{*}{C}H(Me)O$	$OC_{12}H_{25}$	12.3			(22.7)		32.4–32.8
$C_9H_{19}CO$	$CH_2CH_2\overset{*}{C}H(Me)Et$	60.2		74.0–74.8	79.6–79.7	—	95.1–96.1
$C_9H_{19}CO$	$O(CH_2)_2CH(Me)Et$	49.5 K_2[f]	67.6–68.2(K_1)	90.9–91.3	—	—	105.6–105.9
NC	$CH_2CH_2\overset{*}{C}H(Me)Et$	53.6			(63.5–64.5)	(65.5)[g]	72.1–74.6

[a] *indicates an optically active compound.

[b] K = crystallization temperature obtained by cooling the melt 2°/min, C = smectic C, A = smectic A, N* = chiral N or cholesteric, BP = cholesteric blue phase and I = isotropic liquid.

[c] A crystal-to-crystal change preceded melting at 31.3–32.6°.

[d] Two interconvertible crystal forms were observed. Cooling the melt gave K_2 at ~12°. On reheating, K_2 went to K_1 at 31.3–32.6° which then melted on further heating.

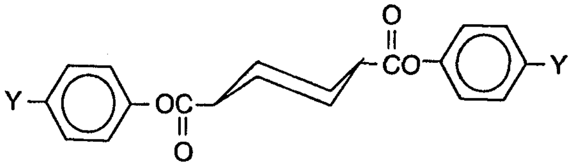
[e] A nematic phase formed on cooling the melt to −1.7. This phase was cooled to −20° without recrystallization so no melting temperature could be obtained. The value in the I column is for N to I.

[f] Two interconvertible crystal forms were observed. Cooling the S_C phase gave K_2 at 49.5°. These converted to K_1 at 59.0–59.7 on reheating and then they melted to the S_C phase.

[g] The blue phase was identified by Peter Crooker at the University of Hawaii.

TABLE III

Transition temperatures (°C) for



Y[a]	K[b]	N	I
$CO_2CH_2\overset{*}{C}H(Me)Et$	121.1	125.5–126.8	132.4–132.6
$(CH_2)_2CO_2CH_2\overset{*}{C}H(Me)Et$	65.4		71.0–72.5

[a] *indicates an optically active compound.

[b] K = crystallization temperature on cooling at 2°/min, N = nematic phase and I = isotropic liquid.

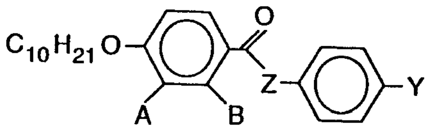
occurred. This monotropic smectic A phase persisted in the esters when the $C_6H_{13}CH(Me)$ moiety was attached to the benzene ring via a $(CH_2)_nCO_2R$ group even when n = 2,[6] although at very low temperatures. No mesophases were seen when n = 1 in agreement with the trends observed for the straight chain esters.[8] The best properties in the esters *2* occurred when Y = $O_2C\overset{*}{C}H(Me)Et$ which showed enantiotropic smectics C and A and nematic phases when X = RO but only a smectic A phase when X = $C_9H_{19}CO$. Among the thioesters, combinations of X = $C_9H_{19}CO$ with either $(CH_2)_2\overset{*}{C}H(Me)Et$ or $O(CH_2)_2\overset{*}{C}H(Me)Et$ gave no smectic C phases; only smectic A and chiral nematics. The X = RO and Y = OCOR′ with R′ = branched chain will be reported in a later paper[20] and the thioesters with X = RO and Y = $CO_2\overset{*}{C}H(Me)R'$ have already been reported to have smectic C phases with large P_s values.[21] Among the lateral substituted esters/thioesters studied, the thioesters with a lateral F substituent and Y = $(CH_2)_2CH(Me)Et$ showed the most interesting mesomorphic properties having smectic C and nematic phases when A = F and an additional smectic A phase when B = F (Table IV). The cyclohexane diesters showed poor mesomorphic properties (Table III). Mixture studies of some of these esters with the thioesters *1* have been done at Hughes Laboratories.[2]

CONCLUSIONS

No mesophases were observed in either the esters or thioesters when X = $C_6H_{13}CH(Me)O$. However, smectic A phases occurred in the esters when Y = $C_6H_{13}CH(Me)O$ suggesting that a branched chain on the phenol side is more favorable for mesophase formation than one on the acid side. The best mesophase combination for FLC materials in the esters occurs when X = C_8O and Y = OCOCH(Me)Et which showed nematic and smectics A and C phases. Longer alkyl chains led to loss of the nematic phase and the addition of a smectic B phase. Among the thioesters, Y = $(CH_2)_2CH(Me)Et$ is the only chain studied that gave a smectic A-C combination. With X = $C_9H_{19}CO$, no nematic phase was observed

TABLE IV

Transition temperatures (°C) for



Z	A	B	Y	K[a]	C	A	N	I
O	H	F	$O\overset{*}{C}H(Me)C_6H_{13}$[b]	[c]				8.7–10.3[c]
O	F	H	$O\overset{*}{C}H(Me)C_6H_{13}$	27.4				40.2–40.8
O	H	F	OCOCH(Me)Et	14.6	(24.9)[d]	(37.7–38.0)		38.3–39.2
S	H	F	$(CH_2)_2\overset{*}{C}H(Me)Et$	−0.6	(24.9)	34.3–34.8	42.1–42.2	42.3
S	H	Me	$(CH_2)_2CH(Me)Et$	14.4				41.2–42.5
S	F	H	$(CH_2)_2CH(Me)Et$	18.4	(27.5–27.8)		(35.2–35.3)	43.0–44.0
S	F	H	$(CH_2)_2\overset{*}{C}H(Me)Et$	14.2	(27.8)		(35.5)	43.1–43.7

[a] K = crystallization temperature obtained on cooling the melt 2°/min, C = smectic C phase, N = nematic phase and I = isotropic liquid.

[b] *indicates an optically active compound. Rotations are given in Table VI. The phases C and N then are chiral.

[c] Crystallization did not occur on cooling to −17°. This material has a smectic A phase below 8.7°. We could not determine whether it was monotropic or enantiotropic. This temperature is for A to I.

[d] The appearance of the microscopic texture was like that for a C rather than a C* phase.

TABLE V

Specific optical rotations in CH_2Cl_2

X	Y	$[\alpha]_D$	Temperature (°C)
$C_6^*CH(Me)O$	CO_2H	$+10.68^a$	22
$C_6^*CH(Me)O$	OH	$+12.77^b$	21
$C_6\overset{*}{C}H(Me)O_2C(CH_2)_2$	OH	+8.00	21
$Et\overset{*}{C}H(Me)CO_2$	$OCH_2C_6H_5$	+17.11	23
$Et\overset{*}{C}H(Me)CO_2$	OH	+23.14	23
$Et\overset{*}{C}H(Me)O_2CCH_2$	OH	+5.33	21
$Et\overset{*}{C}H(Me)CH_2O_2C(CH_2)_2$	OH	−2.67	21
$Et\overset{*}{C}H(Me)CH_2CH_2$	SH	+18.67	22

$^a[\alpha]_D^{25} = +8.8°$ ($CHCl_3$) reported in Reference 3.
$^b[\alpha]_D^{25} = +11.4°$ ($CHCl_3$) reported in Reference 3.

whereas with X = $C_{10}O$ and B = F all three desired phases (N, S_A and S_C) were seen but the smectic C became monotropic. Unlike the biphenyl phenyl esters, the phenylbenzoates and phenylthiobenzoates showed poor mesomorphic properties when either X or Y = $OCH(Me)C_6H_{13}$ suggesting that an additional benzene ring is necessary for stabilizing mesophases with this substituent.

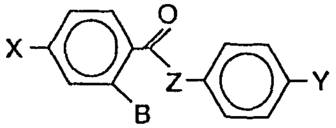
EXPERIMENTAL

The synthesis of the following intermediates were previously reported: 4-alkylphenols,[22,23] thiols[22] and benzoyl chlorides (or acids),[24] 4-alkoxyphenols[25] and thiols,[13,26] 4-acyl acids[6] and phenols,[7] and 4-acyloxy acids[9] and phenols.[10] The 4-alkoxybenzoic acids were purchased from Frinton Laboratories, R(−) and S-(+)-2-octanol, S-(−)-2-methyl-1-butanol, S-(+)-2-methylbutyric acid and 1,4-*trans*-cyclohexane dicarboxylic acid were purchased from Aldrich Chemical Company. Synthesis of the lateral substituted acids will be discussed in a later paper. All organic extracts were dried over anhyd Na_2SO_4.

TLC data were obtained using Anal-Tech silica gel GHLF-Uniplates with $CHCl_3$ as the solvent and I_2/UV light as the detectors. Silica gel for flash chromatography was purchased from Aldrich Chemical Company. Melting temperatures (°C) were determined using a Thomas-Hoover melting point apparatus and are corrected. IR spectra were run on a Pye Unicom 3-200 instrument. NMR spectra were determined using either a Varian EM360 (EM) or a General Electric GN300 (GN) instrument with TMS as an internal standard. These spectra were identical to those previously reported for the analogous straight chain compounds except for the CH multiplet at δ 4.6–4.2 and the methyl protons in the aliphatic region. All structures were

TABLE VI

Specific optical rotations in CH_2Cl_2



Z	B	X	Y	$[\alpha]_D$[a]	Temperature (°C)
O	H	$C_6H_{13}\overset{*}{C}H(Me)O$	OC_7H_{15}	+4.25	23
O	H	$C_6H_{13}\overset{*}{C}H(Me)O$	COC_9H_{19}	+2.44	22
O	H	$C_6H_{13}\overset{*}{C}H(Me)O$	$CO_2C_9H_{19}$	+2.19	22
O	H	$C_6H_{13}\overset{*}{C}H(Me)O$	$OCOC_9H_{19}$	+1.37	22
S	H	$C_6H_{13}\overset{*}{C}H(Me)O$	C_7H_{15}	+1.33	21.5
S	H	$C_6H_{13}\overset{*}{C}H(Me)O$	$OC_{12}H_{25}$	−3.86	22
O	H	$C_{10}H_{21}O$	$O\overset{*}{C}H(Me)C_6H_{13}$	+2.33	21
O	H	$N{\equiv}C$	$O\overset{*}{C}H(Me)C_6H_{13}$	+8.31	22
O	H	$C_{10}H_{21}O$	$CO_2\overset{*}{C}H(Me)C_6H_{13}$	+16.36	24
O	H	$C_{10}H_{21}O$	$CH_2CO_2\overset{*}{C}H(Me)C_6H_{13}$	+5.52	21
S	H	$C_9H_{19}CO$	$CH_2CH_2\overset{*}{C}H(Me)Et$	+10.43	21
O	H	C_4H_9O	$CO_2CH_2\overset{*}{C}H(Me)Et$	−4.0	21
O	H	$C_8H_{17}O$	$CO_2CH_2\overset{*}{C}H(Me)Et$	+2.67	21
O	H	$C_{10}H_{21}O$	$CO_2CH_2\overset{*}{C}H(Me)Et$	+4.00	21
O	H	$C_8H_{17}O$	$(CH_2)_2CO_2CH_2\overset{*}{C}H(Me)Et$	+4.57	21
O	H	$C_{10}H_{21}O$	$(CH_2)_2CO_2CH_2\overset{*}{C}H(Me)Et$	+16.0	22
O	H	$C_{10}H_{21}O$	$(CH_2)_2CO_2CH_2\overset{*}{C}H(Me)Et$	+4.0	22
O	H	$C_8H_{17}O$	$O_2C\overset{*}{C}H(Me)Et$	+13.51	22
O	H	$C_{10}H_{21}O$	$O_2C\overset{*}{C}H(Me)Et$	+7.06	22
O	H	$C_9H_{19}O$	$O_2C\overset{*}{C}H(Me)Et$	+7.95	23
S	F	$C_{10}H_{21}O$	$O\overset{*}{C}H(Me)C_6H_{13}$	+6.71	22
S	F	$C_{10}H_{21}O$	$OCO\overset{*}{C}H(Me)Et$	+6.90	21
S	H	CN	$(CH_2)_2CH(Me)Et$	+13.3	22

[a] Since many of the measured rotations were very small, rotations <0.1 probably have an error of ~ ±0.05. All compounds were of the S configuration.

confirmed by IR and NMR. Optical rotations were determined using a Polyscience polarimeter in a 1 dm cell in CH_2Cl_2.

All esters *2*, *3* and *4* were purified by recrystallization from abs EtOH and/or by flash chromatography on silica gel (always followed by recrystallization) until only one spot was seen by TLC; the clearing temperature range was <0.6 and the melting temperature range 3.5°.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 Pol polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a rate of 2°/min as described previously[27] unless otherwise indicated. Temperatures for monotropic phases were obtained by reheating these phases to obtain more accurate heating temperatures. Samples were cooled at 2°/min until they crystallized so no monotropic phases before this temperature were missed. Melting temperatures were obtained by reheating this crystallized sample at 2°/min. Mesophases were identified by the observed textures typical of these phases as described earlier.[27–29] The smectic B phase with Y = OCO$\overset{*}{\mathrm{C}}$H(Me)Et had the same characteristic texture as that observed when Y = OCOR and shown to be a crystalline smectic B phase by x-ray diffraction studies.[10] DSC data were obtained at a rate of 2°/min using a Perkin-Elmer DSC7 instrument.

R-(–)-2-Octyl-*p*-toluenesulfonate

To a cooled (0°) stirred solution of R-(–)2-octanol (74.2 g, 0.57 mole) in pyridine (290 g) was added within 30 min tosyl chloride (104.9 g, 0.55 mole). The reaction mixture was stirred at 20° for 2 hr, RT for 6 hr, poured into a mixture of ice and H_2O (1 l) containing concd HCl (300 ml) and extracted twice with Et_2O. The Et_2O layer was dried, filtered and the filtrate rotovaped to give 132.9 g (93.5%) of the crude tosylate. Excess alcohol was easier to separate from the product than excess tosyl chloride. Unreacted starting alcohol was removed from this material by molecular distillation at 47° (0.15 mm) to give 128.7 g (90.5%) of the purer tosylate as a colorless liquid: TLC R_f = 0.67 (starting alcohol R_f = 0.21 and tosyl chloride = 0.75); IR (film) 1600 cm^{-1} (str, Ar) and no OH at 3400 and ^1H NMR ($CDCl_3$, EM) δ 7.77 (d, J = 8.0 Hz, 2, ArH ortho to S), 7.30 (d, J = 8.0 Hz, 2, ArH ortho to Me), 4.85–4.28 (m, 1, CH), 2.40 (s, 3, $ArCH_3$) and 1.62–0.67 (m, 16, C_6H_{13} and CH_3).

S-(+)-*p*-(1-Methylheptyloxy)benzoic Acid

This material was prepared in the same manner previously reported.[3] Alkylation of the methyl ester of 4-hydroxybenzoic acid with the above tosylate gave the ether in a crude yield of 64.0%. Purification was by column chromatography on silica gel using CH_2Cl_2 as the eluting solvent (CH_2Cl_2-hexane would probably be a better choice) to give 30.0 g (60.3%) of the purified liquid methyl ester: TLC R_f = 0.59 (R_f for starting phenol = 0.06 and tosylate = 0.69); IR (film) 1720 (str, CO_2R) and 1600 cm^{-1} (med, Ar) and ^1H NMR ($CDCl_3$, EM) δ 7.99 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R), 6.87 (d, J = 9.0 Hz, 2, ArH ortho to OR), 4.60–4.12 (m, 1, CH), 3.82 (s, 3, OMe) and 1.79–0.64 (m, 16, C_6H_{13} and CH_3).

Hydrolysis of this ester gave the crude acid in a yield of 77.3%. This material was recrystallized twice from ligroine at dry ice/acetone bath temperature (a dark insoluble material was removed from the hot solution during the first recrystallization) to give the purified acid (65.4%): mp 61–63° (lit[2] mp 62–63°); TLC R_f = 0.02 (R_f for starting ester = 0.59); IR ($CHCl_3$) 3000 (br, acid OH), 1700 (str, CO_2H) and 1600 cm^{-1} (med, Ar); ^1H NMR (CCl_4, EM) δ 8.02 (d, J = 9.0 Hz, 2, ArH ortho to CO_2H), 6.80 (d, J = 9.0 Hz, 2, ArH ortho to OR), 4.63–3.96 (m, 1, CH) and 1.82–0.43 (m, 16, C_6H_{13} and CH_3), transition temperatures (°C) 64.1–64.9 (K-I) and 15.2 (I-K) and $[\alpha]^{22}_{D}$ = +10.68 (CH_2Cl_2) [lit[2] value at 25° = +8.88 (c = 10.4, $CHCl_3$)].

S-(+)-*p*-(1-Methylheptyloxy)phenol

This phenol was prepared in the same manner as described earlier.[3] Alkylation of 4-hydroxybenzyloxybenzene with the 2-octyloxysulfonate gave a quantitative yield of the crude diether. Purification was by flash chromatography on silica gel using 2% EtOAc-hexane as the eluting solvent to give 442 g (93.1%) of the liquid S(+)-*p*-benzyloxy (1-methylheptyloxy)benzene: TLC R_f = 0.71 (starting phenol R_f = 0.19 and tosylate = 0.67); IR (film) 1500 cm^{-1} (str, Ar) and ^1H NMR ($CDCl_3$, EM) δ 7.28 (s, 5, C_6H_5), 6.78 (s, 4, ArH ortho to OR), 4.90 (s, 2, CH_2Ar), 4.33–3.90 (m, 1, CH) and 1.66–0.60 (m, 16, C_6H_{13} and CH_3).

Debenzylation of this diether gave the crude phenol in a quantitative yield. Purification was by distillation at 160° (0.5 mm) (lit[3] bp = 129–130.5/0.5 mm) to give 80.7% of the purified phenol): TLC R_f = 0.16 (starting diester R_f = 0.71); IR (film) 3400 (str, OH) and 1600 cm^{-1} (med, Ar) and ^1H NMR ($CDCl_3$, EM) δ 6.73 (s, 4, ArH), 6.03 (s, 1, OH), 4.37–4.00 (m, 1, CH) and 1.79–0.66 (m, 16, C_6H_{13} and CH_3).

S-(+)-4-(2-Methylbutanoyloxy)phenol

This phenol was made using the method described previously for the analogous straight chain phenols.[10] The crude benzyloxy protected ester was purified by filtering through a short column of silica gel to remove unreacted phenol using 40% CH_2Cl_2-hexane as the eluting solvent followed by two recrystallizations from abs EtOH to give 14.8 g (61.5%) of purified S-(+)-4-(2-methylbutanoyloxy)-benzyloxyphenol: mp 46–48°; TLC ($CHCl_3$) R_f = 0.69 (starting phenol = 0.23); IR (Nujol) 1740 (str CO_2R), 1590 (med, Ar) and 1500 cm^{-1} (str, Ar); ^1H NMR ($CDCl_3$, GN) δ 7.44–7.26 (m, 5, C_6H_5), 7.01–6.90 (m, 4, ArH ortho to OR and OCOR), 5.00 (s, 2, $PhCH_2O$), 2.68–2.52 (m, 1, CH), 1.91–1.72 (m, 1, CH_2), 1.68–1.51 (m, 1, CH_2), 1.26 (d, 3, J = 6.76 Hz, $CH\underline{CH_3}$) and 1.00 (t, 3, J = 7.82 Hz, $CH_2\underline{CH_3}$) and $[\alpha]_D^{23}$ = +17.11° (CH_2Cl_2).

Hydrogenolysis of this benzyl ether gave a quantitative yield of the crude phenol. This material was purified by flash chromatography on silica gel using 90% CH_2Cl_2-hexane as the eluting solvent followed by recrystallization from ligroine (60–80°) to give 8.84 g (93.0%) of the purified phenol): mp 49–51°, TLC ($CHCl_3$) R_f = 0.12; IR (Nujol) 3370 (str, br, OH), 1700 (str, CO_2R) and 1610 cm^{-1} (str, Ar); ^1H NMR ($CDCl_3$, GN) δ 6.83 (d, 2, J = 8.28 Hz, ArH ortho to OCOR), 6.67 (d, 2, J = 9.06 Hz, ArH ortho OH), 2.70–2.55 (m, 1, CH) 1.90–1.72 (m, 1, CH_2), 1.69–1.53 (m, 1, CH_2), 1.26 (d, 3, J = 5.67 Hz, $CH\underline{CH_3}$) and 1.00 (t, 3, J = 7.54 Hz, $CH_2\underline{CH_3}$) and $[\alpha]_D$ = +23.14 (CH_2Cl_2, 23°).

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