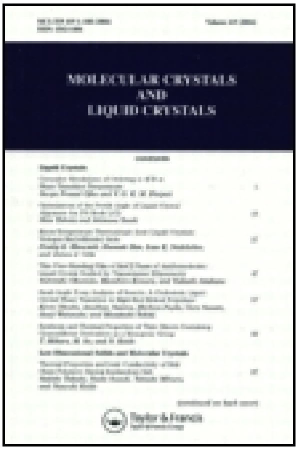


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Effect of 2- and 3-Lateral Substituents on the Acid Side of 4,4′-Disubstituted Phenylbenzoates and Phenylthiobenzoates on Mesomorphic Properties

M. E. Neubert [a] , S. S. Keast [a] , Y. Dixon-polverine [a b] , F. Herlinger [a] , M. R. Jirousek [a c] , K. Leung [a d] , K. Murray [a e] & J. Rambler [a f]

[a] Liquid Crystal Institute, Kent State University, Kent, OH, 44242-0001

[b] Hoescht-Celanese, Sommerville, NJ

[c] Eli Lilly Co., Indranapolis, Ind.

[d] HP Smith, Inc., Bedford Park, IL

[e] Lubrizol Corporation, Cleveland, OH

[f] Engelhard Industries, Cleveland, OH

To cite this article: M. E. Neubert , S. S. Keast , Y. Dixon-polverine , F. Herlinger , M. R. Jirousek , K. Leung , K. Murray & J. Rambler (1994): The Effect of 2- and 3-Lateral Substituents on the Acid Side of 4,4′-Disubstituted Phenylbenzoates and Phenylthiobenzoates on Mesomorphic Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 250:1, 109-123

To link to this article: http://dx.doi.org/10.1080/10587259408028197

Mol. Cryst. Liq. Cryst., 1994, Vol. 250, pp. 109–123
Reprints available directly from the publisher
Photocopying permitted by license only

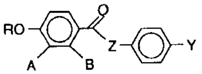
Printed in the United States of America

The Effect of 2- and 3-Lateral Substituents on the Acid Side of 4,4′-Disubstituted Phenylbenzoates and Phenylthiobenzoates on Mesomorphic Properties

M. E. NEUBERT, S. S. KEAST, Y. DIXON-POLVERINE,* F. HERLINGER,
M. R. JIROUSEK,* K. LEUNG,* K. MURRAY* and J. RAMBLER*

Liquid Crystal Institute, Kent State University, Kent, OH 44242-0001

(Received July 23, 1993)



A variety of esters/thioesters of the type where A or B=F, Cl, Me; Z=O, S and Y=C_{10}, OC_{10}, COC_9, CO_2C_9 and $OCOC_9$ for Z=O and C_5, C_{10}, OC_7, OC_{10} for Z=S and R=C_8H_{17}, $C_{10}H_2$, $C_{12}H_{25}$ were synthesized and their mesomorphic properties determined by hot-stage polarizing microscopy. These properties were compared with those for the parent compounds having no lateral substituents. Melting temperatures decreased in most, but not all, of the esters but decreased in all the thioesters studied whereas clearing temperatures always decreased. The amount of temperature depression varied considerably for both transitions. Melting temperature depressions in the esters were similar for the 2- and 3-fluorine isomers but were larger in the 2- than the 3-isomers with larger lateral substituents. Clearing temperature depressions were usually more for the 2-F ester than for the 3-isomer but not always. This difference was less in the thioesters. Often clearing temperature depressions were greater than melting temperature depressions giving narrower mesophase ranges.

Nematic and smectic C phases were found more often in the lateral substituted esters than in the parent compounds whereas the smectic A phase occurred less frequently. Thioesters showed a better suppression of smectics and a predominance of nematics than the esters. More smectic phases with larger phase ranges occurred in the 2- than the 3-F esters. As lateral substituent size increased the reverse became true.

A few lateral substituted thioesters containing branched chains (A or B=F, Me), Y=$CH_2CH(Me)Pr$ or $(CH_2)_2CH(Me)Et$ were also synthesized, mesomorphic properties determined and these properties compared to those for the parent thioesters. Lateral substituents lowered transition temperatures more than the branched chain did but unlike the branched chain, the clearing temperatures decreased more than the melting temperatures giving narrower mesophase ranges and fewer mesophases.

INTRODUCTION

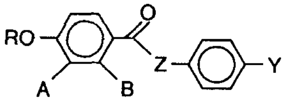
The incorporation of lateral substituents into rigid-rod type liquid crystalline molecules has been known to lower transition temperatures for some time.[1] More recently,

---

* Current address: Y. D.-P., Hoescht-Celanese, Sommerville, NJ; MRJ, Eli Lilly Co., Indranapolis, Ind. KL, HP Smith, Inc., Bedford Park, IL: K. M., Lubrizol Corporation; and J. R., Engelhard Industries, Cleveland, OH.

considerable interest has been directed at studying the effect of lateral fluorine substituents on mesomorphic properties because of the small difference in size between the hydrogen and fluorine atoms,[2] its ability to suppress smectic phases both in single materials[3,4] and in mixtures[5,6] giving wide range nematic phases and the tendency of a lateral fluorine atom to increase the dielectric anisotropy with a minimal increase in viscosity.[7] Although single nematic phases often predominate, smectic phases do occur in many compounds. It appears that the tilted smectic phases such as smectic C are more favored than the non-tilted ones with the size of the substituent determining whether the more highly ordered smectic phases of a parent compound will disappear.[8]

We were interested in determining what effect combining lateral substituents on the acid side of phenylbenzoates with carbonyl containing substituents on the phenolic side 1 would have on mesomorphic properties.



1 $Z{=}O$; $Y{=}C_{10}H_{21}, C_{10}H_{21}O, COC_9H_{19}, CO_2C_9H_{19}, OCOC_9H_{19}$

a $A{=}F, Cl, Me$; $B{=}H$

b $A{=}H$; $B{=}F, Cl, Me$

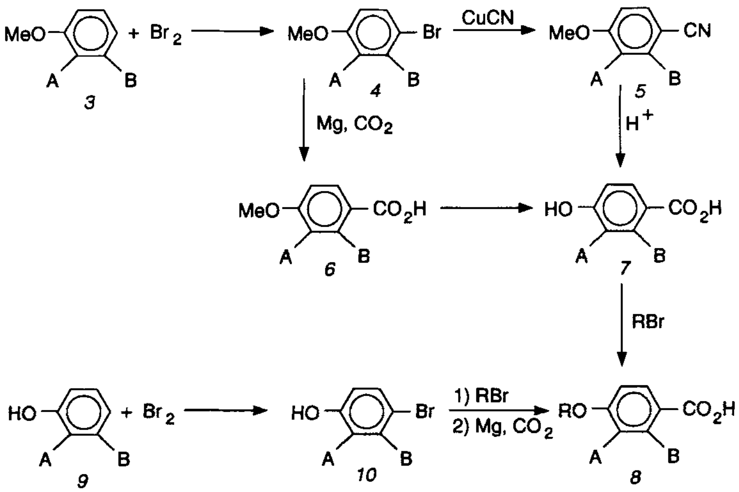
2 $Z{=}S$; $Y{=}C_5H_{11}, C_{10}H_{21}, OC_7H_{15}$

Equally interesting was to compare the temperature lowering effects of lateral substituents with those of branched chains and the effect of combining both modifications in one molecule. Some of this work has been submitted for publication;[9] additional studies will be published elsewhere.[10] Since only a few lateral substituted (fluorine only) thioesters have been studied[11] (not enough to establish structure-property relationships), a few simple thioesters containing lateral substituents 2 were also studied.

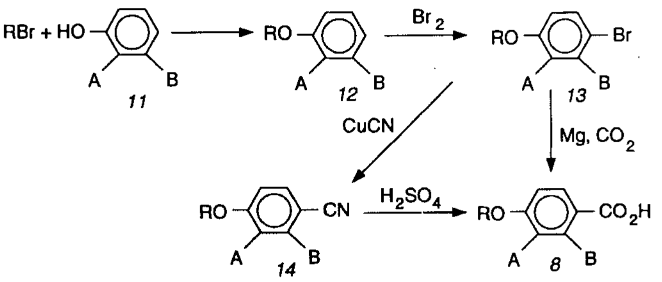
SYNTHESIS

Several methods for preparing the lateral fluoro[1,5,11–16] and methyl[15,17,18] substitued acids were available in the literature with the most popular approach proceeding through the bromides 4 or 10 (Scheme 1). Since we needed only a couple of terminal chain lengths (C_{10} was chosen as the primary one since the parent compounds were usually known), we chose to introduce the long terminal chain first (Scheme 2). Both isomers of the lateral fluorine and methyl acids were synthesized in this manner. Difficulties were encountered due to lower reactivity ortho to the lateral substituent or solubility problems although all acids were successfully prepared. Since both isomers of 4-chlorohydroxybenzoic acid are commercially available, only the alkylation of these acids was necessary to obtain the desired alkoxy acids 8 (A or $B{=}Cl$).[1] Purification of all the acids was by recrystallization.

The esters/thioesters 1,2 were prepared by esterification of the acids 8 with the appropriate phenol/thiol using the carbodiimide method.[19] These were purified by



SCHEME 1



SCHEME 2

recrystallization or a combination of recrystallization and flash chromatography on silica gel with mixtures of hexane in CH_2Cl_2 until they showed only one spot by thin layer chromatography and had sharp clearing ($\leq 0.8°$)* and melting ($< 2.5°$) temperatures. Structures of all compounds were confirmed by IR and NMR whenever feasible; elemental analyses were obtained when NMR was not possible due to low solubility. With our previous extensive knowledge on NMR data for 4,4′-disubstituted phenylbenzoates and thiobenzoates[20–24] and use of a Gemini 200 MHz instrument, all protons could be assigned (sometimes using 2D-NMR) providing what we consider as convincing confirming evidence for the proposed structures. A lateral fluorine atom usually caused additional splitting of the other protons on the benzene ring to which it was attached and gave a larger coupling constant for the proton adjacent to it. Typical examples of data are provided in the experimental section to illustrate this difference. Interpretation of the remaining protons in the spectra agreed with those reported earlier. Thus, we did not feel it was necessary to include all the data in this paper.

---

* During the course of this work our standards on purity and ability to purify have improved so that our current standard is $< 2.0°$ for C–M, $< 0.3°$ for N–I and $< 0.5°$ for S–I for most compounds.

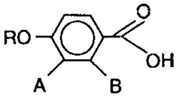
MESOMORPHIC PROPERTIES

Transition temperatures (°C) and mesophase identification were accomplished using hot-stage polarizing microscopy as described in the experimental section. All the laterally substituted acids that were synthesized were checked for possible mesophases and transition temperatures compared to earlier data when available (Table I). Usually a short range nematic phase (often monotropic) was observed and sometimes a smectic C phase. Transition temperatures were rarely sharp which is also true for the parent acids containing no lateral substituents.[26] These parent acids also show nematic and smectic C phases but with higher transition temperatures and wider phase lengths (all are enantiotropic illustrating the typical effects of lateral substituents). Data for the lateral substituted esters are given in Tables II and III and the thioesters in Table IV. Differences in the melting and clearing temperatures from those reported in the parent compounds are also given in these tables. Data for the parent esters/thioesters containing no lateral substituents were reported earlier.[19,21,22,26–29]

Melting temperatures in the esters/thioesters were often lowered by a lateral substituent with fewer exceptions occurring in the thioesters than in the esters. Clearing

TABLE I

Transition Temperatures (°C) for



R	A	B	K[a]	C	N	I
C_{10}	F	H	106.7 (K^1)[b]	109.0–109.6 (K^1)	110.9–112.4	115.7–116.6
				108[c,d]	112	116.5
C_{10}	H	F	93.4[e]		94.3–95.3	112.1–113.5
C_8	Cl	H	87.6[f]		(95.2–95.5)	96.4–98.4 (K^1)
				(86)[c]	(93)	94[d]
C_{10}	Cl	H	83.4	(85.5–86.6)	(92.0–92.3)	99.3–100.5
				(86)[c]	(90.5)	100.5
C_{10}	H	Cl	57.1		(66.2–66.9)	83.4–85.6
C_{12}	Cl	H	85.9		(87.6–88.0)	102.7–103.6
				(83.5)	(88)	101.5[g]
	H	Cl	75.1			90.4–91.3
C_{10}	Me	H	93.7		(95.2–96.6)	106.6–107.0
C_{10}	H	Me	60.4		(61.3–63.6)	73.5–75.4

[a] Abbreviations for phases are as follows: K = crystallization temperature obtained on cooling the melt 2°/min, C = smectic C, N = nematic and I = isotropic liquid.

[b] Shows a crystal-to-crystal change on cooling further to 72.1–72.0 (K_2). K_2 converted to K_1 on reheating at 104.3–104.9.

[c] Smectic was not identified.

[d] Data from Reference 1.

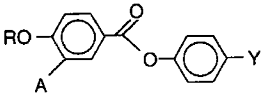
[e] Possibly shows another crystal form with mp 93.9–96.1°.

[f] When the crystallized melt was reheated, a transition occurred which suggested that the nematic phase might be enantiotropic although none was observed. Since another possibility was that a crystal–crystal change occurred before the melting transition, the crystallized melt was allowed to stand at room temperature for several days. Reheating at 2°/min then gave an obvious crystal–crystal change at 93.8–94.3° and then the isotropic liquid at the higher melting temperature confirming that the nematic phase was monotropic. We did not see the reported smectic phase probably because our cystallization temperature was too high.

[g] Data from Reference 25.

TABLE II

Transition Temperatures (°C) for



A	R	Y	K[a]	C	A	N	I	Δmb[b]	Δclp[b]
F	C_{10}	C_{10}	50.0	(58.5–58.9)	–	–	67.4–69.9	8.3	– 16.2
		COC_9	91.6	(97.6–98.2)	102.1–105.7	–	116.0–116.4	– 2.5	– 4.3
		CO_2C_9	51.9		63.4–63.8[c]		63.4–63.6	– 6.0	– 10.9
		OC_{10}	68.0	73.7–74.0			79.5–79.6	3.2	– 10.8
		$OCOC_9$	81.0	(88.9–90.0)			94.9–95.0	25.6	– 6.8
Cl	C_8	C_{10}	53.4				59.3–60.0	5.2	
		OC_{10}	39.3	(56.7–56.8)		(62.9–63.0)	63.7–64.0	8.9	– 27.2
		$OCOC_9$	53.8	(75.5–75.8)		(76.0–76.2)	76.3–76.7	9.4	– 19.6
Cl	C_{10}	C_{10}	47.2				65.8–66.5	4.9	
		COC_9	59.1		86.4–87.3	–	89.6–91.1	– 20.3	– 29.6
		CO_2C_9	53.8				63.7–63.9	– 5.5	
		OC_{10}	56.4	(59.2–59.7)	–	(62.8–63.1)	65.2–65.6	– 5.2	– 27.3
		$OCOC_9$	58.6	(77.1–77.6)	–	–	77.2–77.5	–8.1	– 19.2
	C_{12}	C_{10}	69.4				71.8–72.8	– 0.8	
		COC_9	74.1		93.4–93.8	–	98.4–98.7	– 18.2	– 20.4
		OC_{10}	58.7	61.1–61.2	–	62.4–62.5	64.0–64.2	– 20.0	– 27.8
		$OCOC_9$	56.0	(76.7–77.2)	–	–	77.7–78.2	+ 6.1	– 20.5
Me	C_{10}	C_{10}	34.0			(43.0–44.2)	45.4–46.0	– 15.6	– 30.9
		COC_9	31.5[c]		54.8–55.1 (K^1)[d]	–	79.5–79.8	– 52.5 – 49.6	– 40.9
		CO_2C_9	32.3		57.8–58.0 (K_2)		55.6–56.7	– 12.7	
		C_{10}	10.0	(26.5–26.7)	–	44.0–44.3	58.9[e]	– 26.5	– 31.5
		OC_{12}	13.6	(35.9–36.1)	–	43.6–44.5	58.3–58.4	– 32.5	– 31.6
		$OCOC_9$	45.4	(49.3–49.6)		60.5–60.8	66.1–66.4	– 8.6	– 30.4

[a] K = crystallization temperature obtained on cooling 2°/min, C and A are smectics C and A, N = nematic, I = isotropic liquid and ( ) indicates a monotropic phase. Details are provided in the experimental section.

[b] Δmp = difference in melting temperature from that for the parent compound, Δclp = difference in clearing temperature from that for the parent compound.

[c] Actually a $K \rightarrow A \rightarrow I$ transition.

[d] Crystals (K_1) were formed on cooling to 31.5°. Reheating to 49.5° gave a partial change to a mixture of two crystals which gave two different melting temperatures.

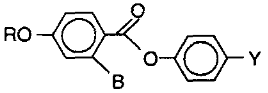
[e] Transition temperature range < 0.1°.

temperatures were always lowered. Usually the clearing temperatures decreased more than the melting temperatures, giving shorter phase lengths. The few exceptions were found only in the esters. When the lateral substituent was ortho to the ester group all but one exception occurred when B=F (Table III) whereas when the lateral substituent was ortho to the alkoxy chain exceptions occurred when A=Me.

The amount of melting temperature depression in the esters usually increased with the size of the lateral substituent and with its location ortho to the central group as expected. Considerable variation occurred even in a series where the lateral substituent was kept constant. Less variation occurred in the thioesters with both size and location possibly because of the lower steric hindrance around the central group in these compounds. However, the fewer number of structure modifications could also explain this difference.

TABLE III

Transition Temperatures (°C) for



R	Y	B	K[a]	C	A	N	I	Δmb[b]	Δclp[b]
C_{10}	C_{10}	F	23.9		46.1–46.7		61.5–61.9	−14.9	−13.2
	COC_9		74.5		85.4–86.5		109.0–109.4	−21.1	−11.3
	CO_2C_9		34.6		53.8–54.6		62.1–62.2	−14.8	−12.5
	OC_{10}		28.5 K_2[c]	54.5–54.9	70.7[d]	72.0[d]	79.5[d]	−15.9	−10.9
	$OCOC_9$		51.5	66.7–68.4		72.4[d]	85.4–85.5	−1.0	−11.3
	C_{10}	Cl	18.9			(21.6–21.7)	39.8–40.1	−21.5	−53.4
	COC_9		38.2		67.5–68.1		72.9–73.1	−39.5	−47.6
	CO_2C_9		23.3				32.5–32.8	−36.6	–
	OC_{10}		21.0			(45.8–45.9)	46.7–47.3	−23.5	−44.5
	$OCOC_9$		14.1	(35.1–35.4)	–	44.0–45.6	54.1–54.3	−15.1	−51.2
C_{12}	C_{10}	Cl	34.7		(~28.6)[e]	(~29.4)	45.0–46.4	−27.2	−45.9
	COC_9		45.7		69.0–69.7		76.9–77.5	−42.3	−41.6
	OC_{10}		34.8	(37.9–38.0)	–	(49.4)[d]	52.5–53.5	−27.7	−42.6
	$OCOC_9$		31.8 K_1[f]	(43.3)		53.1–54.5	57.1–57.3	−17.6	−40.4
C_{10}	C_{10}	Me	9.0			(18.3)	34.8–35.5	−26.1	−56.8
	COC_9		52.2 K_2[g]			(61.3–61.6)	65.5–66.4	−41.2	−59.1
	CO_2C_9		8.9 K_1[h]				39.2–39.9 (K_1) 37.9 (K_2)	−29.5	–
	OC_{10}		39.6			(40.2–40.4)[i]	54.5–56.3	−14.5	−50.0
	$OCOC_9$		30.3			(48.5)[d]	47.7–50.0	−19.4	−48.3

[a] K = crystallization temperature obtained on cooling 2°/min. C and A are smectics C and A, N = nematic, I = isotropic liquid and ( ) indicates a monotropic phase.

[b] Δmp = difference in melting temperature from that for the parent compound, Δclp = difference in clearing temperature from that for the parent compound.

[c] The first crystals K_2 formed quickly and then changed to a second crystalline form K_1 which melted to the C phase when reheated.

[d] Transition temperature range was < 0.1°.

[e] These mesophases were rarely seen due to higher crystallization temperatures. When observed, crystallization occurred before the phase could be reheated to obtain a heating transition.

[f] On reheating, these crystals changed to another crystal form K_2 at 47.1–49.9°

[g] The original crystals showed two crystal forms with two melting temperatures which was not observed in the crystals formed on cooling the melt.

[h] Two crystal forms with two different melting temperatures were observed.

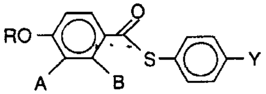
[i] Crystals begin to grow about the same time as the nematic phase formed. Thus, this phase may not always be seen.

Clearing temperatures showed similar trends except the amount of temperature depression for the 2- and 3-F isomers varied little in both the esters and thioesters. Less variation occurred in a specific series as expected. There seemed to be no consistent trends that could be attributed to the effect of the carbonyl containing chains ($Y{=}COC_9$, CO_2C_9 and $OCOC_9$) on transition temperatures.

The effect of lateral substituents on the types of mesophases and their phase lengths is shown by the examples given in Table V. Interestingly, a fluorine substituent ortho to the central group (2-isomer) has a tendency to give more mesophases with wider temperature ranges than a fluorine atom ortho to the alkoxy chain (3-isomer) despite

TABLE IV

Transition Temperatures (°C) for



R	A	B	Y	K[a]	C	A	N	I	Δmb[b]	Δclp[b]
C_{10}	F	H	C_5	49.0			(57.7)-(57.8)	72.2-73.1	12.8	−27.8
			C_{10}	29.7			59.5-59.6	63.2-63.3	−6.7	−23.4
C_8	Cl	H	C_5	26.9			35.3-35.4	48.0-48.4	−23.2	−38.1
			C_{10}	25.0	(33.2-33.4)	–	39.3-40.0	44.8-44.9	−20.6	−39.3
C_{10}	Cl	H	C_5	38.4				45.9-46.2	−14.1	–
			C_{10}	29.6	(38.7-38.8)	–	40.0-41.0	47.1[c]	−25.3	−39.6
			OC_7	63.1				75.3-76.4	5.0	–
			OC_{10}	55.6	(56.0-56.1)	–	(64.8-64.9)	67.6-68.0	13.3	−33.4
C_{12}	Cl	H	C_5	39.7[d]			(40.4-40.5)	52.0-52.5	−9.9	−46.2
			C_{10}	19.0	(40.4-40.6)	–	43.4-44.1	48.2-48.3	−31.6	−40.7
C_{10}	Me	H	C_5	7.0			(26.8)[c]	42.3-44.7	−15.6	−58.8
			C_{10}	12.0			(22.3-22.4)	41.4-42.3	−24.0	−64.3
			$CH_2CH(Me)Pr$	20.7			(38.0)[c]	42.7-44.8	−15.5	−47.6
C_{10}	H	F	C_5	16.5		45.6-46.6[e]	46.3[c]	59.6-59.8	−13.7	−25.8
			C_{10}	23.9		44.1-44.6	57.9-58.0	64.1-64.2	−21.7	−22.5
		Cl	C_5	21.7				49.4-50.0	−10.3	–
			C_{10}	34.8				44.8-45.4	−20.9	–
		Me	C_5	21.5			(22.3-22.4)	42.3-44.1	−16.2	−63.2
			C_{10}	15.8			(26.6-26.7)	44.7-45.7	−20.6	−60.0

[a] K = crystallization temperature obtained on cooling 2°/min. C and A are smectics C and A, N = nematic, I = isotropic liquid and () indicates a monotropic phase. The observance of these phases depends on the crystallization temperature which varies with cooling conditions. Therefore, these phases are not always seen when they occur close to the crystallization temperature.

[b] Δmp = difference in melting temperature from that for the parent compound, Δclp = difference in clearing temperature.

[c] Transition temperature range < 0.1°.

[d] These crystals (K_2) show a crystal-to-crystal transition to K_1 at 48.7–51.2° on reheating which then melt to the isotropic liquid.

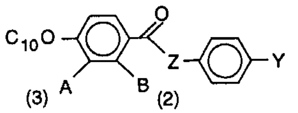
[e] This is actually a continuous S_{ANI} transition.

the greater steric hindrance between the fluorine atom and the central group than with the alkoxy chain. Some enhancement of nematic and smectic C phases occur in the esters with the smectic A phase being less preferred. In the thioesters, nematic phases definitely are preferred over the smectic phases, a tendency previously reported for other compounds containing lateral fluorine atom.[5] Conceivably, even better nematic phases would occur with shorter terminal chains on the acid side. The position of the fluorine atom also affected the type of smectic phase observed. The smectic C phase occurred more in the 3-F esters whereas the smectic A phase occurred more in the 2-F esters and thioesters with the 3-F thioesters showing only nematic phases. As the size of the lateral substituent increases, the 3-isomer begins to show wider mesophases as is quite evident in the 3-Me esters. However, since the mesophases are more likely to be monotropic, comparisons become more difficult. The 2-keto chain (Y=COC_9) gave wider range smectic A phases than the parent ester (Y=$C_{10}H_{21}$).

A comparison of the temperature lowering effect of a lateral substituent with that for a terminal branched chain (Table VI) shows that the branched chain lowers the clearing

TABLE V

Mesophase Range (°C) for



Z=O		A=B=H				A=F B=H				A=H B=F		
Y	C[a]	A	N	Total	C	A	N	Total	C	A	N	Total
C_{10}		13.5		13.5	m			m		15.2		15.2
COC_9		13.1		13.1	m	11.3		11.3		22.9		22.9
CO_2C_9		5.3		5.3		m		m				0
OC_{10}	16.7	1.5		19.6	3.8			3.8	15.8	1.3	7.5	24.6
$OCOC_9$	22.1	–		27.4	m			m	4.0		13.1	17.1
			Z=0			A=Cl	B=H			A=H	B=Cl	
C_{10}								0			m	m
COC_9						3.8		3.8		5.0		5.0
CO_2C_9								0				0
OC_{10}					m		m	m			m	m
$OCOC_9$					m			m			m	m
			Z=0			A=Me	B=H			A=H	B=Me	
C_{10}							m	m			m	m
COC_9						24.7		24.7			m	m
CO_2C_9								0				0
OC_{10}					m	15.1		15.1				0
$OCOC_9$					m		5.6	5.6			m	m
			Z=S			A=F	B=H			A=H	B=F	
C_5	2.4	16.9	6.0	25.3			m	m		~0.1	~0.1	~0.2
C_{10}	13.3	7.0	–	20.4			3.7	3.7		13.4	6.2	19.6

[a] C=smectic C, A=smectic A and N=nematic; m indicates a monotropic phase. Data for the parent esters with A=B=H were obtained from References 19, 21, 27–29.

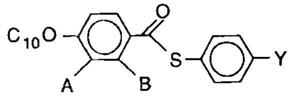
temperature about the same amount as the melting temperature whereas the lateral substituent decreases the clearing temperature much more than the melting temperature. A comparison of the observed temperatures for the thioesters in which both of these modifications are incorporated into one molecule with that calculated by adding the lowering effects observed in the two parent compounds once again shows the inaccuracy of predicting melting and clearing temperatures by assuming an additive effect. Obviously, this is not the approach to take to lower only melting temperatures and achieve wider range mesophases.

CONCLUSIONS

These studies indicate that lateral substituents, even the small fluorine atom on the acid side of phenylbenzoates and phenylthiobenzoates, generally give poor mesomorphic properties. Melting temperatures were usually lowered in the esters and always in the thioesters studied whereas clearing temperatures were always lowered. The amount of temperature depression varied considerably for both transitions. It was similar for the

TABLE VI

Comparison of the Effect of Lateral Substituents and Branched Terminal Chains on the Melting and Clearing Temperatures (°C) for



A	B	Y	ΔT(°C)[a]	
			melting	clearing
F	H	C_5H_{11}	+ 12.8	− 27.8
H	H	$(CH_2)_2CH(Me)Et$[b]	− 22.1	− 14.2
F	H	$(CH_2)_2CH(Me)Et$		
		calcd[c]	− 9.3	− 42.0
		obsd[d]	− 16.3	− 50.3
H	F	C_5H_{11}	− 13.7	− 25.8
H	F	$(CH_2)_2CH(Me)Et$		
		calcd	− 35.8	− 40.0
		obsd[d]	− 25.5	− 43.3
Me	H	C_5H_{11}	− 17.5	− 58.8
H	H	$CH_2CH(Me)Pr$	− 16.2	− 15.7
Me	H	$CH_2CH(Me)Pr$		
		calcd[c]	− 33.7	− 74.5
		obsd[d]	− 15.5	− 47.6
H	Me	C_5H_{11}	− 16.2	− 63.2
H	Me	$(CH_2)_2CH(Me)Et$		
		calcd[c]	− 38.3	− 77.4
		obsd[d]	− 17.8	no mesophases

[a] Calculated by subtracting the transition temperature of the modified thioesters from that for the unsubstituted parent thioesters. Values for the latter were obtained from Reference 29.

[b] Data obtained from Reference 30.

[c] Obtained by adding ΔT for the lateral substituted thioester and ΔT for the branched chain thioester.

[d] Data obtained from Reference 9.

melting transition in the 2- and 3-F esters but more for the 2- than the 3-isomers with larger substituents. Clearing point depression was often lower for the 2- than the 3-ester isomers but not always. The difference was less in the thioesters.

Nematic and smectic C phases seemed to be more preferred than for the esters/thioesters containing no lateral substituents. Thioesters showed a better suppression of smectic phases and a predominance of nematic phases. More smectic phases showing larger phase ranges occurred in the 2-F than in the 3-F esters. As the lateral substituent size increases, the 3-isomer shows the wider mesophase ranges but the mesophases tend to become monotropic hampering comparisons.

Lateral substituents lower transition temperatures by larger amounts than terminal branched chains. However, they also tended to lower the clearing temperature more than the melting temperature, decreasing the mesophase range more than a branched-chain which tends to lower melting and clearing temperatures by about the same amount. Thus, neither of these modifications provide the desired melting point lowering only with an increase in the mesophase range.

EXPERIMENTAL

Anhydrous Na_2SO_4 was used to dry all organic extracts. The solvent 1-methyl-2-pyrrolidinone was dried over Linde #4A molecular sieves and distilled before use. TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with UV light and I_2 as detectors. Flash chromatography was done on Aldrich grade 60, mesh 230–240 silica gel using the method previously described.[31] All compounds were purified by recrystallization and/or chromatography until they showed one spot by TLC, no impurities in their NMR spectra and melting temperatures within 3°. Melting points (°C) of intermediates were determined using a Thomas–Hoover melting point apparatus and are corrected. Purity for the phenylbenzoates and phenylthiobenzoates was also checked by the sharpness of the clearing temperature ($< 0.8°$ for clearing, $< 2.5°$ for melting; see the text) by microscopy. GLC was performed on a 3% SP-200 on 80/100 Supelcoport 6′ × 1/8″ SS column using a Varian 3700 instrument. HPLC was done using a Burdick and Jackson silica gel column and a Waters Prep 3000 instrument.

IR spectra were run using a Pye-Unicam 3–200 instrument and NMR spectra were obtained in $CDCL_3$ using a General Electric GN-300 (GN) or a Varian Gemini 200 instrument with TMS as the internal standard. Published NMR data for the corresponding esters and thioesters without lateral substituents[18,19–23] were used to assist in peak identification. An elemental analysis was obtained from Oneida Research Services, Inc., Whitesboro, NY when NMR could not be used for structure confirmation due to poor solubility.

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 heating rate of 2°/min as previously described.[32] Samples were cooled at 2°/min until they crystallized to obtain the crystallization temperature and so no monotropic phases occurring below this temperature were missed. Mesophases were identified by the observance of known textures.[33,34]

Laterally Substituted Decyloxybenzenes, 12

All these ethers were synthesized using the following typical procedure for:

3-Fluorodecyloxybenzene, 12 ($R{=}C_{10}H_{21}$, A=H, B=F)

To a stirred mixture of 3-fluorophenol (49.9 g, 0.44 mole) and KOH (56.1 g = 0.58 mole) in 112 ml H_2O and 890 ml abs EtOH at RT was added dropwise bromodecane (113.1 g = 0.51 mole). This mixture was then refluxed for 48 hr, cooled to RT and rotovaped. The remaining liquid was dissolved in $CHCl_3$ washed with H_2O 5% aq KOH and H_2O dried, filtered and the filtrate rotovaped to give 187.3 g of the crude ether. Distillation of this material at 117° (0.25 mm) gave 89.5 g (79.7%) of the purified ether 12: TLC ($CHCl_3$) $R_f = 0.82$, IR (film) 1600, 1580 and 1500 cm^{-1} (str Ar); GLC (200°) $t_R = 0.98$, estd purity = 99.5%; HPLC (hexane) $t_R = 3.93$ estd purity = 99.6% and ^1H NMR (GN) 7.23 – 7.11 (m, 1, 5-ArH), 6.72 – 6.54 (m, 3, 2-, 4- and 6-ArH), 3.97 – 3.85 (m, 2, $ArOCH_2$), 1.82 – 1.70 (m, 2, OCH_2CH_2), 1.50 – 1.17 (m, 14, $2CH_2$) and 0.88 (s, 3, CH_3).

Data for the other ethers 12 prepared in this manner are as follows:

2-Fluorodecyloxybenzene 12 (R=$C_{10}H_{21}$, A=F, B=H): 87.7%, bp 155–160° (0.66 mm); TLC ($CHCl_3$) $R_f = 0.82$; IR (film) 1600 and 1580 cm^{-1} (weak Ar) and ^{1}H NMR $\delta 7.25 - 6.80$ (m, 4, ArH), 4.02 (t, 2, $J = 6.63$ Hz, OCH_2), 1.82 (quint, 2, $J = 6.67$ Hz, $OCH_2\mathit{CH}_2$), 1.60–1.10 (m, 14, $7CH_2$) and 0.88 (t, 3, J=6.42 Hz, Me).

2-Decyloxytoluene 12 (R=$C_{10}H_{21}$, A=Me, B=H): 73.2%, bp 122° (0.20 mm); TLC ($CHCl_3$) $R_f = 0.80$ (R_f for starting material = 0.30); IR (film) 1600 cm^{-1} (med, Ar) and ^{1}H NMR (GN) $\delta 7.14 - 7.09$ (m, 2, 4 and 6-ArH), 6.83 – 6.78 (dd; 2; J = 7.35, 7,90 Hz, 3- and 5-ArH) 3.93 (t, 2, $J = 6.6$ Hz, $ArOCH_2$), 2.22 (s, 3, $ArCH_3$), 1.81 – 1.75 (m, 2, $OCH_2\mathit{CH}_2$), 1.47 – 1.19 (m, 14, $7CH_2$) and 0.88 (t, 3, J = 6.6 Hz, CH_3).

3-Decyloxytoluene 12 (R=$C_{10}H_{21}$ A=H, B=Me): 82.5%, bp 125° (0.2 mm); TLC($CHCl_3$) $R_f = 0.79$ (R_f for starting material = 0.25); IR (film) 1600, 1590 and 1500 cm^{-1} (str Ar) and ^{1}H NMR (GN) 7.12 (dd; 1; J = 7.92 Hz, 5-ArH), 6.73 – 6.66 (m, 3, 2-, 4- and 6-ArH), 3.90 (t, 2, J = 6.78 Hz, $ArOCH_2$), 2.30 (s, 3, $ArCH_3$), 1.82 – 1.68 (m, 2, $OCH_2\mathit{CH}_2$), 1.52 – 1.14 (m, 14, $7CH_2$) and 0.88 (t, 3, J = 6.12 Hz, CH_3).

Laterally Substituted 4-Bromodecyloxybenzenes, 13

Bromination of the ethers 12 was achieved using the following method described for:

4-Bromo-3-fluorodecyloxybenzene, 13 (R=$C_{10}H_{21}$, A=H, B=F):

Bromine (55.6 g = 0.35 mole) was added dropwise to a stirred solution of the ether 12(87.8 g = 0.35 mole) in $CHCl_3$ at RT. This mixture was refluxed for 2.5 hr, cooled to RT, additional $CHCl_3$ added and washed with H_2O, 5% aq KOH and H_2O. The organic layer was dried, filtered and the filtrate rotovaped to give 155 g of the crude bromide. Distillation of this material at 137° (0.15 mm) gave 105.6 g (91.6%) of the purified bromide 13: TLC ($CHCl_3$), $R_f = 0.82$; GLC (200°) $t_R = 2.11$, estd purity = 90% with the remainder consisting of 4% of the starting ether and 6% of an unknown and ^{1}H NMR (GN) $\delta 7.38$ (dd, 1, J = 8.34, 8.47 Hz, 5-ArH), 6.68 (dd, 1, J = 2.80, 10.50 Hz, 2-ArH), 6.59 (dd, 1, J = 2.95, 8.73 Hz, 6-ArH), 3.90 (t, 2, J = 6.53 Hz, $ArOCH_2$), 1.77 (quint, 2, J = 7.18 Hz, $OCH_2\mathit{CH}_2$), 1.50 – 1.20 (m, 14, $7CH_2$) and 0.88 (t, 3, 6.31 Hz, CH_3).

4-Bromo-2-fluorodecyloxybenzene, 13 (R=$C_{10}H_{21}$, A=F, B=H): 81.4%, bp 140–145° (0.1 mm), GLC (180–250°) $t_R = 2.14$, estd purity = 99.4%, and IR (film) 1605 and 1595 cm^{-1} (med, Ar).

5-Bromo-2-decyloxytoluene, 13 (R=$C_{10}H_{21}$, A=Me, B=H): 93.7%, bp 151° (0.18 mm); TLC ($CHCl_3$) $R_f = 0.79$; GLC (210°) $t_R = 1.28$, estd purity = 99% and ^{1}H NMR (GN) $\delta 7.22$ (s, 1, 6-ArH), 7.20 (d, 1, J = 8.54 Hz, 4-ArH), 6.63 (d, 1, J = 7.36 Hz, 3-ArH), 3.89 (t, 2, J = 6.00 Hz, OCH_2), 2.18 (s, 3, $ArCH_3$), 1.80 – 1.74 (m, 2, $OCH_2\mathit{CH}_2$), 1.50 – 1.27 (m, 14, $7CH_2$) and 0.88 (t, 3, J = 6.4 Hz, CH_3).

2-Bromo-5-decyloxytoluene, 13 (R=$C_{10}H_{21}$, A=H, B=Me): 42.6%, bp 169° (0.15 mm), TLC ($CHCl_3$) $R_f = 0.79$, HPLC (hexane) $t_R = 2.81$ sec, estd purity = 99.9% and ^{1}H NMR $\delta 7.36$ (d, 1, J = 8.79 Hz, 4-6.77 (d, 1, J = 2.93 Hz, 6-ArH), 6.59, 6.58 (dd, 1,

$J = 8.50$, 8.67 Hz, 3-ArH), 3.88 (t, 2, $J = 6.49$ Hz, $ArOCH_2$), 2.34 (s, 3, $ArCH_3$), 1.75 (quint, 2, $J = 7.14$ Hz, OCH_2CH_2), 1.60 – 1.15 (m, 14, $7CH_2$) and 0.88 (t, 3, $J = 6.41$ Hz, CH_3).

Laterally Substituted Decyloxybenzonitriles, 14

All these nitriles were synthesized using the following procedure for:

4-Decyloxy-3-methylbenzonitrile, 14 ($R{=}C_{10}H_{21}$, A=Me, B=H)

A mixture of the bromide *13* (10.0 g, 0.03 mole) and CuCN (5.55 g = 0.62 mole) in 1-methyl-2-pyrrolidinone (31 ml) was refluxed for 1.5 hr, cooled to RT, poured into a solution of 12.4 g $FeCl_3$ in 155 ml 1*N* HCl, stirred for 40 min and extracted with Et_2O. The organic layer was washed with Et_2O, dried, filtered and the filtrate rotovaped to give 8.31 g (98.1%) of the crude nitrile; TLC ($CHCl_3$) showed 3 spots with $R_f = 0.65$ (major), 0.37 and 0.03. This material was purified by flash chromatography using a 1:2 petroleum ether (30–60°)-$CHCl_3$ (CH_2Cl_2 would be better) mixture as the eluting solvent followed by recrystallization from abs EtOH to give 6.20 g (73.2%) of the purified nitrile 14: mp 31.5–33°; TLC ($CHCl_3$) $R_f = 0.62$; IR (Nujol) 2250 (med, CN) and 1620 cm^{-1} (med, Ar) and ^{1}H NMR (GN) δ7.45 (d, 1, $J = 7.45$ Hz, 6-ArH), 7.38 (s, 1, 2-ArH), 6.82 (d, 1, 6.82 Hz, 5-ArH), 4.00 (t, 2, $J = 6.18$ Hz, OCH_2), 2.21 (s, 3, $ArCH_3$), 1.84 – 1.75 (m, 2, OCH_2CH_2), 1.55 – 1.18 (m, 14, $7CH_2$) and 0.88 (t, 3, $J = 6.28$ Hz, CH_3).

4-Decyloxy-2-methylbenzonitrile, 14 ($R{=}C_{10}H_{21}$, A=H, B=Me): 89.8%, 30% CH_2Cl_2 in hexane used in flash chromatography; TLC ($CHCl_3$) $R_f = 0.79$; IR (film) 2200 (str, CN) and 1600, 1500 cm^{-1} (str Ar) and ^{1}H NMR δ7.49 (d, 1, $J = 8.34$ Hz, 6-ArH), 6.79 (m, 1, 3-ArH), 6.74 (d, 1, $J = 8.43$ Hz, 5-ArH), 3.97 (t, 2, $J = 6.41$ Hz, OCH_2), 2.50 (s, 3, $ArCH_3$), 1.90 – 1.71 (m, 2, OCH_2CH_2), 1.56 – 1.20 (m, 14, $7CH_2$) and 0.89 (t, 3, $J = 6.26$ Hz, CH_3).

4-Decyloxy-2-fluorobenzonitrile, 14 ($R{=}C_{10}H_{21}$, A=H, B=F): 47.2%, recrystallized from abs EtOH with charcoal treatment (it would probably be better to chromatograph the crude material first); mp 36–38°C; TLC ($CHCl_3$), $R_f = 0.63$; IR (Nujol) 2240 (str, CN) and 1610 cm^{-1} (str, Ar) and ^{1}H NMR δ7.50 (dd, 1, 7.81 and 8.55 Hz, 6-ArH), 6.75 (dd, 1, $J = 2.52$, 8.63 Hz, 3-ArH), 6.69 (dd, 1, $J = 2.36$, 10.34 Hz, 5-ArH), 3.99 (t, 2, $J = 6.49$ Hz, OCH_2), 1.80 (quint, 2, $J = 7.14$ Hz, OCH_2CH_2), 1.53 – 1.20 (m, 14, $7CH_2$) and 0.88 (t, 3, $J = 6.41$ Hz, CH_3).

Laterally Substituted 4-Alkoxybenzoic Acids, 8

The 2- and 3-chloro acids were prepared by alkylation of the commercially available 2- and 3-chloro-4-hydroxybenzoic acids using the method of Gray and Jones.[1] Purification was by recrystallization from abs EtOH. Transition temperatures for all the acids prepared are given in Table I. Additional data are as follows:

2-Chloro-4-decyloxybenzoic Acid, 8 ($R{=}C_{10}H_{21}$, A=H, B=Cl): 73.2% recrystallized from benzene: IR (Nujol) 3180 – 2800 (broad, acid OH), 1700 (str, CO_2H) and 1600 cm^{-1} (str, Ar) and ^{1}H NMR, δ8.04 (d, 1, $J = 8.89$ Hz, 6-ArH), 6.99 (d, 1,

$J = 2.45$ Hz, 3-ArH), 6.84 (dd, 1, $J = 2.48$, 8.91 Hz, 5-ArH), 4.00 (t, 2, $J = 6.51$ Hz, OCH_2), 1.80 (quint, 2, OCH_2CH_2), 1.60 – 1.10 (m, 14, $7CH_2$) and 0.88 (t, 3, $J = 6.13$ Hz, CH_3).

3-Chloro-4-octyloxybenzoic Acid, 8 ($R{=}C_{10}H_{17}$, A=Cl, B=H): 52.6%, recrystallized twice from abs EtOH, TLC ($CHCl_3$) $R_f = 0.04$.

3-Chloro-4-decyloxybenzoic acid, 8 ($R{=}C_{10}H_{21}$, A=Cl, B=H): 48.0%, recrystallized from benzene; IR ($CHCl_3$), 3600 – 2400 (br, acid OH), 1680 (str, CO_2H) and 1600 cm^{-1} (str, Ar) and ^1H NMR, δ8.03 (d, 1, $J = 2.04$ Hz, 2-ArH), 7.92 (dd, 1, $J = 2.07$, 8.59 Hz, 6-ArH), 6.95 (d, 1, $J = 8.63$ Hz, 5-ArH), 4.09 (t, 2, $J = 6.49$ Hz, OCH_2), 2.75 – 2.00 (quint, 2, OCH_2CH_2), 1.70 – 1.10 (m, 14, $7CH_2$) and 0.88 (t, 3, $J = 6.41$ Hz, CH_3). The remaining acids were prepared either by a Grignard reaction on the bromide 13 or by hydrolysis of the nitrile 14 using the following typical procedures:

4-Decyloxy-3-fluorobenzoic Acid, 8 ($R{=}C_{10}H_{21}$, A=F, B=H): A mixture of the bromide 13 (40.0 g, 0.12 mole) and bromopropane (14.8 g, 0.12 mole) was added dropwise to a stirred mixture of Mg (7.2 g, 0.3 mole) in anhyd Et_2O (60 ml) under a N_2 atmosphere. Warming was necessary to initiate the reaction which later become vigorous enough to require cooling. After completion of the addition, the reaction mixture was refluxed for 1 hr and cooled to – 10°. Dry CO_2 gas was bubbled through this mixture for 2 hr and the resulting thick liquid poured with stirring into ice cold 1*N* HCl. The resulting precipitate was extracted into Et_2O (2 × 300 ml), washed with H_2O, dried, filtered and the filtrate rotovaped to give 35.0 g (98.0%) of the crude acid. Three recrystallizations of this material from abs EtOH gave 22.0 g (61.6%) of the purified acid 8: IR (Nujol) 3200–2200 (broad acid OH), 1680 (str but broadened and split, CO_2H), 1615 (str Ar) and 1590 cm^{-1} (med, Ar) and NMR (DMSO-d_6) δ7.75 (d, 1, $J = 8.59$ Hz, 6-ArH), 7.76 (dd, 1, $J = 2.03$, 11.88 Hz, 2-ArH), 7.25 (d, 1, $J = 8.54$ Hz, 5-ArH), 4.11 (t, 2, $J = 6.43$ Hz, OCH_2), 1.75 (quint, 2, $J = 6.82$ Hz, OCH_2CH_2), 1.50 – 1.15 (m, 14, $7CH_2$) and 0.85 (t, 3, $J = 6.37$ Hz, CH_3).

4-Decyloxy-3-methylbenzoic Acid, 8 ($R{=}C_{10}H_{21}$, A=Me, B=H): A mixture of the nitrile 14 (5.71 g = 0.021 mole) and 70 ml HOAc in 70 ml 50% H_2SO_4 was refluxed for 24 hr, poured into ice and extracted twice with CH_2Cl_2. The organic layer was washed with H_2O, dried and the filtrate rotovaped to give 6.4 g of a white solid. This material was recrystallized from abs EtOH to give 4.11 g (67.3%) of the purified acid 8: TLC ($CHCl_3$) $R_f = 0.04$; IR (Nujol) 3000 (br, acid OH) 1680 (str, CO_2H), 1610 and 1500 cm^{-1} (str Ar) and ^1H NMR: ($CDCl_3$-DMSO) δ7.84 (d, 1, $J = 8.79$ Hz, 6-ArH) 7.80 (s, 1, 2-ArH), 6.83 (d, 1, $J = 8.43$ Hz, 5-ArH), 4.02 (t, 2, $J = 6.26$ Hz, OCH_2), 2.23 (s, 3, ArMe), 1.82 (quint, 2, $J = 6.96$ Hz, OCH_2CH_2), 1.59 – 1.20 (m, 14, $7CH_2$) and 0.88 (t, 3, $J = 6.26$ Hz, CH_3).

The 2-isomer was prepared in the same manner:

4-Decyloxy-2-methylbenzoic Acid, 8 ($R{=}C_{10}H_{21}$, A=H, B=Me): 28.2% recrystallized from CH_3CN: TLC ($CHCl_3$) $R_f = 0.05$; IR (Nujol) 3400 (br, acid OH), 1665 (str, CO_2H), 1600 and 1500 cm^{-1} (str Ar) and ^1H NMR δ7.92 (d, 1, $J = 9.37$ Hz, 6-ArH), 6.79 – 6.76 (m, 2, 3- and 5-ArH), 4.03 (t, 2, $J = 6.37$ Hz, $ArOCH_2$), 2.58 (s, 3, ArMe), 1.90 – 1.71 (m, 2, OCH_2CH_2), 1.59 – 1.20 (m, 14, $7CH_2$) and 0.89 (t, 3, $J = 5.31$ Hz,

CH_3). A better yield (41.6%) of this acid was obtained using the Grignard reaction with hexane as the recrystallizing solvent.

Phenylbenzoates 1 and Phenylthiobenzoates 2

These esters/thioesters were prepared using the carbodiimide method as previously described.[19] Purification was by recrystallization from abs EtOH and if necessary by flash chromatography on silica gel using hexane-CH_2Cl_2 mixtures as the eluting solvent. Transition temperatures are given in Tables II–IV. ^{1}H NMR spectra were consistent with structures agreeing with spectra observed for the lateral substituted intermediates and the trends observed for the parent compounds. The aliphatic protons beyond the α-protons all had the following chemical shifts: δ2.00 – 1.70 (m, $ArOCH_2CH_2$), 1.70 – 1.55 ($ArCH_2CH_2$), 1.55 – 1.20 (m, remaining CH_2) and 0.88 (t, CH_3). Protons on the two benzene rings were easily differentiated by the influence of the lateral substituent. This was especially true for the lateral fluorine esters which often showed doublet of doublet sets for the protons on the fluorine ring and a large coupling constant for the proton ortho to the fluorine atom as shown by the following examples: compound 1b ($R{=}C_{10}H_{21}$, B=F, $Y{=}C_{10}$) δ8.03 (dd, 2, J = 8.58, 8.79 Hz, ArH ortho to CO_2Ar), 7.21 (d, 2, J = 8.5 Hz, ArH ortho to C_{10}), 7.10 (d, 2, J = 8.42 Hz, ArH ortho to OCOAr), 6.76 (dd, 1, J = 2.48, 8.87 Hz, ArH ortho to OR and H), 6.67 (dd, 1, J = 2.34, 12.67, ArH ortho to OR and F), 4.01 (t, 2, J = 6.45 Hz, OCH_2), 2.61 (t, 2, J = 7.58 Hz, $ArCH_2$), compound 2 ($R{=}C_{10}H_{21}$, A=H, B=F and $Y{=}C_{10}H_{21}$), δ7.89 (dd, 2, J = 8.46 and 8.75 Hz, ArH ortho to CO_2Ar), 7.41 (d, 2, J = 8.06 Hz, ArH ortho to S), 7.26 (d, 2, J = 7.41 Hz, ArH ortho to C_{10}), 7.37 (dd, 1, J = 8.87, 10.0 Hz, ArH ortho to OC_{10}), 6.66 (d, 1, J = 12.82 Hz, ArH ortho to F), 4.00 (t, 2, J = 6.04 Hz, OCH_2), and 2.64 (t, 2, J = 7.88 Hz, $ArCH_2$, compound 1a (A=F, $Y{=}C_{10}H_{21}$) δ7.95 (d,1, J = 9.36 Hz, ArH ortho to CO_2Ar), 7.89 (dd, 1, J = 2.34, 13.69 Hz, ArH ortho to F), 7.22 (d, 2, J = 8.51 Hz, ArH ortho to C_{10}), 7.09 (d, 2, J = 8.71 Hz, ArH ortho to OCOAr), 6.70 (d, 1, J = 6.60 Hz, ArH meta to F), 4.11 (t, 2, J = 6.60 Hz, $ArOCH_2$) and 2.62 (t, 2, J = 7.70 Hz, $ArCH_2$) and compound 1a (A=F, $Y{=}OC_{10}H_{21}$) δ7.94 (d, 1, J = 9.08 Hz, ArH ortho to CO_2Ar), 7.88 (dd, 1, J = 2.57, 13.55 Hz, ArH ortho to F), 7.09 (d, 2, J = 8.95 Hz, ArH ortho to OCOAr), 7.00 (d, 1, J = 8.51 Hz, ArH meta to F), 6.92 (d, 2, J = 9.08 Hz, ArH ortho to OC_{10}), 4.11 (t, 2, J = 6.53 Hz, $ArFOCH_2$) and 3.95 (t, 2, J = 6.53 Hz, $ArOCH_2$).

Acknowledgement

This material is based on work supported in part by the National Science Foundation—Solid State Chemistry Grants DMR81-15544, DMR83-09739, DMR85-15221 and DMR88-18561 and ALCOM-STC DMR89-20147. Contributions made to the synthesis and characterization of these materials by C. Citano, R. Dollinger, P. Greer, W. Jones, J. Paulin, W. Saupe, B. Williams and B. Ziemnicka are acknowledged. We thank the Chemistry Department for the use of their NMR instrument and ARPA National Center for Intergated Photonic Technology Contract MDA972-90C-0037 for financial support for the Gemini 200 MHz instrument.

References

1. G. W. Gray and B. Jones, *J. Chem Soc.*, 2556 (1954).
2. G. W. Gray and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, **75**, 109 (1981).

3. R. Eidenschink, *Mol. Cryst. Liq. Cyst.*, **123**, 57 (1985).
4. G. W. Gray, D. Lacey, J. E. Stanton and K. J. Toyne, *Liq. Cryst.*, **1**, 407 (1986).
5. G. W. Gray, C. Hogg and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **67**, 1 (1981).
6. D. G. McDonnell, E. P. Raynes and R. A. Smith, *Mol. Cryst. Liq. Cryst.*, **123**, 169 (1985).
7. J. E. Fearon, G. W. Gray, A. D. Ifill and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **124**, 89 (1985).
8. G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *J. Chem Soc.*, **PT II**, 2041 (1989).
9. M. E. Neubert, S. S. Keast, M. C. Ezenyilimba, C. A. Hanlon and W. C. Jones, *Mol. Cryst. Liq. Cryst.*, (in press, 1993).
10. M. C. Ezenyilimba, Kent State University, M. S. Thesis (1990).
11. M. F. Nabor, H. T. Nguyen, C. Destrade, J. P. Marcerou and R. J. Twieg, *Liq. Cryst.*, **10**, 785 (1991).
12. J. S. DuBois, A. Zann and A. Béguin, *Mol. Cryst. Liq. Cryst.*, **42**, 139 (1977).
13. D. Coates, *Liq. Cryst.*, **2**, 423 (1987).
14. T. Gunjima, Y. Nakogawa and Y. Masuda, *Rep. Res. Lab.*, Asahi Glass Co., Ltd., **32**, 87 (1982).
15. V. S. Bezborodov, V. I. Lapanik, P. V. Adomenas and R. Sirutkaitis, *Liq. Cryst.*, **11**, 373 (1992).
16. S. M. Kelly, *Helv. Chim. Acta*, **67**, 1572 (1984).
17. B. K. Sadashiva, *Mol. Cryst. Liq. Cryst.*, **53**, 253 (1979).
18. D. Coates and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **37**, 249 (1976).
19. M. E. Neubert, P. J. Wildman, M. J. Zawaski, C. A. Hanlon, T. L. Benyo and A. de Vries, *Mol. Cryst. Liq. Cryst.*, **145**, 111 (1988).
20. M. E. Neubert, M. R. Jirousek and C. A. Hanlon, *Mol. Cryst. Liq. Cryst.*, **133**, 223 (1986).
21. M. E. Neubert, B. Ziemnicka-Merchant, M. R. Jirousek, S. J. Laskos, Jr., D. Leonhardt and R. B. Sharma, *Mol. Cryst. Liq. Cryst.*, **154**, 209 (1988).
22. M. E. Neubert, K. Leung, M. R. Jirousek, M. C. Ezenyilimba, S. Sabol-Keast, B. Ziemnicka-Merchant and R. B. Sharma, *Mol. Cryst. Liq. Cryst.*, **197**, 21 (1991).
23. M. E. Neubert, C. M. Citano, M. C. Ezenyilimba, M. R. Jirousek, S. Sabol-Keast and R. B. Sharma, *Mol. Cryst. Liq. Cryst.*, **206**, 103 (1990).
24. M. E. Neubert, S. S. Keast, M. C. Ezenyilimba, P. B. Greer, W. C. Jones, D. Leonhardt and I. Shenouda, "The Effect of Carbonyl Containing Chains on Mesomorphic Properties in 4,4′-Disubstituted Phenylbenzoats and Thiobenzoates. 8." *Mol. Cryst. Liq. Cryst.*, (in press, 1993).
25. D. Demus, H. Demus and H. Zaschke, "Flüssige Kristalle in Tabellen" (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974), p. 59.
26. M. E. Neubert and A. de Vries, *Mol. Cryst. Liq. Cryst.*, **145**, 1 (1987).
27. T. T. Blair, M. E. Neubert, M. Tsai and C. Tsai, *J. Phys. Chem. Ref.*, **20**, 189 (1991).
28. M. E. Neubert, F. C. Herlinger, M. R. Jirousek and A. De Vries, *Mol. Cryst. Liq. Cryst.*, **139**, 299 (1986).
29. M. E. Neubert, R. E. Cline, M. J. Zawaski, P. J. Wildman and A. Ekachai, *Mol. Crtyst. Liq. Cryst.*, **76**, 43 (1981).
30. M. E. Neubert, K. Leung, S. J. Laskos, Jr., M. C. Ezenyilimba, M. R. Jirousek, D. Leonhardt, B. A. Williams and B. Ziemnicka-Merchant, *Mol. Cryst. Liq. Cryst.*, **166**, 181 (1989).
31. W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).
32. M. E. Neubert and L. J. Maurer, *Mol. Cryst. Liq. Cryst.*, **43**, 313 (1977).
33. D. Demus and L. Richter, "Textures of Liquid Crystals" (Verlag Chemie, NY, 1978).
34. G. W. Gray and J. W. Goodby, "Smectic Liquid Crystal Textures and Structures" (Leonard Hill, Glasgow, 1984).