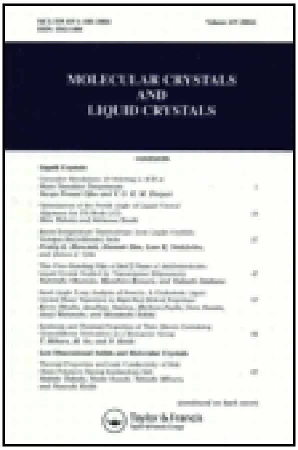

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The Effect of Methyl Group Position in Branched Alkyl Chains on the Thiolic End of 4,4′-Disubstituted Thiophenylbenzoates on Mesomorphic Properties and Some Optically Active Analogs as New Ferroelectric Liquid Crystals

Mary E. Neubert [a] , Ktherine Leung [a b] , Stanley J. Laskos Jr. [a c] , Matthew C. Ezenyilimba [a] , M. R. Jirousek [a d] , Darrin Leonhardt [a] , Brian A. Williams [a] & Barbara Ziemnicka-merchant [a e]

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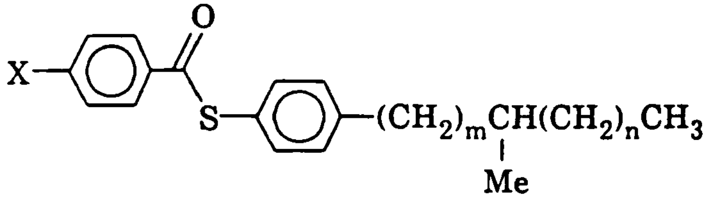
The Effect of Methyl Group Position in Branched Alkyl Chains on the Thiolic End of 4,4′-Disubstituted Thiophenylbenzoates on Mesomorphic Properties and Some Optically Active Analogs as New Ferroelectric Liquid Crystals†

MARY E. NEUBERT, KATHERINE LEUNG,‡ STANLEY J. LASKOS, JR.,‡ MATTHEW C. EZENYILIMBA, M. R. JIROUSEK,‡ DARRIN LEONHARDT, BRIAN A. WILLIAMS and BARBARA ZIEMNICKA-MERCHANT‡

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

(*Received March 18, 1988*)

The effect of the methyl group position in the branched alkyl chains of the thioesters



where X = C_8H_7, RO, and C_9CO_2; m = 1–3 and n = 0–2 on mesomorphic properties is reported. These thioesters were prepared by esterification of the appropriate acid or acid chloride with the branched chain thiol. Synthesis of the thiols was via a Friedel-Crafts acylation of benzene with the branched alkyl chain acid chloride, catalytic reduction, sulfonation in sulfuric acid, conversion to the sulfonyl chloride and reduction to the thiol with zinc and sulfuric acid. Transition temperatures and types of mesophases were determined using hot-stage polarizing microscopy. The same types of mesophases observed in the analogous straight chain thioesters were also found in these compounds, including two unidentified smectic phases like those now believed to be S_G and S_J phases in the straight chain series. Branching always lowered the clearing temperatures but not always the melting ones. Clearing temperatures do not always increase with increasing distance between the methyl group and the benzene ring as was reported earlier for branched chain phenylbenzoates with a four carbon backbone. Branching

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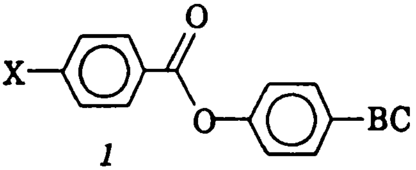
enhances the S_C phase, but the S_A phase is less favored although it does not completely disappear. The nematic phase is enhanced the most when the branch is on the second carbon atom and the least when it is on the third one. Additional comparisons to the straight chain thioesters are made as well as the effect of branching on the phenolic end of the analogous phenylbenzoates.

An optically active isomer of the series with the branching methyl group in the 3-position was also prepared for possible use in ferroelectric liquid crystal displays. Compounds having various combinations of cholesteric, smectic A, and chiral S_C phases, some with the S_C^* phase near room temperature, were obtained.

INTRODUCTION

The observance of improved mesomorphic properties and N, S_A, and S_C phases in branched chain (BC) phenylbenzoates *1*[1]



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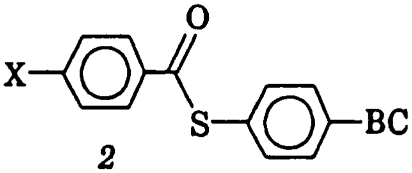
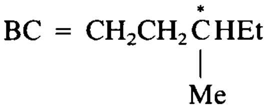
suggested that the analogous thioesters *2*



2

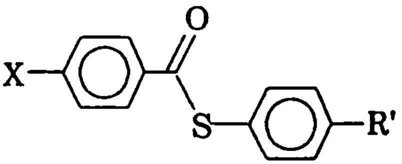
should also be studied since earlier work on straight chain (SC) thioesters indicated that these have more smectic phases with wider temperature ranges than the esters.[2] If these also occurred in the BC thioesters, more smectic phases on which the effect of a methyl branch on the thiolic end on mesomorphic properties could be studied in addition to studying this effect on another series. Also, since some of the SC thioesters have a S_C phase close to room temperature (for example $\bar{7}$S5 at 36.9°),[2] it seemed likely that the temperature lowering effect often observed for BC compounds would give a thioester with a room temperature smectic C phase. If S_A and N phases were observed as well, this would give the desired combination for a ferroelectric smectic C phase if the branched chain was optically active rather than racemic. Mesomorphic properties for only a few BC thiophenylbenzoates have been reported but these are all dialkoxy compounds.[3,4] Thus, it was necessary for us to prepare a variety of homologs to determine mesomorphic properties and trends.

The synthesis of optically active thioesters is limited by the availability of optically active starting materials which can be used to prepare these thioesters. The easiest one to prepare is the analog where



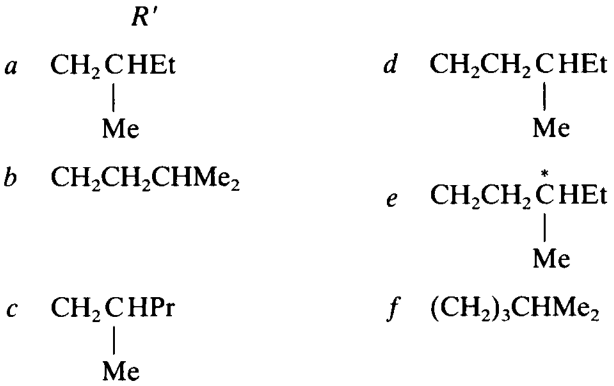
$$\mathrm{BC} = \mathrm{CH_2CH_2}\underset{\substack{|\\ \mathrm{Me}}}{\overset{*}{\mathrm{C}}}\mathrm{HEt}$$

Thus, we synthesized the following BC thioesters *3–5*:



	X
3	R
4	RO
5	C_9CO_2

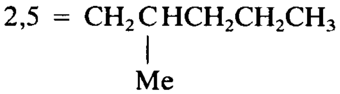
with



	R'		
a	$\mathrm{CH_2}\underset{\substack{|\\ \mathrm{Me}}}{\mathrm{C}}\mathrm{HEt}$	*d*	$\mathrm{CH_2CH_2}\underset{\substack{|\\ \mathrm{Me}}}{\mathrm{C}}\mathrm{HEt}$
b	$\mathrm{CH_2CH_2CHMe_2}$	*e*	$\mathrm{CH_2CH_2}\underset{\substack{|\\ \mathrm{Me}}}{\overset{*}{\mathrm{C}}}\mathrm{HEt}$
c	$\mathrm{CH_2}\underset{\substack{|\\ \mathrm{Me}}}{\mathrm{C}}\mathrm{HPr}$	*f*	$\mathrm{(CH_2)_3CHMe_2}$

and determined their mesomorphic properties. These were compared with those reported previously for the SC thioesters[2] and the BC phenylbenzoates.[1,5-7] The 1-methyl BC thioesters were not prepared since earlier results indicated these would probably not have good mesomorphic properties whereas more work would be needed to prepare them. However, our current results suggest that better properties might be found than anticipated so that synthesis of some of these compounds is now in progess.

To simplify our discussion, the following abbreviations will be used for the branched chains:



$$2{,}5 = \mathrm{CH_2}\underset{\substack{|\\ \mathrm{Me}}}{\mathrm{C}}\mathrm{HCH_2CH_2CH_3}$$

2-indicates the position of the branching methyl group
5-indicates the number of carbon atoms in the backbone of the BC alkyl group
BC = branched chain
SC = straight chain
BB = backbone

Abbreviations used for mesophases are given in the Experimental Section.

SYNTHESIS

These BC thioesters were prepared by esterification of the BC thiol *7* (Scheme 1) with the appropriate acid or acid chloride *6* using the carbodiimide or acid chloride/Et_3N methods previously reported[8] and purified by recrystallization from absolute ethanol. Purified yields were in the range of 45–75%.

The BC thiols *7* were synthesized from the BC sulfonates *3* by the method reported earlier for the synthesis of sodium 4-decylbenzene-sulfonate[9] (Scheme 1). Purified yields and boiling points for these thiols and the intermediate sulfonyl chlorides are given in Table I. Yields are not given for the sulfonates since these were not always purified before being converted to the sulfonyl chloride. If too much inorganic salt was present in the sulfonates, additional phosphoryl chloride was used to obtain a stirrable mix. Yields were, of course, lower for the crude salts. These salts could be recrystallized from water except when R′ = $(CH_2)_3CHMe_2$ which was recrystallized from H_2O—EtOH. Since these sulfonates are soaps, foaming occurs and care must be taken to use a large enough flask to avoid material loss. The optically active thiol was prepared in the same manner from (+)-3-methylpentylbenzene which was synthesized from (−)-2-methylbutanol by the method

SCHEME 1

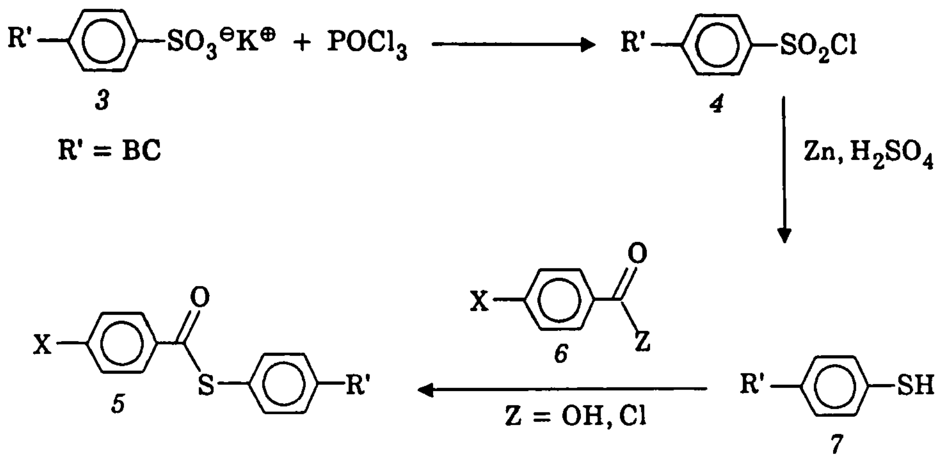
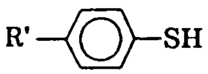


TABLE I

Purified Yields and Boiling Points (°C) for R'—



R'		X	Yield (%)	bp (mm)
EtCHCH$_2$-	(±)	SO_2Cl	81.0	170 (6)
Me		SH	89.4	100-103 (0.8)
Me$_2$CH(CH$_2$)-	(±)	SO_2Cl	71.0	124 (1.1)
		SH	68.1	86-90 (0.5)
PrCHCH$_2$-	(±)	SO_2Cl	53.1	145 (1.5)
Me		SH	90.4	not recorded
EtCH(CH$_2$)$_2$	(±)	SO_2Cl	78.5	150 (2.0)
|	(+)	SO_2Cl	88.5	138 (0.8)
Me	(±)	SH	89.4	90 (0.1)
	(+)	SH	92.2	110 (1.5)
Me$_2$CH(CH$_2$)$_3$-	(±)	SO_2Cl	61.5	135 (0.4)
		SH	90.4	120 (1.2)

described earlier.[1] All thiols were checked for purity by TLC and GLC and found to contain only one component. Optical rotation for the sulfonyl chloride was +12.7° at 23° and +14.9° at 24° for the thiol. Optical purity was not determined.

NMR spectra were obtained for all compounds prepared in this work. Spectra for the sulfonyl chlorides and thiols were the same as those reported for the SC compounds[9] except for the aliphatic proton region. NMR data for this region for the BC C_5 BB phenols were reported earlier[1]; spectra for the thiols were identical. Spectra for this region in the BC C_4 BB thiols are given in Figure 1 which also shows the SH peak at 3.18δ. NMR spectra for the BC thioesters were the same as for the analogous SC thioesters except for this aliphatic proton region. A comparison of spectra for all four R/RO series of SC thioesters is given in Figure 2.

Mesomorphic Properties

Transition temperatures for these BC thioesters as determined by hot-stage microscopy are presented in Tables II–V. When X is an alkyl group, series *3*, near room temperature monotropic N phases predominated although a low temperature monotropic S_A phase occurred when R' = 3,5 *3d* (Table II). When X = RO, series *4*, more mesophases were found, as expected, with N, S_A, S_C, and at least one more highly ordered S phase occurring in a variety of combinations (Table

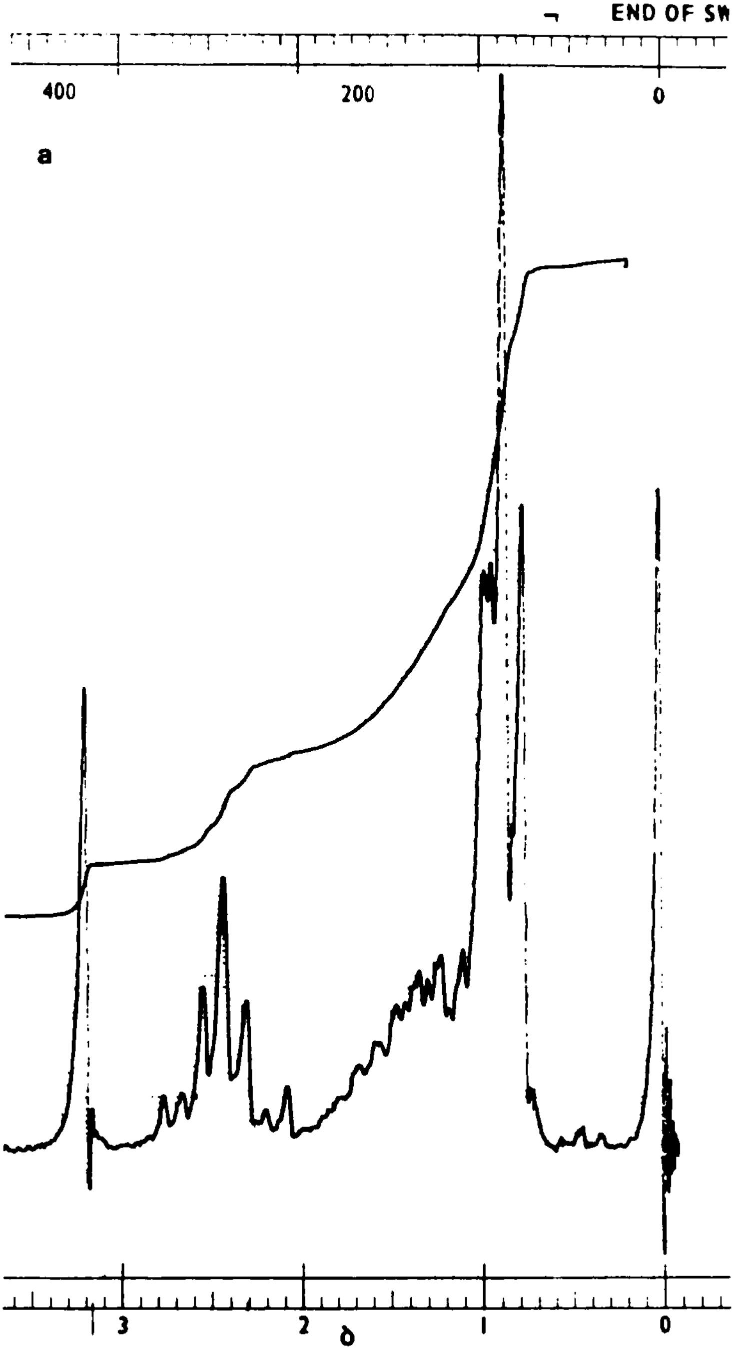
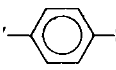


FIGURE 1 NMR spectra for aliphatic proton region of R'—  —SH

a. $R'{=}CH_2\underset{\underset{Me}{|}}{C}HEt$

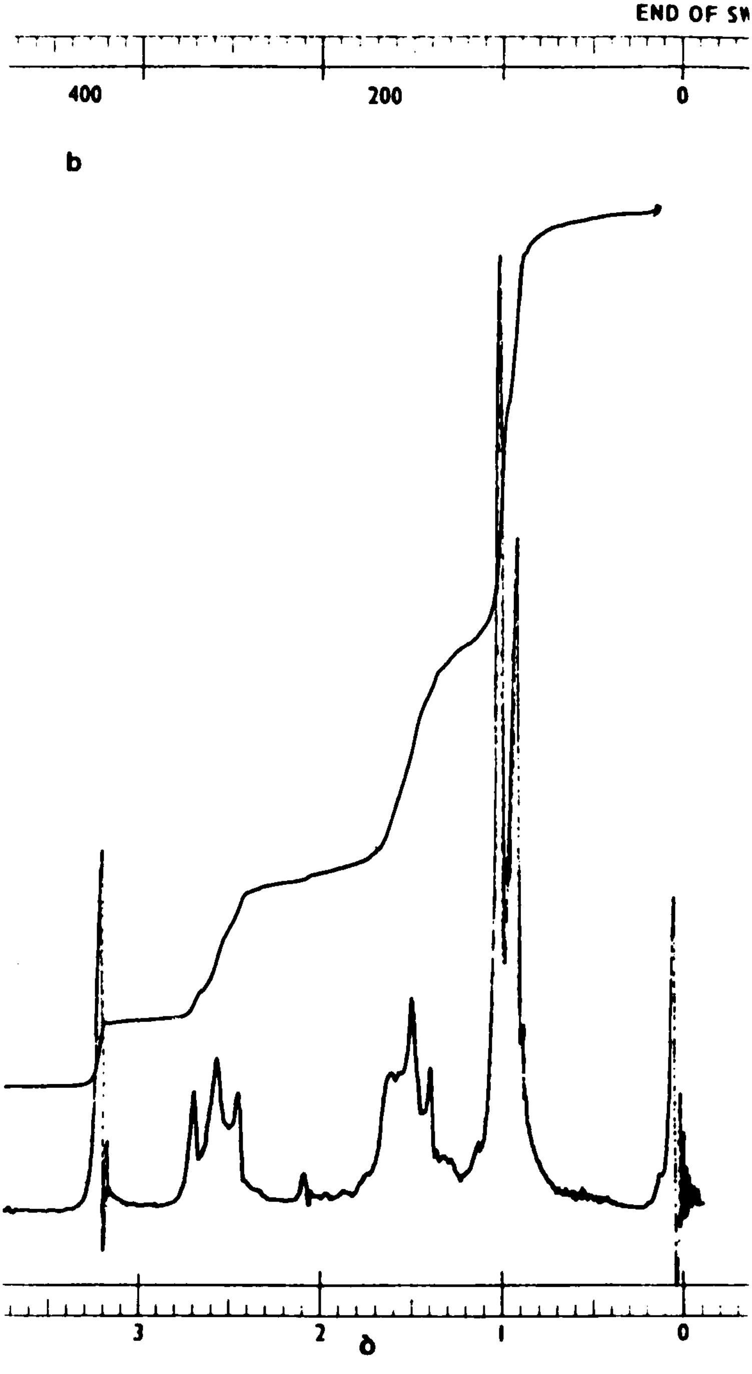


FIGURE 1 (*continued*)

b. R′=$CH_2CH_2CHMe_2$

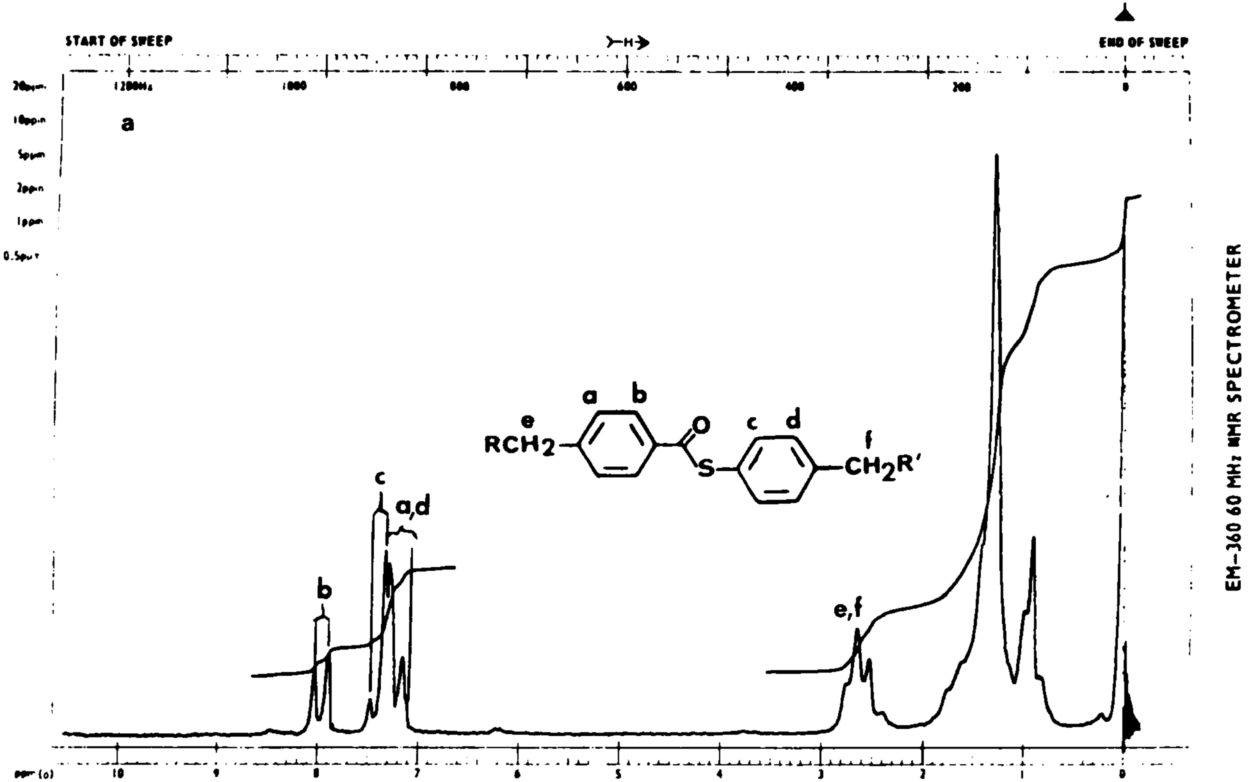
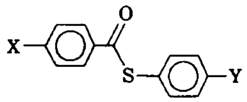


FIGURE 2 NMR spectra for



a. X = Y = alkyl;

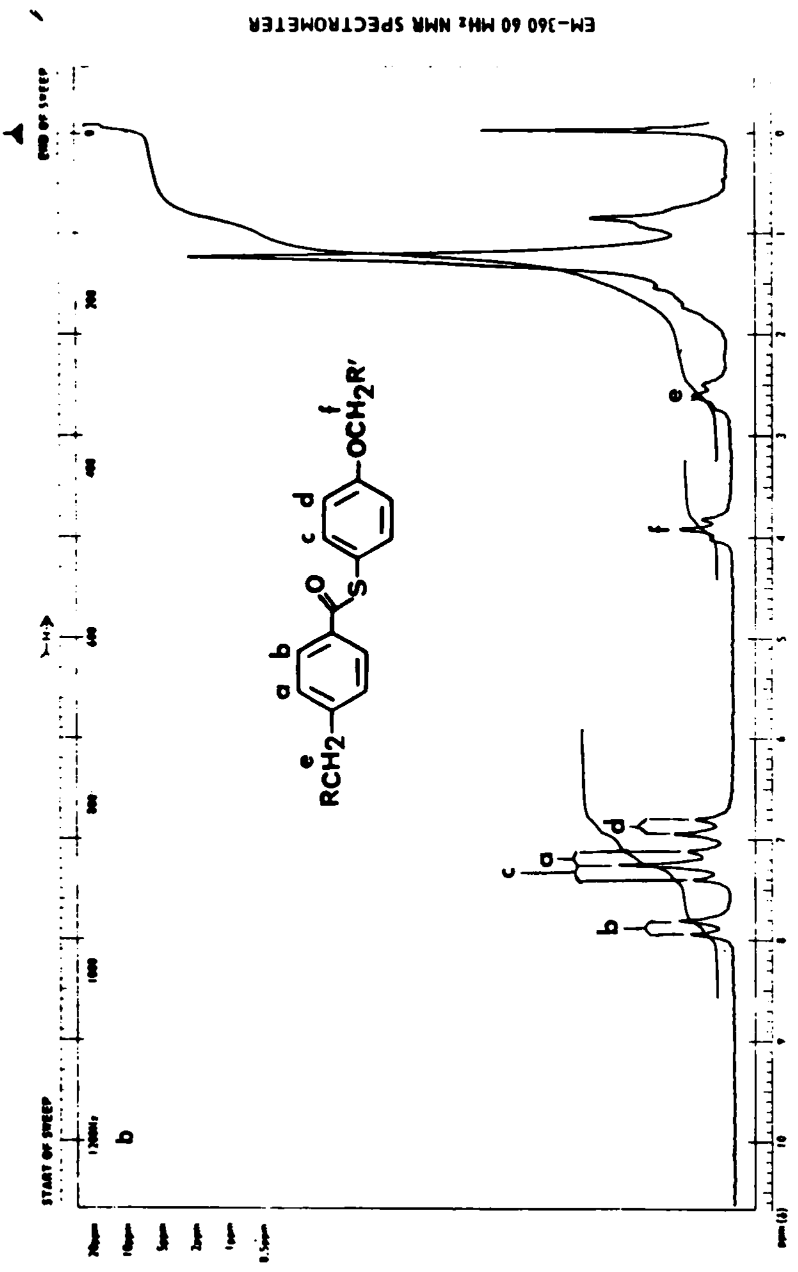


FIGURE 2 (*continued*)

b. X = alkyl, Y = alkoxy;

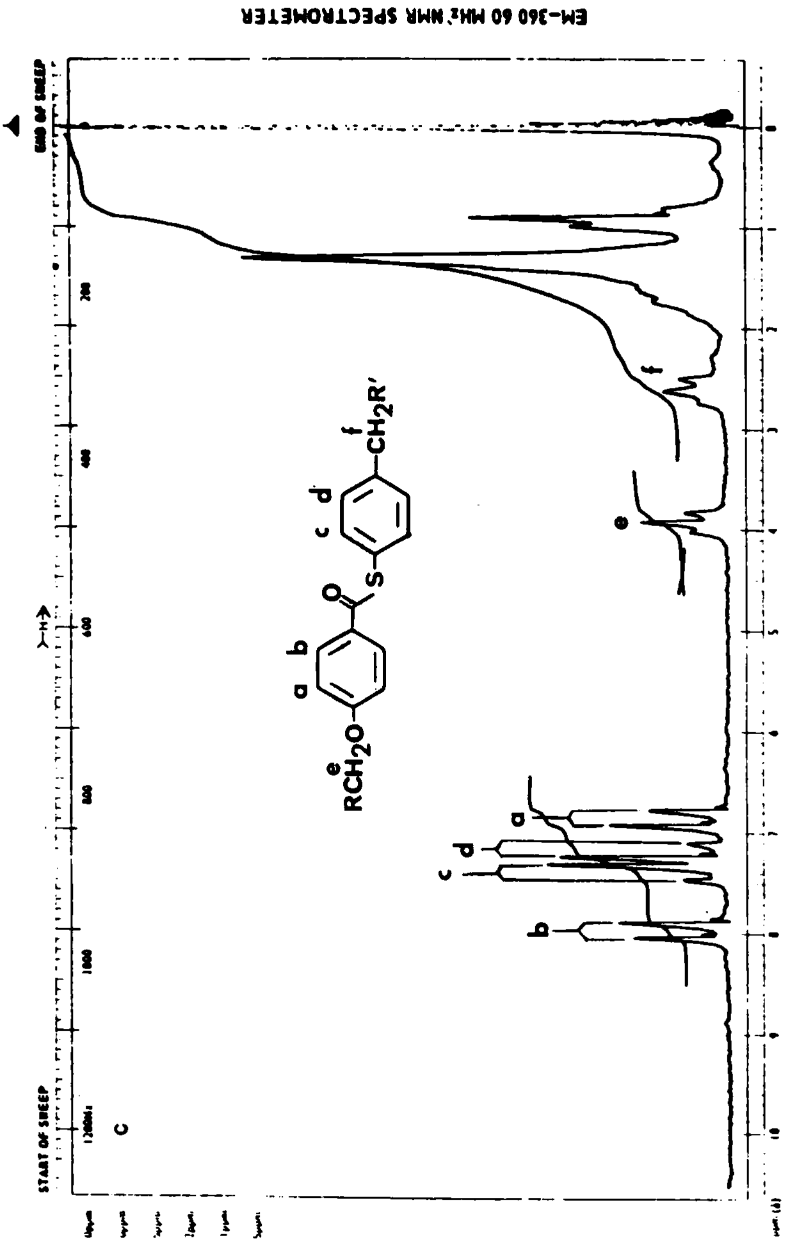


FIGURE 2 (continued)

c. X = alkoxy, Y = alkyl

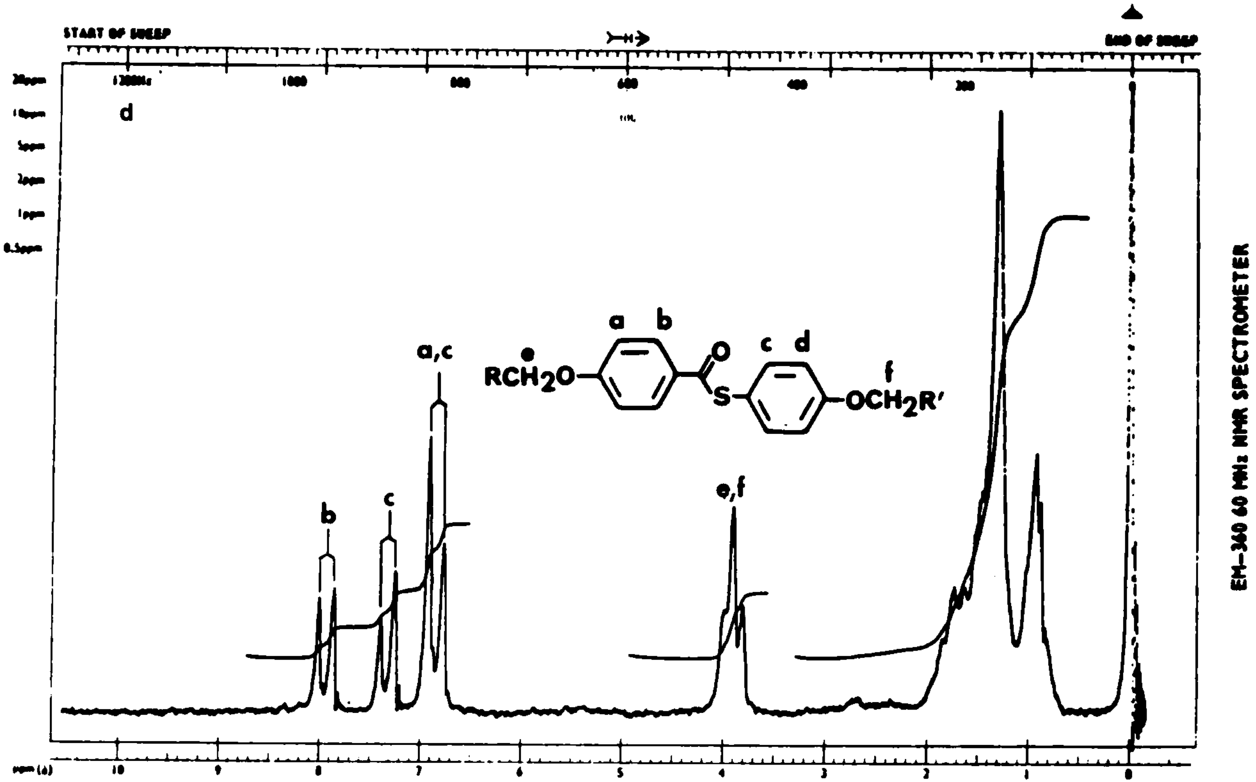


FIGURE 2 (*continued*)

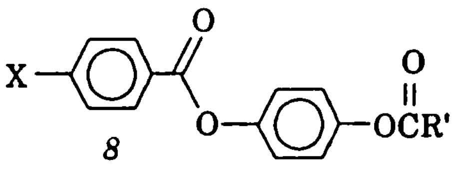
d. X = Y = alkyl

III). All these phases were observed in the 3,5 series (*4d*) and therefore an optical isomer of many of the homologs were prepared (Table IV). Several of these were found to contain a Ch—S_A—S_C^* sequence with the longer homologs having only S_A–S_C^* transitions. Although some of these S_C^* phases occurred at 35–38°, none were at room temperature except on cooling. However, mixtures of some of these homologs should give a RT S_C^*.† When X = C_9CO_2, series *5*, no S_A phases were observed although all the remaining mesophases were (Table V).

The melting temperature for the R = C_{11} homolog in the 3,5 series *4e* could not be obtained from a cooled sample of this material making it difficult to determine if the S phase was monotropic or enantiotropic. Both DSC and microscopy showed a melting temperature of ~47° for fresh crystals suggesting that this phase is monotropic. Fresh crystals, of course, are not always identical to cooled ones which might give a different melting temperature. The R = C_8 homolog of the 3,5 alkyl series *3e* showed an interesting melting behavior. Crystals obtained by recrystallization from ethanol (fresh) melted to the isotropic liquid at 50.2°. On cooling this liquid, a Ch phase was observed which on reheating gave the isotropic liquid at 46.3°. Cooling the Ch phase gave fine crystals converted to larger crystals before the Ch phase was formed. These melted to the isotropic liquid at the same temperature as the fresh crystals. Thus these transitions can be diagrammed as follows:

$$\begin{tikzcd}
C_1 \arrow[r, "50.2^\circ"] & I \arrow[d, leftrightarrow, "46.3^\circ"] \\
C_2 \arrow[u] \arrow[r, shift left, "35.0^\circ"] \arrow[r, leftarrow, shift right, "\sim 21^\circ"'] & Ch
\end{tikzcd}$$

Identification of the unknown biaxial smectic phases by microscopy was not possible. In many cases, the texture of the growth of the S_3‡ from the S_C phase was similar to that observed for growth of the S_B phase in the dialkoxyphenylbenzoate, $\overline{9}\text{O}\overline{4}$[10] (Figure 3).§‖ Growth of the S_B phase in this ester occurred as a front of spears (Figure 3a) or lines moving across the fans. When growth was completed, a mosaic texture was observed (Figure 3b). Similar textures were also reported in the growth of the S_B phase from the S_C phase in the acyloxy esters *8*.[8]



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†Mixture studies are being done by Hughes Laboratories.

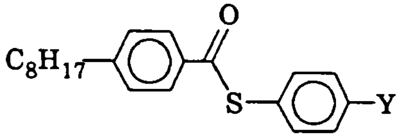
‡Used to designate all of the S phases which occur directly below a S_C phase.

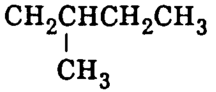
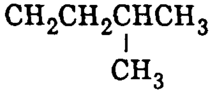
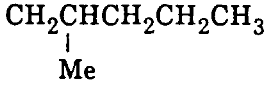
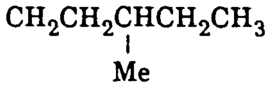
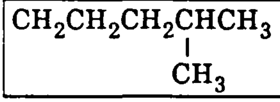
§Although this particular homolog was not reported in Reference 10, data for a variety of homologs such as $\overline{10\text{O}5}$ were given. It is unlikely that this smectic phase differs from the S_B phase observed in these homologs. However, a check of the textures seen in $\overline{10\text{O}5}$ showed a typical S_C–S_B transition from S_C fans through transition bars to S_B fans.

‖The abbreviation used here is the same system as used by Reynolds for the thioesters.[11]

TABLE II

Transition Temperatures (°C) for



Y	C	S_A	N	I
 $\mathrm{CH_2\underset{CH_3}{CH}CH_2CH_3}$	3.2		(25.4-25.5)	27.8-30.1
 $\mathrm{CH_2CH_2\underset{CH_3}{CH}CH_3}$	25.4		(25.5-25.7)	52.6-52.9
 $\mathrm{CH_2\underset{Me}{CH}CH_2CH_2CH_3}$	11.1		(31.5-31.7)	34.4-36.2
 $\mathrm{CH_2CH_2\underset{Me}{CH}CH_2CH_3}$	15.3 33.6	(19.4-19.6)[a]	(25.8-25.9)[a]	45.3-46.4 43.4-45.3
 $\mathrm{CH_2CH_2CH_2\underset{CH_3}{CH}CH_3}$	22.7		(34.5)	42.9-43.2

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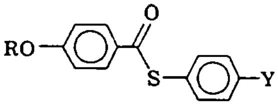
[a] Observation of these mesophases depended on the crystallization temperature.

TABLE III

Transition Temperatures (°C) for



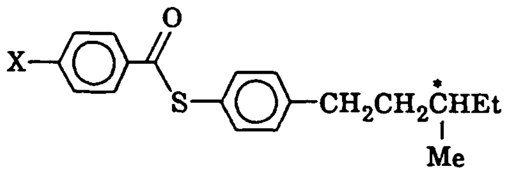
R	C	S	S_C	S_A	N	I
$Y = CH_2CHCH_2CH_3$ Me 2,4						
C_7	22.6		(31.9-32.0)	- -	42.9-44.2	62.1-62.2
C_8	20.3		(43.2-43.3)	- -	51.7-53.0	66.1-66.2
C_9	23.5		(47.8-49.6)	(51.2-52.2)	63.3-65.2	65.2-65.4
C_{10}	30.3		48.1-48.6	52.1-52.7	59.3-59.4	66.9-67.2
C_{12}	26.4		51.9-52.2	53.9-54.8	67.7-66.7	67.3-68.3
$Y = CH_2CH_2CHCH_3$ Me 3,4						
C_6	43.4		(45.7-46.1)	(50.9-51.0)	60.5-62.4	69.1-69.3
C_7	37.5	(45.3-45.5)	47.1-48.1	64.5-64.6	69.3-69.4	71.5-71.7
C_8	30.0	(34.8-35.5)	(55.2-55.3)	57.1-57.4	57.5-57.6	66.3-66.4
C_9	42.5	(43.0-43.5)	59.6-61.0	67.9-68.2	- -	71.4-71.9
C_{10}	24.3	(48.3-48.6)	50.9-53.0	70.4-70.6	- -	74.7-74.9
C_{12}	~22	(52.8-53.1)	55.7-56.6	72.5-72.7	- -	75.4-75.6
$Y = CH_2CHCH_2CH_2CH_3$ Me 2,5						
C_6	8.8		(9.9-10)		32.6-33.5	69.2-69.3
C_7	2.4		(23.2-23.3)		35.8-36.5	65.1-65.2
C_8	39.7 (C_1) 7.3 (C_2)	(0.7-0.8)	(39.2-39.3)	$C_1 \to N$ $C_2 \to C_1 \to N$	46.1-47.2 45.0-46.7	69.3-69.5

R	C	S	S	S_C	S_A	N	I
C_9	23.4			(46.5-46.7)†	(49.4-49.5)†	61.1-63.1	67.7-67.8
C_{10}	5.1		(11.3-11.5)	43.3-44.1	51.4-51.5	59.4-59.5	69.8-69.9
C_{12}	~4		(23.0-23.2)	37.7-40.0	54.1-54.5	67.8-68.0	70.5-70.8
$\mathrm{Y=CH_2CH_2\underset{\underset{Me}{\mid}}{C}HCH_2CH_3}$ 3,5							
C_7	18.6			40.1-40.7	49.9-50.1	51.9-52.1	62.8-62.9
C_8	~5.8		(31.7-31.8)	35.3-35.9	60.6-60.8	64.9-65.0	68.2-68.3
C_9	22.9	(31.5-31.8)	(32.1-32.3)	50.3-51.3	64.5-65.2	67.5-67.7	68.4-68.5
C_{10}	~2.2		37.3-38.2	38.8-38.9	68.4-68.8	- -	71.2-71.4
$\mathrm{Y=CH_2CH_2CH_2\underset{\underset{Me}{\mid}}{C}HCH_3}$ 4,5							
C_6	35.0					54.0-54.1	72.2-72.6
C_7	31.6			(44.8-44.9)	- -	55.9-56.3	67.0-67.3
C_8	19.1		(23.6-23.8)	42.6-44.3	54.6-54.9	61.2-61.3	71.7-71.8
C_9	15		(29.3-29.5)	43.3-44.5	61.5-61.7	66.3-66.4	72.1
C_{10}	10.9		(38.0-38.2)	44.6-46.7	64.9-65.8	71.2-71.4	73.2-73.4
C_{12}	44.9		(48.1-48.5)	65.9-66.5	70.2-70.9	- -	75.6-75.8

† not always seen

TABLE IV

Transition Temperatures (°C) for



X	$[\alpha]_D$	T(°C)	C[a]	S	S	S_C*	S_A	Ch	I
C_8	+5.44	22.5	18.3				(19.4)[b]	(26.0)	46.1-46.8
C_3O	+16.7	22.7	21.1					34.1-35.0	49.0-50.2 46.2-46.3[b]
C_7O	+8.0	23.5	19.1		(~20.5)	40.3-40.9	50.5-50.7	51.4-51.8	63.2-63.3
C_8O	+8.0		6.0		(31.7)	35.3-35.9	60.5-61.1	65.1-65.5	68.3-68.4
C_9O	+11.5	22.7	31.3	(~32.2)	(32.6-32.8)	50.0-50.9	64.8-65.1	67.5-67.6	68.1-68.3
$C_{10}O$	+8.35	23.5	~7.5		37.5-38.0	38.2-38.3	68.9-69.0	--	71.3-71.5
$C_{11}O$	+9.85	22.7	<-16.0		(36.8-37.1)	45.1-46.5[b]	68.7-69.5	--	71.2-71.7
$C_{12}O$	+15.0	23.5	<-20.0		46.0-46.6[c]	46.0-46.2[c]	72.6-72.8	--	74.4-74.6

---

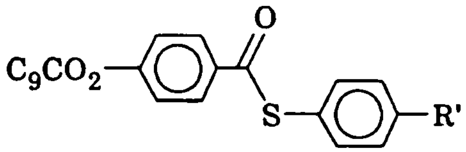
[a] Crystallization temperature on cooling 2°/min.

[b] See discussion in text.

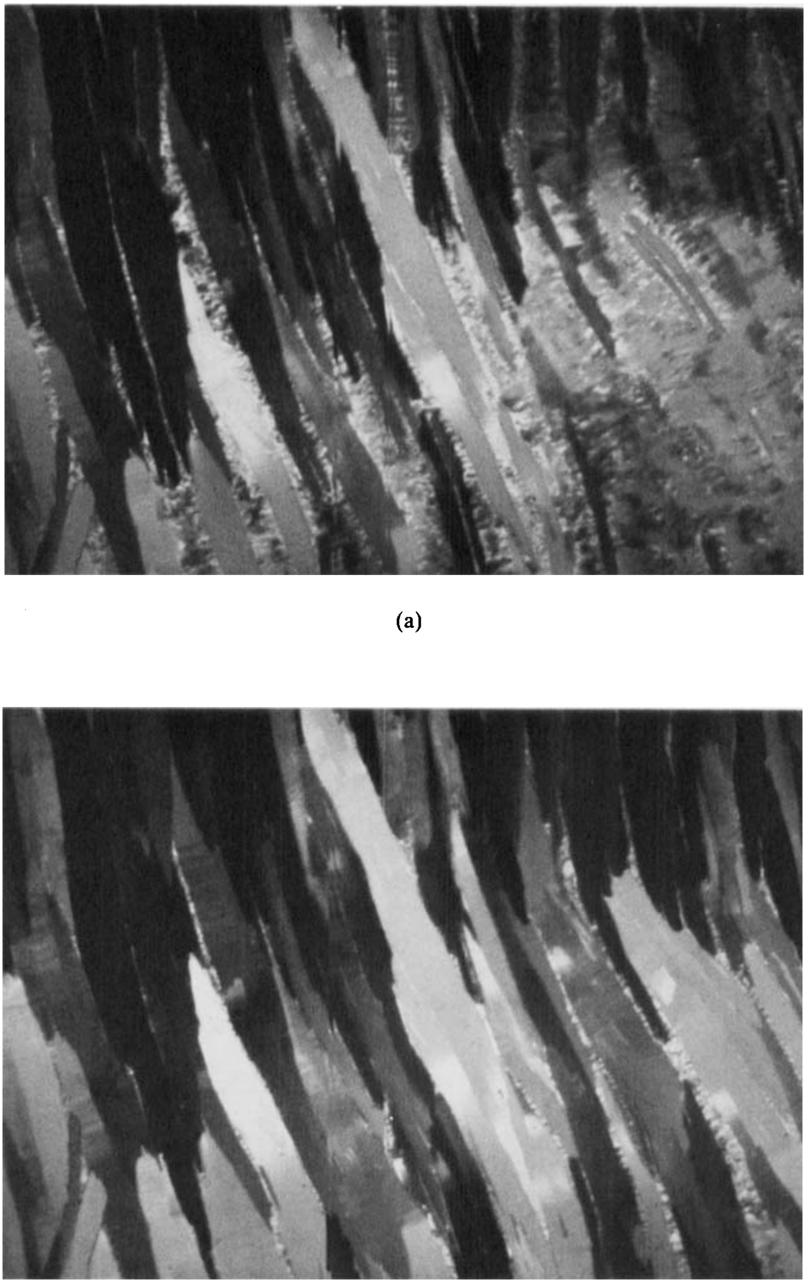
[c] Overlapping transitions. Value under S_C^* obtained by reheating S formed on cooling to S_C^*.

TABLE V

Transition Temperatures (°C) for



R'	C	S	S	S_C	N	I
$CH_2CH_2CH_2CH_2CH_3$	40.3		(52.0-52.2)	(60.3-60.4)	62.4-62.8	79.2-79.6
$CH_2\underset{\substack{\vert\\ Me}}{CH}CH_2CH_3$	31.0			40.4-41.9	45.7-45.9	60.1-60.2
$CH_2CH_2\underset{\substack{\vert\\ Me}}{CH}CH_3$	49.8		(55.6-55.8)	(63.8-64.0)	(65.2-65.4)	65.3-65.9
$CH_2\underset{\substack{\vert\\ Me}}{CH}CH_2CH_2CH_3$	3.7	(18.1-18.4)	(19.4-19.5)	36.0-38.7	45.2-45.3	63.9-62.8
$CH_2CH_2\underset{\substack{\vert\\ Me}}{CH}CH_2CH_3$	25.9		(46.5-46.9)	59.5-60.1	60.8-61.2	62.5-62.6
$CH_2CH_2CH_2\underset{\substack{\vert\\ Me}}{CH}CH_3$	45.9		(47.4-48.0)	(59.8-59.9)	65.0-65.6	67.2-67.3



(a)

(b)

FIGURE 3 Growth of the S_B phase from the S_C phase in $\bar{9}0\bar{4}$. a. Spears of S_B phase growing across the S_C phase. b. Completed S_B phase.

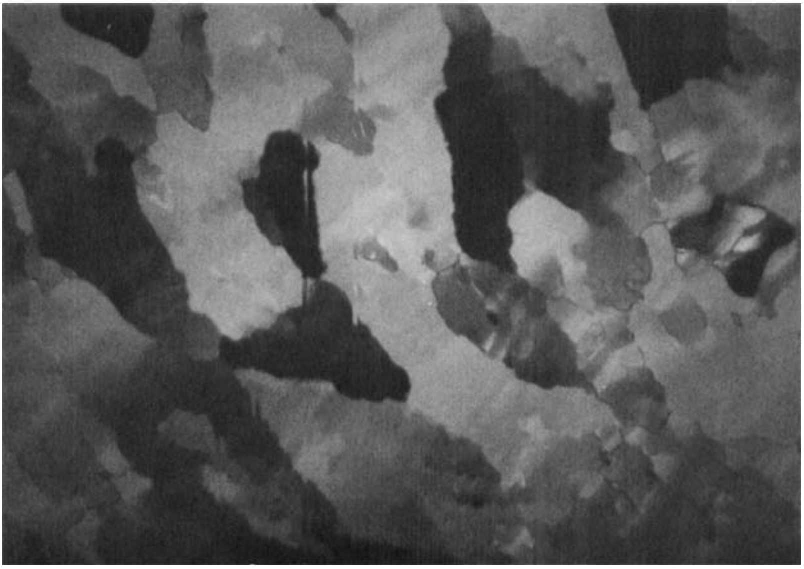
where the S_B phase was confirmed by x-ray crystallography. In other instances, the S_3 phase grew like the S_y phase in $\bar{8}S5$ where mosaic spots appeared (Figure 4a), grew, and coalesced to give a mosaic texture (Figure 4b). Growth of the S_3 phase seems also to vary with the chain length of R. For example, in the 4,5 series *4f*, growth of this phase in the C_8 homolog appeared like that in the S_y phase in $\bar{8}S5$ (Figure 5) but in the C_9 homolog, a front of lines was observed (Figures 6a–c) which yielded a block-like mosaic texture in the S_3 phase (Figure 6c) quite different from that observed in the C_8 homolog (Figure 5c). Growth of this phase in the C_{10} homolog is similar (Figures 7a and b) but yields a spiral mosaic texture (Figure 7c). This raises the question as to whether all these S_3 phases are the same or these textural differences are just variations in textures for the same phase. No homeotropic or schlieren textures were observed in these phases despite repeated attempts to obtain them. However, the lack of a homeotropic texture in a phase below a S_C one does not eliminate the possibility this phase is a S_B one since it is often difficult to obtain this texture in S_B phases which occur below a S_C phase and this is true of some of these phases in the SC thioesters.[12]

Contact mixture studies with the standards $\bar{9}O\bar{4}$ and $\bar{8}S5$ provided inconclusive results since all the smectic phases involved have mosaic textures. A mixture of $\bar{9}O\bar{4}$ with the R = C_{10} homolog of the 4.5 series (*4f*) showed the growth of identical textures for the S_B phase of $\bar{9}O\bar{4}$ and the S phase of the BC thioester (Figure 8) with disappearance of the interface when growth was complete suggesting these two phases are the same. A mixture of $\bar{9}O\bar{4}$ and $\bar{8}S5$ showed the growth of two different textures in the S_B (front of lines) and the S_y (mosaic) phases but the S_B phase becomes more mosaic near the interface so the differences between the two textures are less definite (Figure 9). Limitations to the use of contact mixture studies due to the miscibility of S_B phases with S_G and S_H phases are also well known.[13] Thus, x-ray studies are needed to identify this S_3 phase.

When X = C_9CO_2 (series *5*), the S_3 phase always occurred below a S_C phase which is directly below a N phase. This makes it difficult to obtain a good fan texture, but we were able to obtain one in the 3,4 compound *5b*. Cooling the broken fan texture of the S_C phase (Figure 10a) to the S_3 phase gave lines across the fans which yielded the mosaic-like fan texture shown in Figure 10b. Other areas showed a more obvious mosaic texture as shown in Figure 10c. A schlieren texture could be obtained in the S_C phase but this yielded a mosaic texture on cooling to the S_3 phase. In the corresponding C_5SC thioester, the smectic phase below the S_C phase was identified as a S_B phase based on the observance of a homeotropic texture (not easily obtained) which showed a uniaxial cross. In this series, the cover slip was easily moved as would be expected for a S_B phase. In the BC compounds, the cover slip was difficult to move and no homeotropic texture could be obtained leaving the structure of this S phase unidentified.

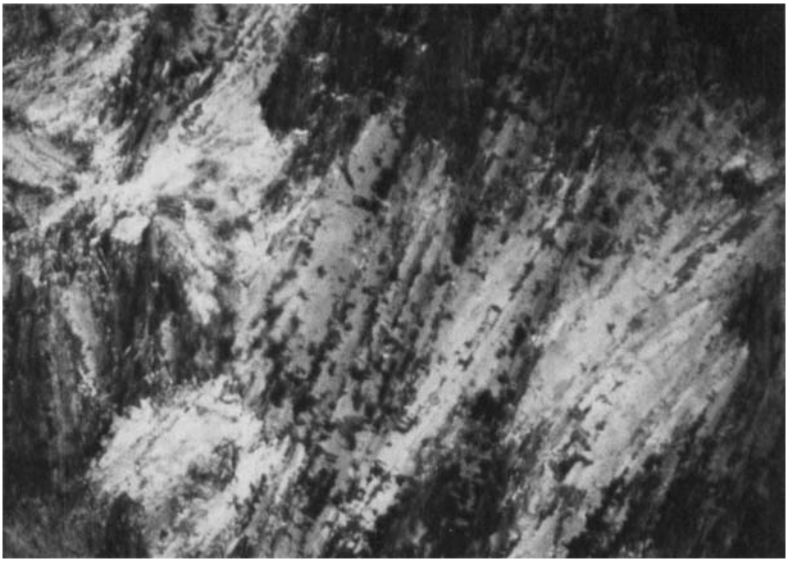
Studies of the textures for the chiral 3,5 series *4e* showed the presence of the Ch and S_C^* phases. Both focal conic and planar textures (sometimes containing oily streaks) were observed in the Ch phases but no blue phases were seen. The C_7 homolog showed brilliant color changes at the Ch to S_A transition. Cooling the pale blue planar texture gave a series of intense color changes beginning with a pale yellow at the Ch → S_A transition and progressing through a series of brilliant

(a)

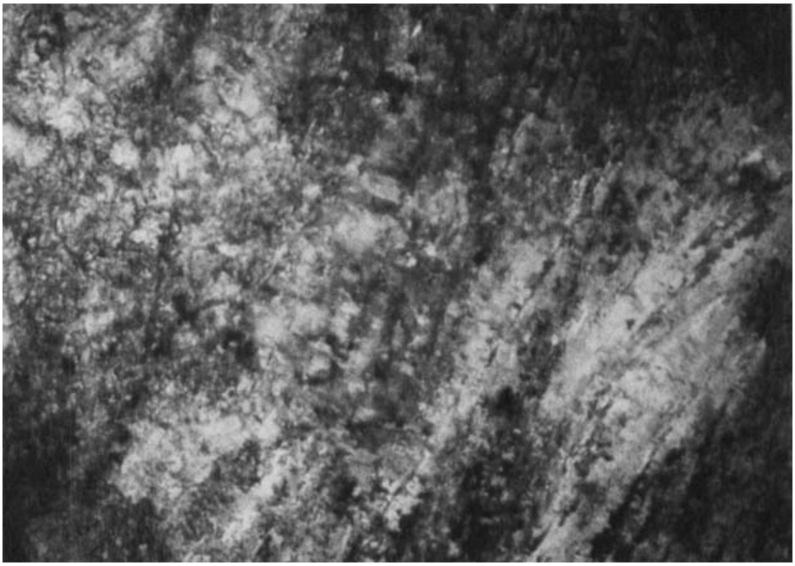


(b)

FIGURE 4 Growth of the S_y phase from the S_C phase in $\bar{8}$S5. a. Beginning of growth of the S_y phase. b. Completed S_y phase.

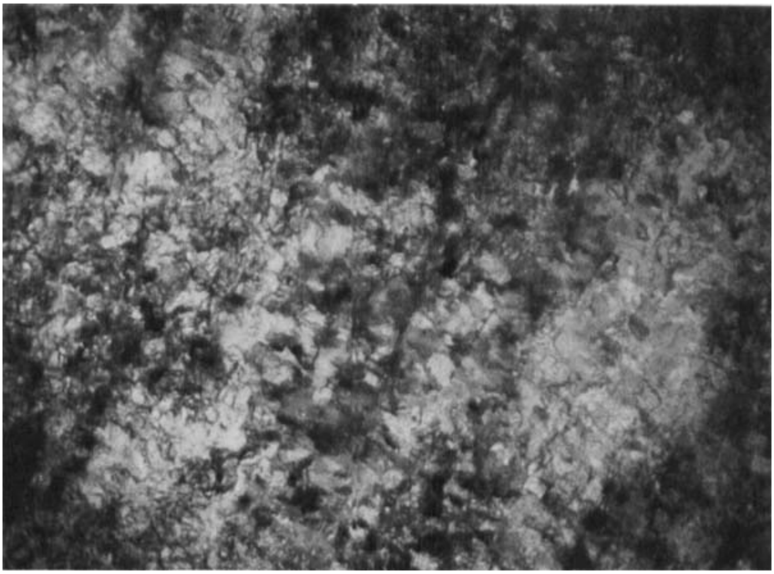


(a)



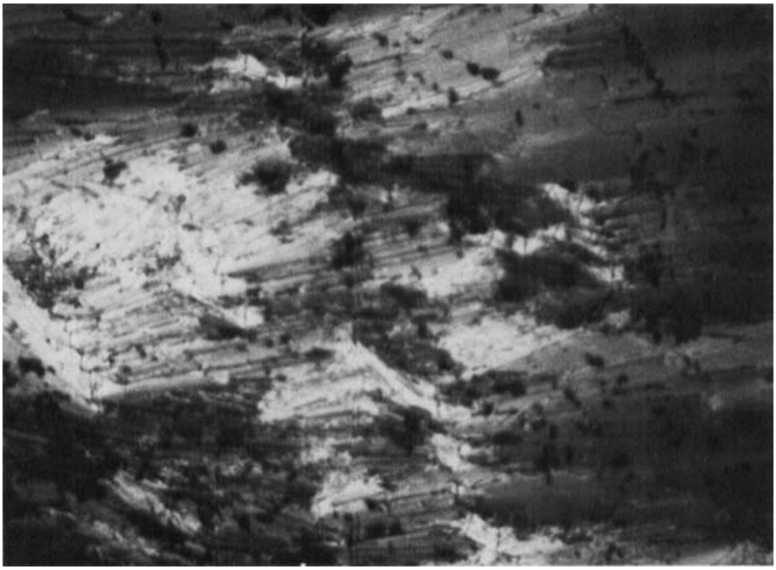
(b)

FIGURE 5 Growth of the S_3 phase from the S_C phase in compound *4f* (R = C_8H_{17}). a. S_C phase just before the transition. b. Beginning of growth of the S_3 phase. c. Completed S_3 phase.



(c)

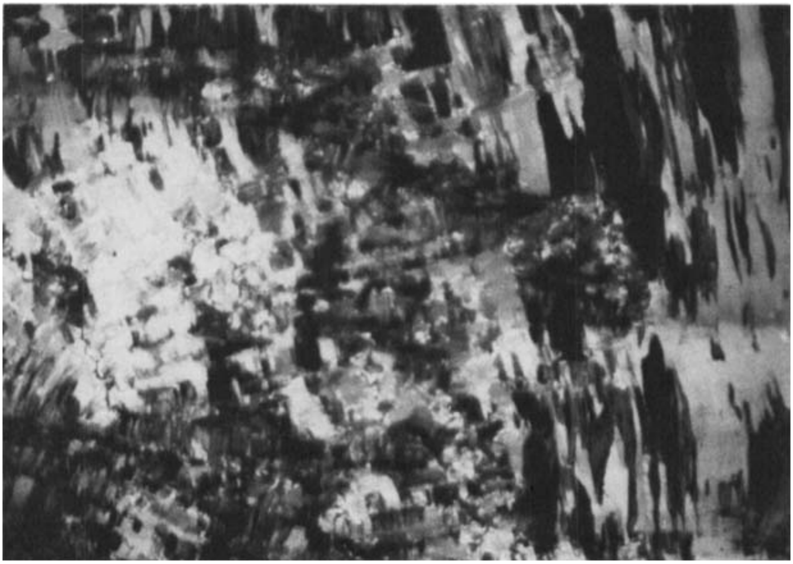
FIGURE 5 (*continued*)



(a)

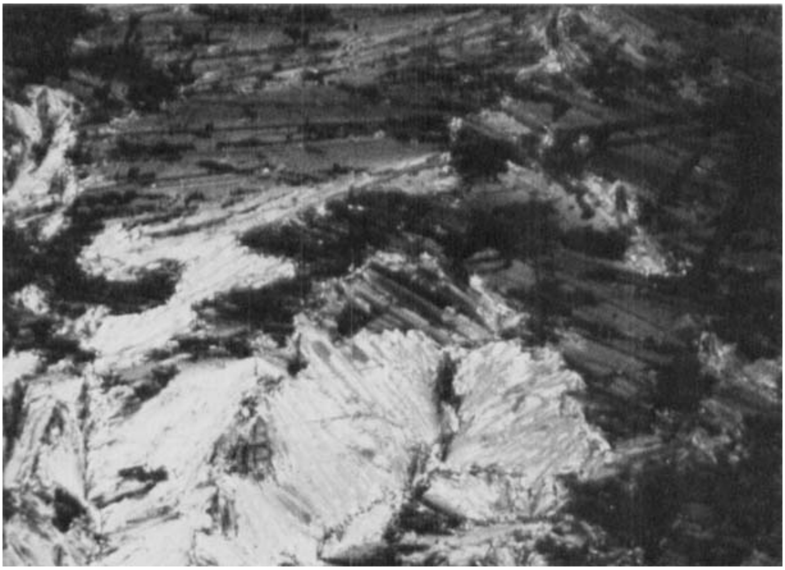
FIGURE 6 Growth of the S_3 phase from the S_C phase in compound *4f* (R = C_9H_{19}). a. S_C phase just before the transition. b. Beginning of growth of the S_3 phase. c. Completed S_3 phase.

(b)

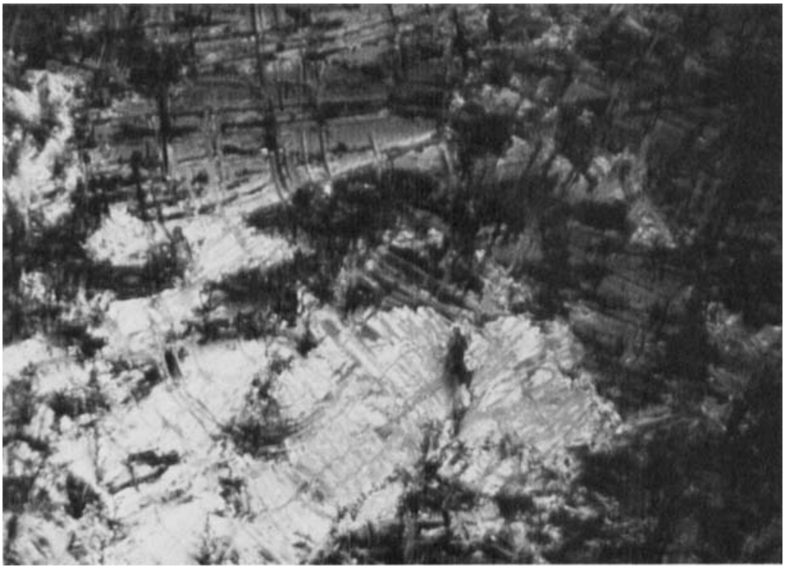


(c)

FIGURE 6 (*continued*)

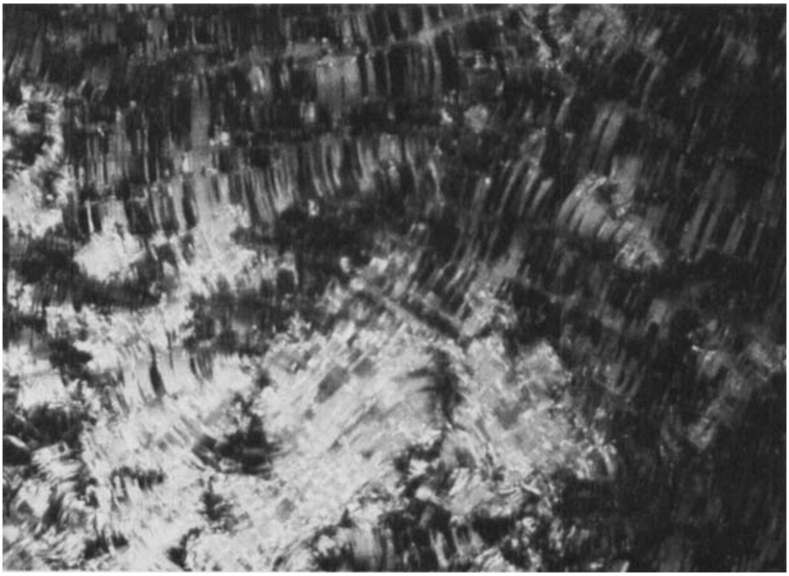


(a)



(b)

FIGURE 7 Growth of the S_3 phase from the S_C phase in compound *4f* (R = $C_{10}H_{21}$). a. S_C phase just before the transition. b. Beginning of growth of the S_3 phase. c. Completed S_3 phase.



(c)

FIGURE 7 (*continued*)

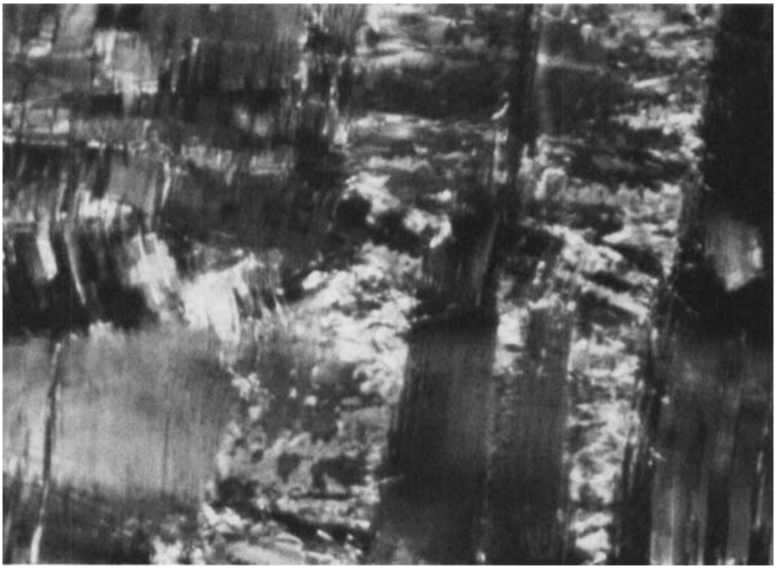
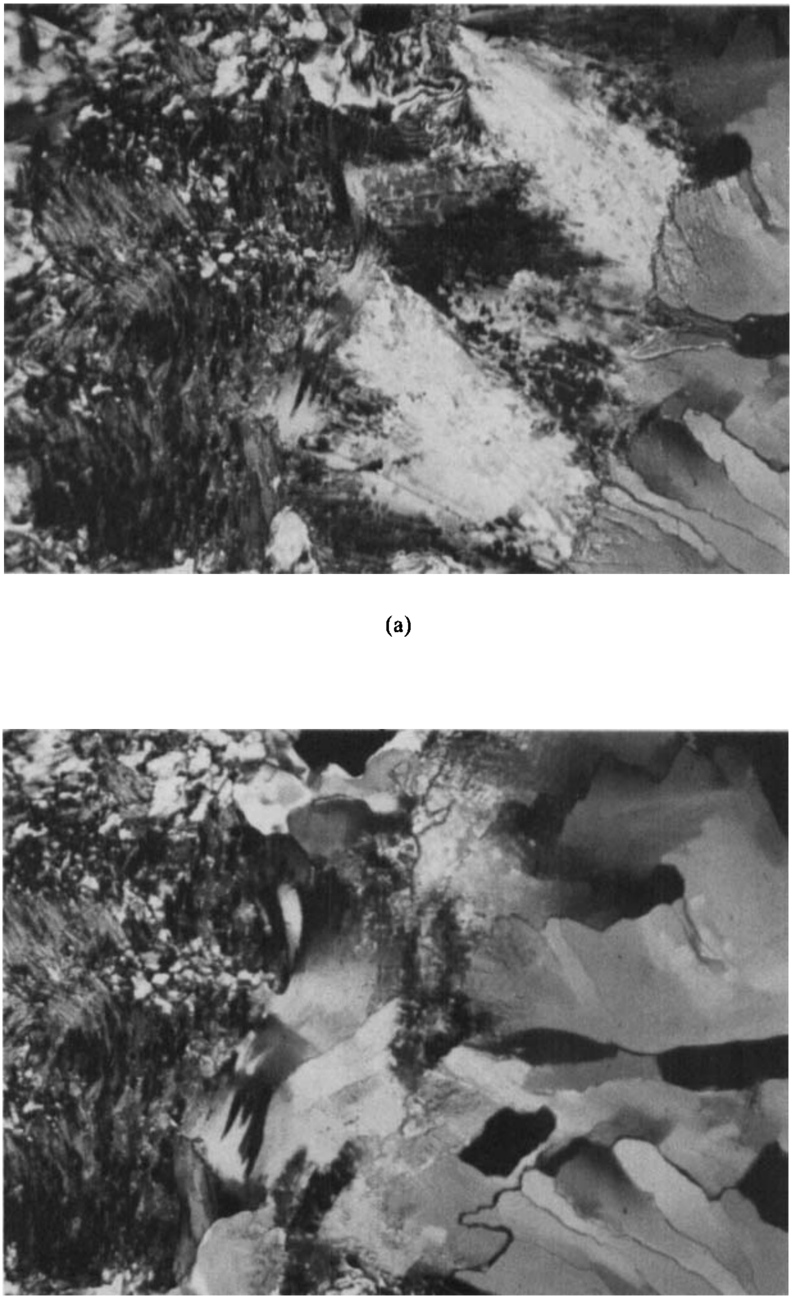


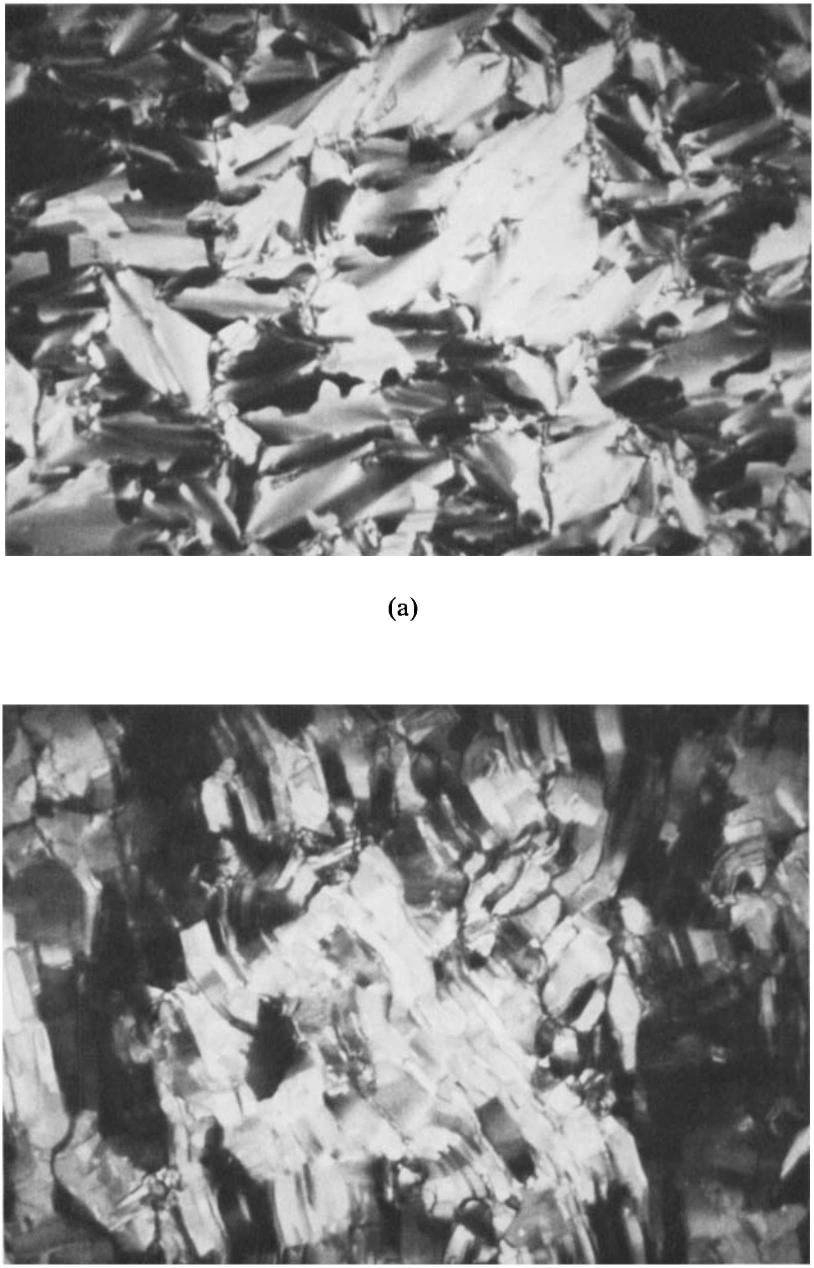
FIGURE 8 Interface in contact mixture study of $\overline{9}O\overline{4}$ and 4,5 BC thioester *4f* (R = $C_{10}H_{21}$) with the S_B phase of $\overline{9}O\overline{4}$ on the left and the S_3 phase growing into the S_C phase of the thioester on the right.



(a)

(b)

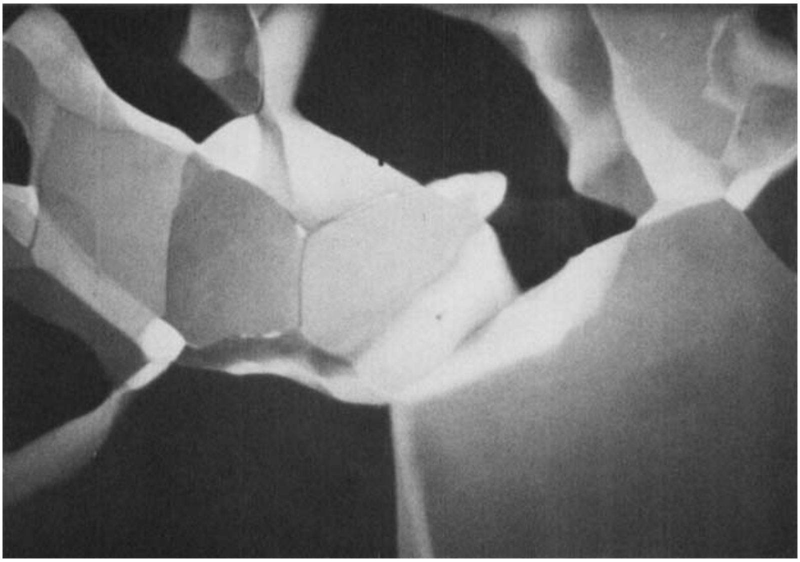
FIGURE 9 Interface in contact mixture study of $\bar{9}O\bar{4}$ and $\bar{8}S5$. a. S_B phase in $\bar{9}O\bar{4}$ (left) and S_y phase in $\bar{8}S5$ (right) growing into the S_C phase of $\bar{8}S5$ (center). b. Same area with growth of S_B and S_y phases completed.



(a)

(b)

FIGURE 10 Growth of the S_3 phase from the S_C phase in the thioester *5b*: a. S_C phase; b. S_3 phase, same area; and c. mosaic texture of the S_3 phase, different area.



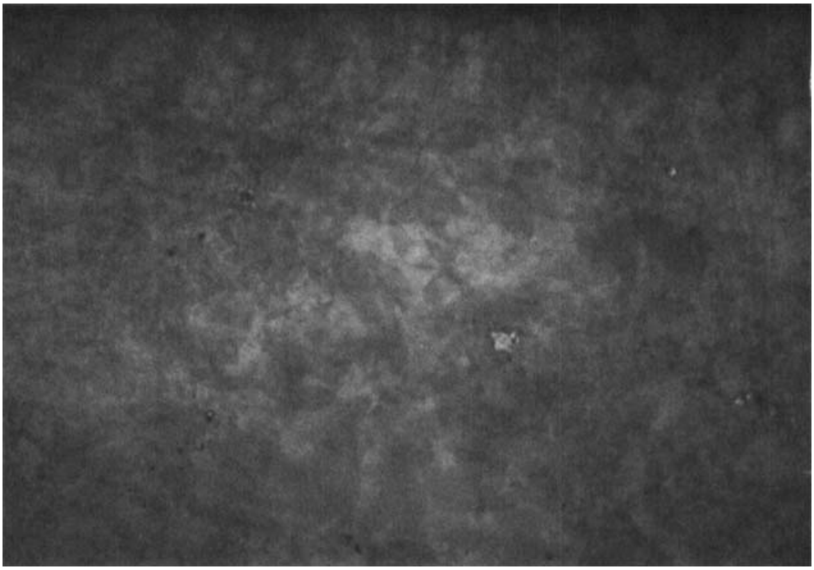
(c)

FIGURE 10 (*continued*)

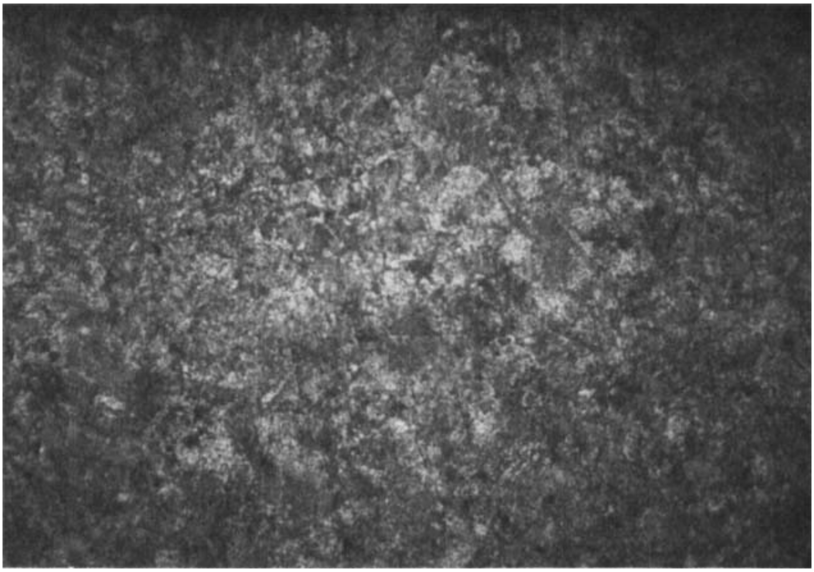
yellow, yellow orange, red, violet, blue, and green first as a platelet texture (Figure 11a), then as a multicolor texture (Figure 11b) for the S_A phase just before the S_A–S_C^* transition and finally converting to the S_C^* texture which showed some areas containing parallel lines (Figure 11c). Since we also studied the racemic compound, we know that these color changes occur in the temperature range of the S_A phase rather than in the Ch phase. Many cholesteric phases show brilliant color changes as the pitch of the helix changes with temperature.[14] We did not observe changes in the color of the Ch planar texture until near the Ch–S_A transition but did observe subtle changes in the focal conic texture in the Ch phase before the Ch–S_A transition. Usually this texture converted to the platelet one as the Ch–S_A transition was approached. This platelet texture resembles the one reported by Gray and Goodby for a chiral S_C phase (see plate 24 in Reference 13) but in our compound occurs in the S_A phase.

These brilliant color changes were not observed at the Ch → S_A transition in the longer homologs although these also have a short range S_A phase sandwiched between Ch and S_C^* phases. Instead, these tended to give a focal conic texture in the Ch phase which converted to a nice fan texture in the S_A phase and was retained on cooling to the S_C^* phase (Figure 12). Often distorted fans were observed at the transition (Figure 13) which sometimes changed to a good fan texture. There was usually some color change at the beginning of the transition but it was brief. A planar Ch texture could be obtained from the focal conic one by moving the cover slip, but this also did not show the brilliant color changes observed in the C_7 homolog.

Microscopic textures for the C_9 homolog showed that the tilt angle of the S_C^* phase is temperature dependent as shown by the change in texture on cooling

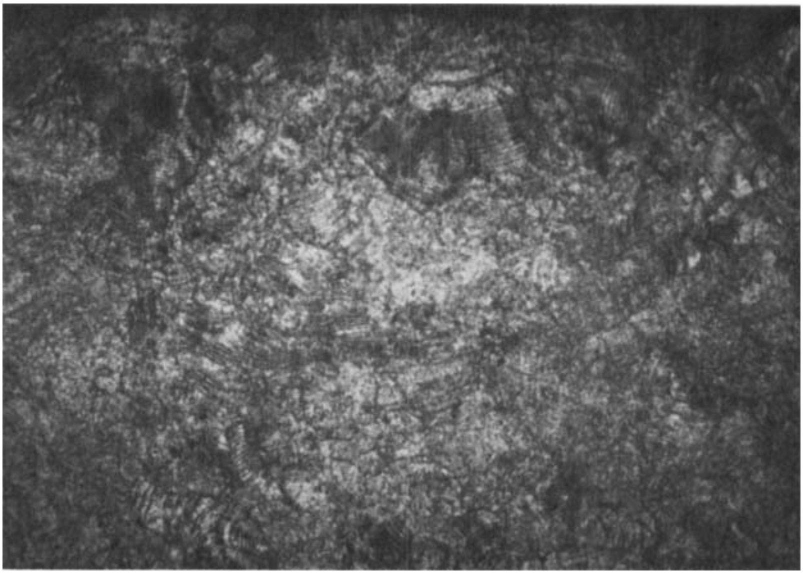


(a)



(b)

FIGURE 11 Microscopic textures for Ch–S_A–S_C^* for the thioester *4e* (R = C_7H_{15}). a. Platelet texture near the beginning of the S_A phase. b. Multicolored texture near the end of the S_A phase. c. Chiral S_C^* texture.



(c)

FIGURE 11 (*continued*)

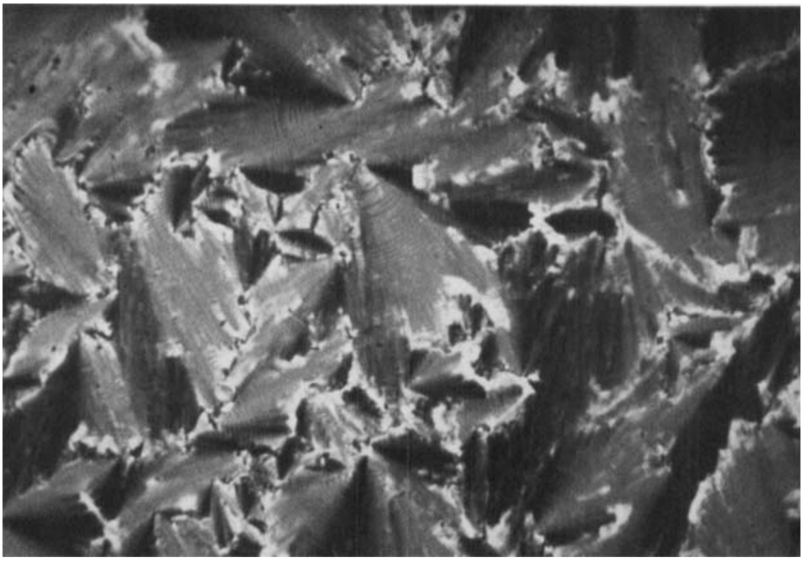


FIGURE 12 Striped fan texture of S_C^* in the thioester *4e* (R = C_9H_{17}).

FIGURE 13 Distorted S_A fan texture at Ch–S_A transition in the thioester *4e* (R = $C_{10}H_{21}$).

(Figures 14a and b). Continued cooling gave the S_B fan texture (Figure 14c) followed by conversion to the S_4^* † fan texture (Figure 14d). Cooling a homeotropic texture in the S_C^* phase to the S_B phase gave a schlieren texture (Figure 14e) which converted to a mosaic texture in the S_4^* phase (Figure 14f). Little difference was observed for the S_3 and S_4 phases in the chiral materials from those seen in the racemic ones although it seemed easier to obtain good fan textures. A good fan texture for the S_C phase in the C_{10} homolog (Figure 15a) gave the fan texture shown in Figure 15b for the S_3^* phase. The homeotropic texture in the lower right hand corner of the S_C^* texture (Figure 15a) changed to a brown mosaic texture in the S_3^* phase (Figure 15b). This is more obvious in another area (Figure 15c) which shows a typical mosaic texture for the S_3 and S_4 phases observed in all these compounds. In the C_7 homolog, a grey mosaic schlieren texture was observed (Figure 16) but this was rarely seen.

X-ray studies of the S_B phase in $\overline{14}$S5 confirmed this structure[12,15] but one of these studies suggests this is not a simple S_B phase.[12] However, it is a crystalline rather than a hexatic S_B phase.[16] It is likely that the S_B phase observed in these BC thioesters is the same type. The S_X phase which occurs below the S_B phase in $\overline{14}$S5 is now believed to be a S_G phase with a small tilt angle.[12] Early studies suggested that the S_y phase which occurs directly below a S_C phase in the SC thioesters was a S_I phase[2] but more recent work indicates it is a S_J phase.[17] It is likely that the S_3 phase observed in these BC thioesters is also the same type as the S_y phase. Thus, the S_3 phase is probably a S_j phase and the S_4 phase a S_G phase

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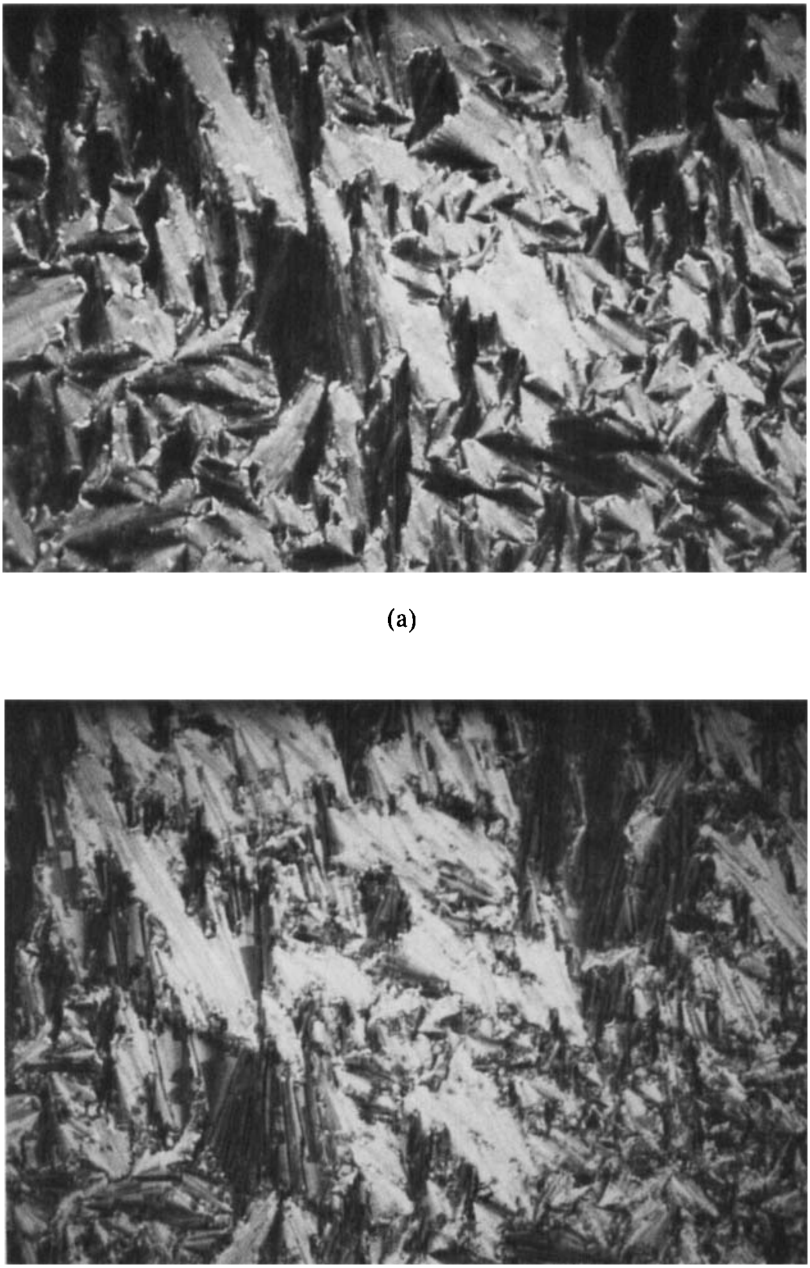
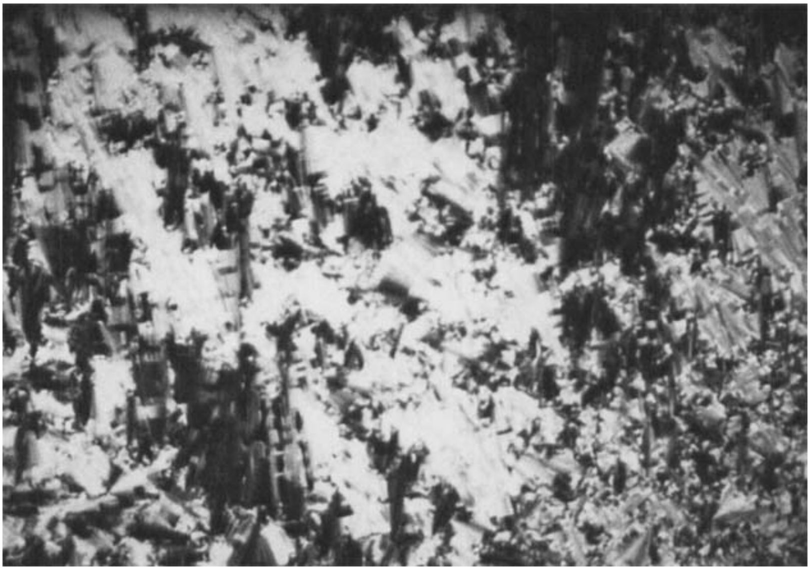
†S_4 is used to designate all unknown smectic phases occurring below what is believed to be a S_B phase.



(a)

(b)

FIGURE 14 Microscopic textures for the S_C^*–S_B–S_4^* transitions in the thioester *4e* (R = C_9H_{17}). a. Fan texture for the S_C^* phase just formed from the S_A phase. b. Fan texture for the S_C^* phase near the end of the S_C^* phase range. c. S_B phase. d. S_4 phase. e. Schlieren texture in S_B phase (different area). f. Same area in the S_4 phase.

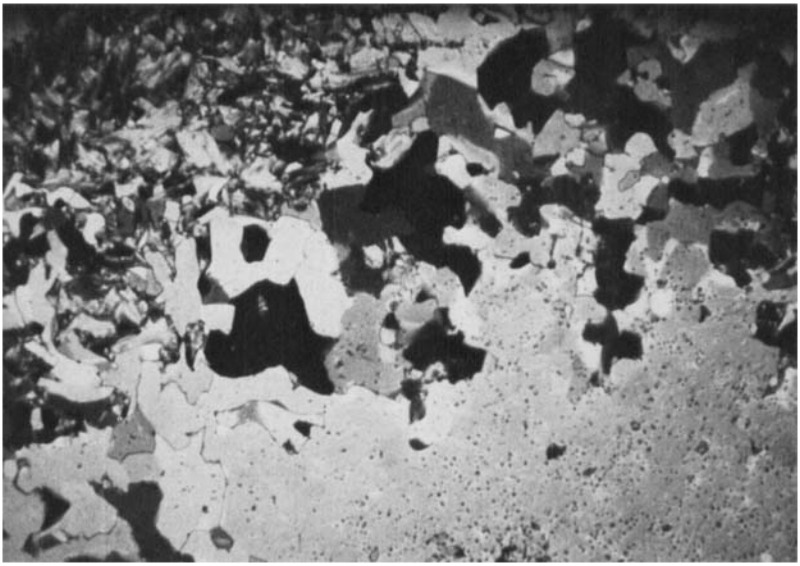


(c)

(d)

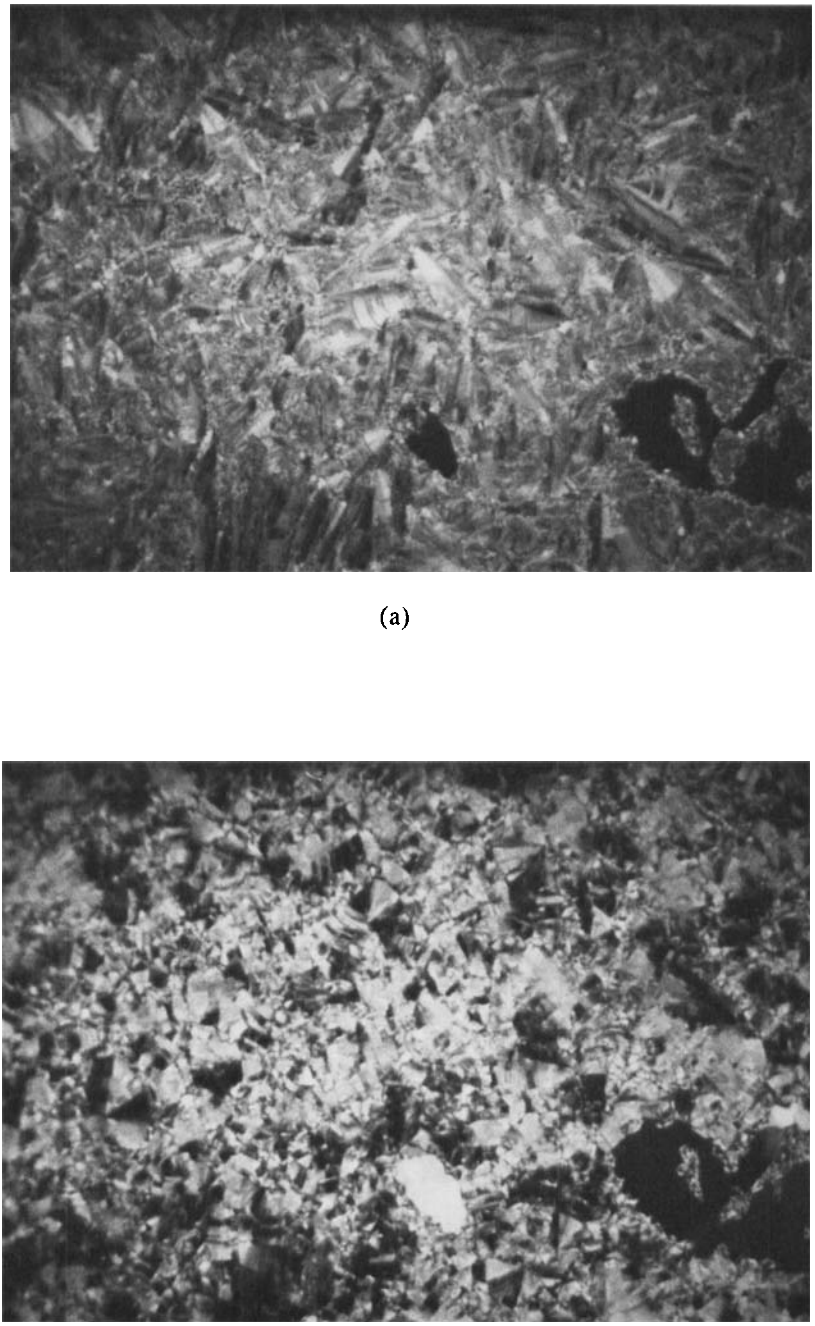
FIGURE 14 (*continued*)

(e)



(f)

FIGURE 14 (*continued*)



(a)

(b)

FIGURE 15 Microscopic textures for the S_C^*–S_3^* transition for the thioester *4e* (R = $C_{10}H_{21}$). a. S_C^* phase. b. S_3^* phase. c. another area of the S_3^* phase.

(c)

FIGURE 15 (*continued*)

and in the optically active compounds, S_J^* and S_G^* respectively. However, if the mosaic textures for the S_3 phase in the C_8 homolog of the 4,5 series *4f* (Figure 17), which is typical of the mosaic textures observed for this phase in all the BC thioesters, is compared with that for the S_G phase in 70.4 (Figure 18) there is an obvious difference. S_G phases usually show some mosaic areas with flower-like shapes and

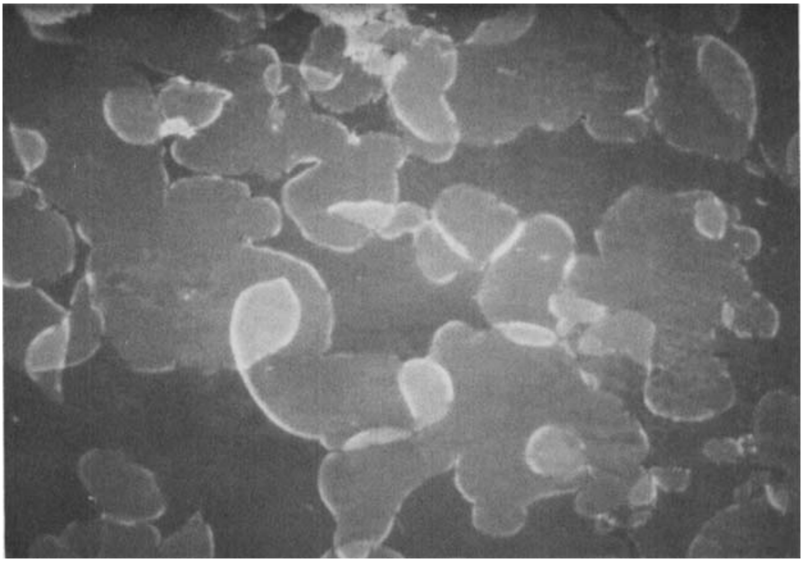


FIGURE 16 Mosaic schlieren texture for the S_3 phase in the thioester *4e* ($R = C_7H_{15}$).

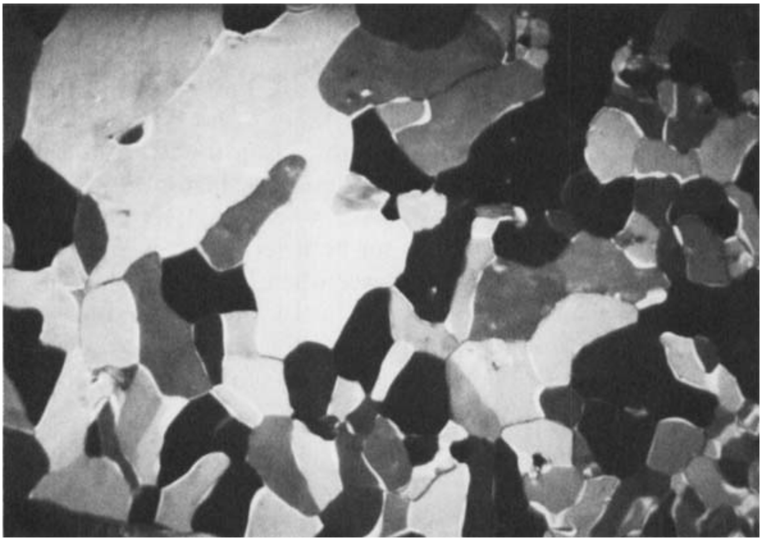


FIGURE 17 Mosaic texture for the S_3 phase in the thioester *4f* (R = C_8).

more lines in the blocks (Figure 17). These were never observed in the BC thioesters. Thus, more x-ray studies are needed to identify these highly ordered smectic phases. Additionally our assignment of the S_B phase is based on analogy with the SC thioesters which yields a weak structural assignment and needs to be confirmed by x-ray studies as well.

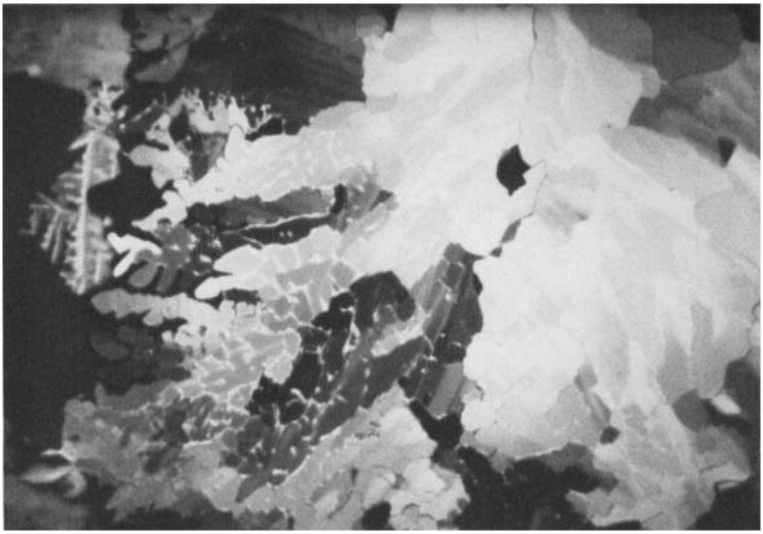
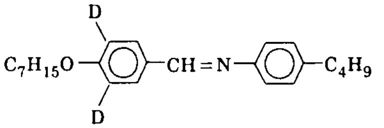


FIGURE 18 Mosaic texture for the S_G phase in



DISCUSSION

A comparison of mesomorphic properties for the BC thioesters with the SC compounds raises the question as to which chain length to use for the SC thioester; the one with the same number of carbon atoms as is in the BB of the BC(C_5) or that with the same total number of carbon atoms (C_6). Figure 19 shows a plot of the transition temperatures for these two series when X = RO for R = C_7–C_{14}. The curves for the clearing temperatures for both series are essentially the same except that the temperatures are a little lower when R′ = C_6. Thus, it does not matter which series is used in comparisons with the BC thioesters as long as absolute values are not compared. However, the two melting curves are different with a definite maximum at R = C_9 for the C_6 series but no obvious one for the C_5 series.

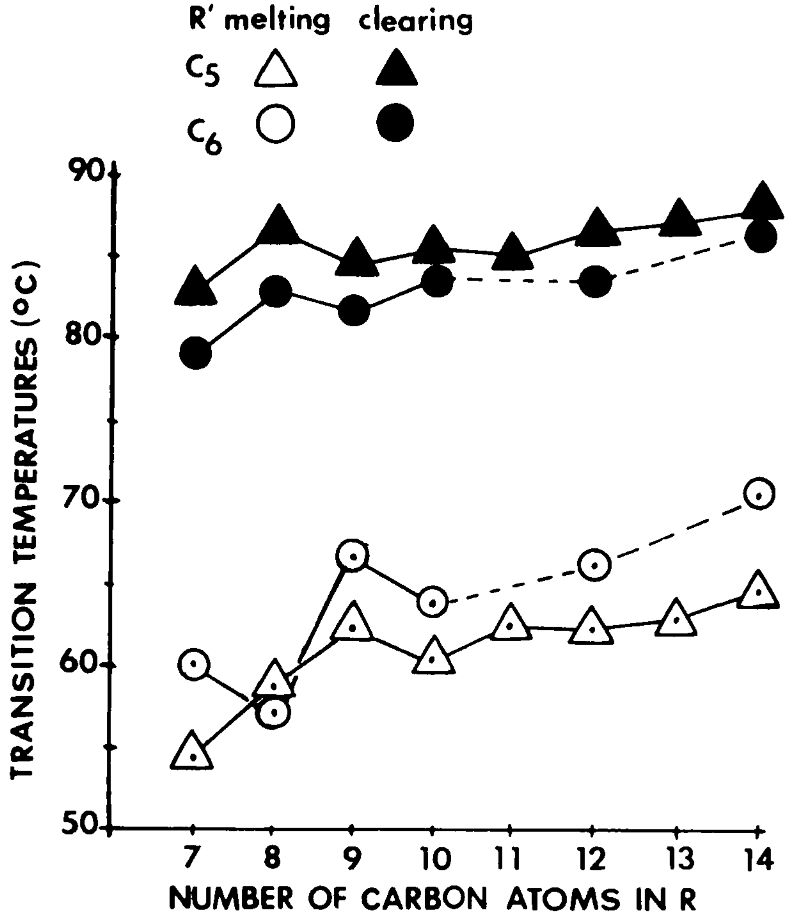
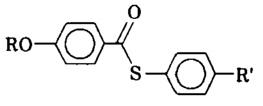


FIGURE 19 Comparison of the transition temperatures for the homologous thioester series



with R′ = C_5 and C_6.

Thus, a comparison in trends in melting temperatures can be affected by which chain length is used for the SC thioester. We chose to use R′ = C_5 since more data were available for this series.

Plots of melting temperatures for both the 4- and 5- BB–BC thioesters (Figures 20 and 21) show a steep maximum at R = C_9 for all the series except the 4,5 one which shows a broad minimum in this area. Since we have data for only one short chain homolog, C_3 (series *4e*), we do not know if this maximum at C_9 is the one for the entire homologous series. However, the melting temperature for the C_3 compound is considerably lower than that for the C_9 homolog suggesting this might be the series maximum. This could, however, vary in the other BC series. Data for the shorter homologs of the SC series with R′ = C_5[11] show a maximum at R = C_2 which is higher than the one at C_9. In the BC series, it is obvious that this C_9 maximum is not just part of an odd–even alternating effect since odd homologs with either shorter or longer chains have much lower melting temperatures whereas in the curves for the SC thioesters, the longer chain homologs have temperatures comparable to those where the maxima occur and thus appear as an odd–even effect (Figure 19). Maxima also occur in the melting curves for the C_9 homolog in the analogous BC esters with a C_5 BB but the SC series also shows a maximum at C_9 and the maxima are not as steep.[1] Such a consistent trend in melting temperatures is very rare. Oscillations in melting temperatures for short chain homologs where the molecule is primarily a rigid rod is common. However, at chain lengths beyond C_8, large oscillations are rare as the molecule becomes primarily a flexible one. This maximum at C_9 suggests a more rigid chain and better packing of the molecules, but why should it occur only at C_9?

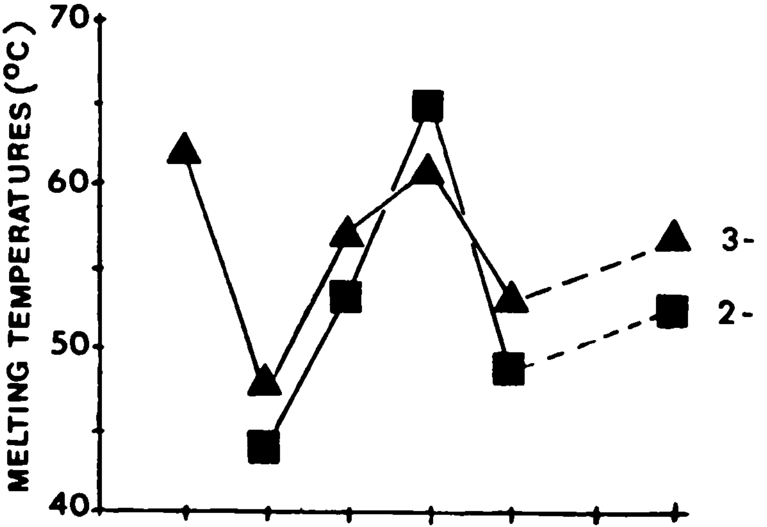


FIGURE 20 Melting temperatures (°C) as a function of the number of carbon atoms in R for the C_4BB series *4*.

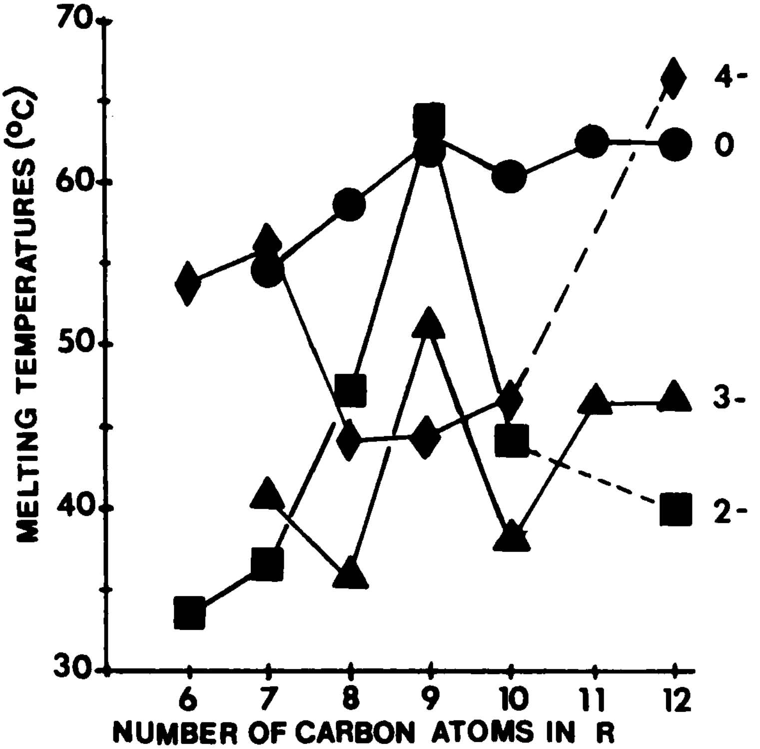


FIGURE 21 Melting temperatures (°C) as a function of the number of carbon atoms in R for the C_5BB series *4*.

The melting curves for the C_5 BB thioesters (Figure 21)† also indicate that the melting temperatures are usually lower for the BC than for the SC compounds. There are, however, enough exceptions to make it difficult to predict whether the melting temperatures will be lowered with the addition of a branched chain. This same variation of the effect of branching on melting temperatures was also observed in the analogous BC esters.[1]

The trend of increasing melting temperatures as the distance between the methyl group and the benzene ring increases holds well in the 4BB series where only the C_9 homolog in the 2,4 series deviates but this trend does not continue in the 5BB series with the 3,5 series usually having lower melting temperatures than the 2,5 one. These results are comparable to those found for the analogous BC esters.[1]

More consistency was observed in the clearing temperatures for these BC thioesters (Figures 22 and 23). In the 5BB series, the clearing temperatures were always lower than those for the SC compounds in all series. This was also true in the analogous BC esters. In both the 4 and 5BB series, clearing temperatures always increased with increasing distance between the methyl group and the benzene ring when R > C_7 whereas when R < C_7 more variability was observed. This trend was

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†Data are not yet available for the SC thioesters with $R'{=}C_4$.

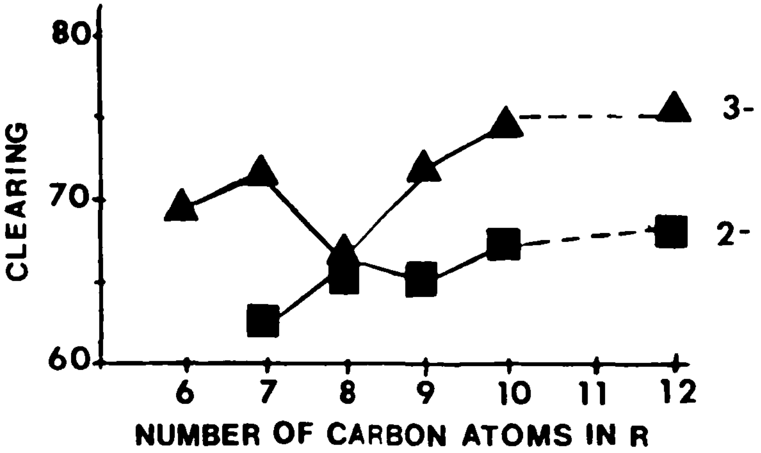


FIGURE 22 Clearing temperatures (°C) as a function of the number of carbon atoms in R for the C_4BB series *4*.

also observed in the 5BB branched chain esters except at R > C_8.[1] Another interesting observation is that the odd-even effect in the clearing temperatures disappears in the 5BB series at longer chain lengths. A plot of transition temperatures for different methyl group positions for R = C_8 (series *4c–f*) (Figure 24) shows that the 3,5 series has the lowest melting and clearing temperatures with the widest enantiotropic mesophase range of all these series. This is fortunate since this is the series that it is the easiest to prepare an optical isomer of for possible use as ferroelectric liquid crystals.

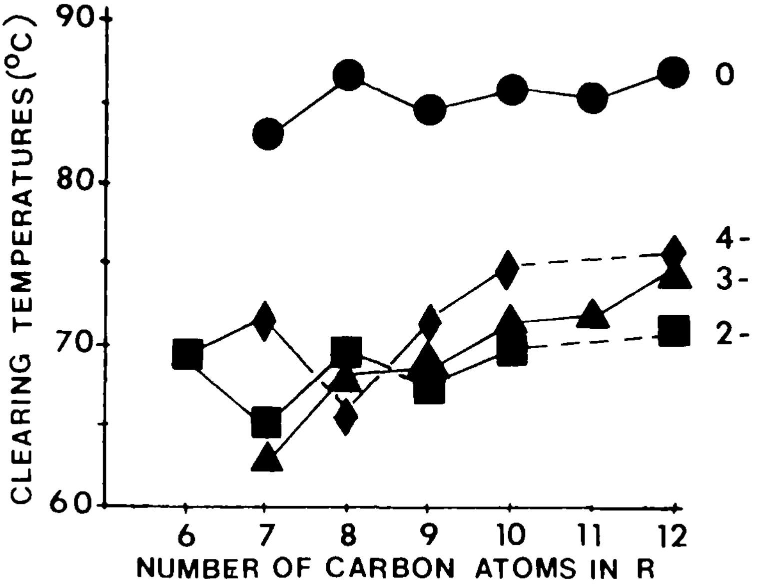


FIGURE 23 Clearing temperatures (°C) as a function of the number of carbon atoms in R for the C_5BB series *4*.

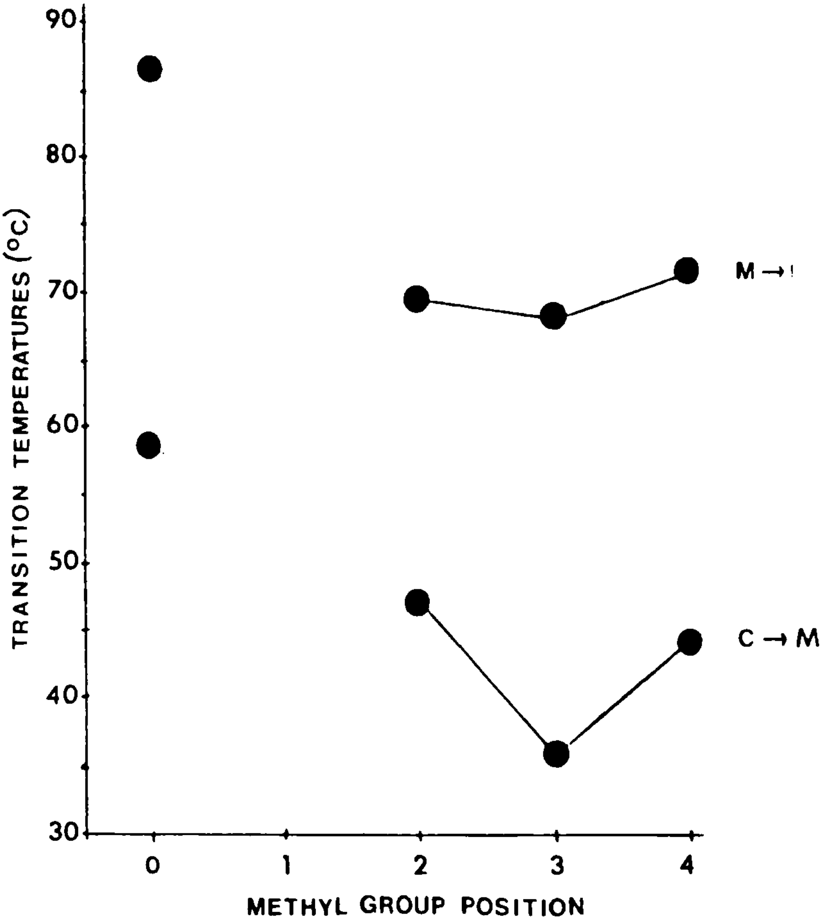


FIGURE 24 The effect of methyl group position on the melting (C → M) and clearing (M → I) transition temperatures for the C_5BB series *4*.

When X = R = C_8, the same trends in the melting and clearing temperatures were observed (Figure 25) *i.e.* clearing temperatures were always lower than those for the analogous SC compounds and melting temperatures were more variable. Again melting and clearing temperatures increased as the distance between the methyl group and benzene ring increased only in the 4BB series. However, unlike the X = RO series, the 3,5 compound has the highest melting temperature, although it still has the lowest clearing temperature.

A comparison of the types of mesophases observed for the BC and SC thioesters shows some interesting results. When X = R = C_8 (Figure 25), only N and S_A phases were observed and these were all monotropic as compared to an enantiotropic N phase in the SC thioesters. The S_A phase was observed only in the 3,5 series. Since the mesomorphic properties are so poor in this series other homologs were not prepared.

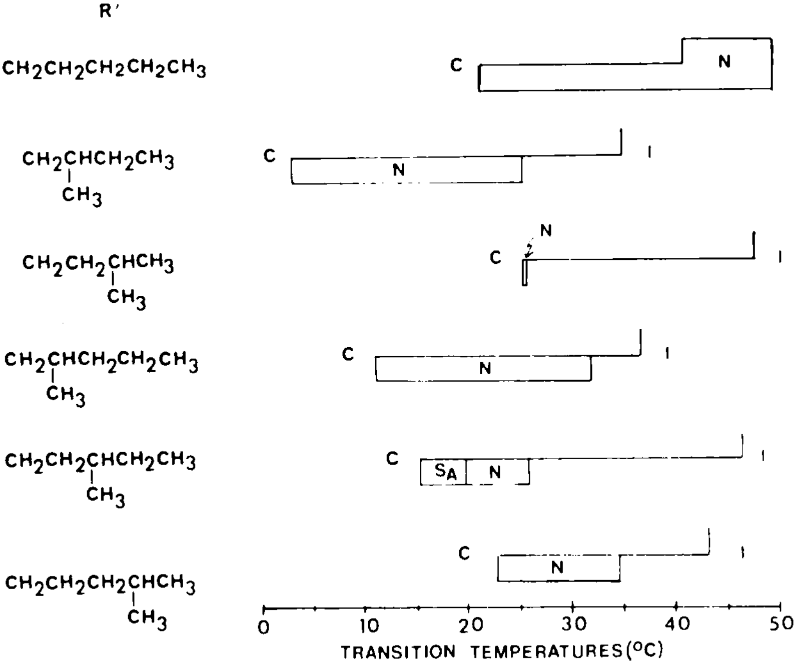
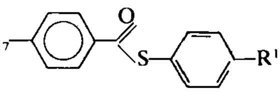


FIGURE 25 Transition temperatures and mesophases for C_8H_{17} 

The BC thioesters with X = RO show good mesomorphic properties with a wide variety of mesophases, some with good phase lengths (Figures 26 and 27). We tried to prepare as many homologs as it seemed were necessary to define the trends in these compounds without preparing the entire homologous series. N, S_A, and S_C phases were observed in all five series and many even showed a more highly ordered smectic phase below a S_C phase. This phase is the least favored in the 2,5 BC compounds (Figure 27b) where the N phase is the most favored often having a longer range and continuing to occur at longer alkoxy chain lengths than in the SC series. In all the 5BB-BC series, the S_A phase is less favored and the S_C phase more so than in the SC series. Crystallization temperatures were generally lower often giving longer monotropic phase ranges. In the 3,5 series (Figure 27c), crystallizations were sometimes so slow that they were not observed by microscopy (e.g. R = C_{11} and C_{12}). Samples of these compounds were allowed to stand at room temperature overnight to crystallize and then reheated to obtain the melting temperatures. This series has wider range S_C phases than occur in the analogous SC thioesters and still show N and S_A phases, although with narrower ranges.

Data for all the C_5BB thioesters (Figure 27) indicate that the mesomorphic properties for the BC compounds are as good, if not better, than the SC thioesters no matter where the methyl group is located. The temperature range over which mesophases occur (*i.e.* between C and I) shifts a little toward lower temperatures but not dramatically so. Interstingly, there is not a gradual increase in mesomorphism as the methyl group is moved further along the chain from the benzene ring.

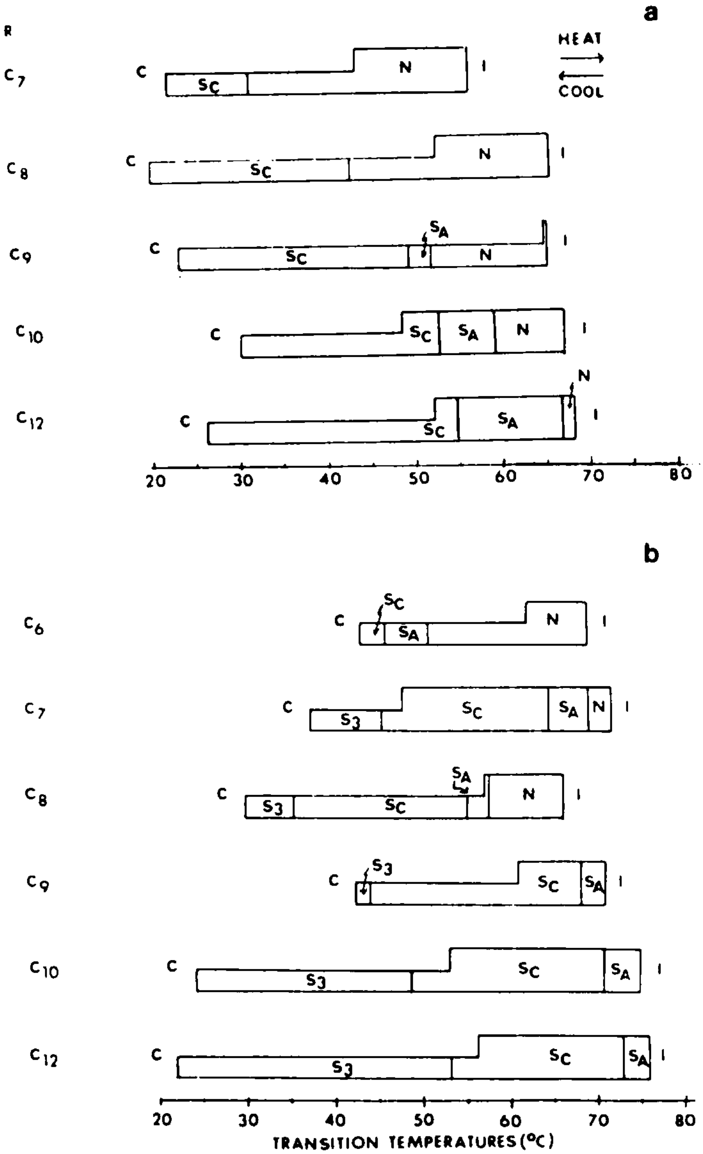
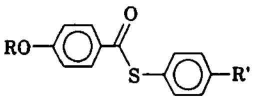
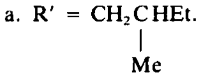


FIGURE 26 Transition temperatures (°C) and mesophases for




a. R' = $CH_2\underset{|\atop Me}{C}HEt$.

b. R' = $(CH_2)_2CHMe_2$.

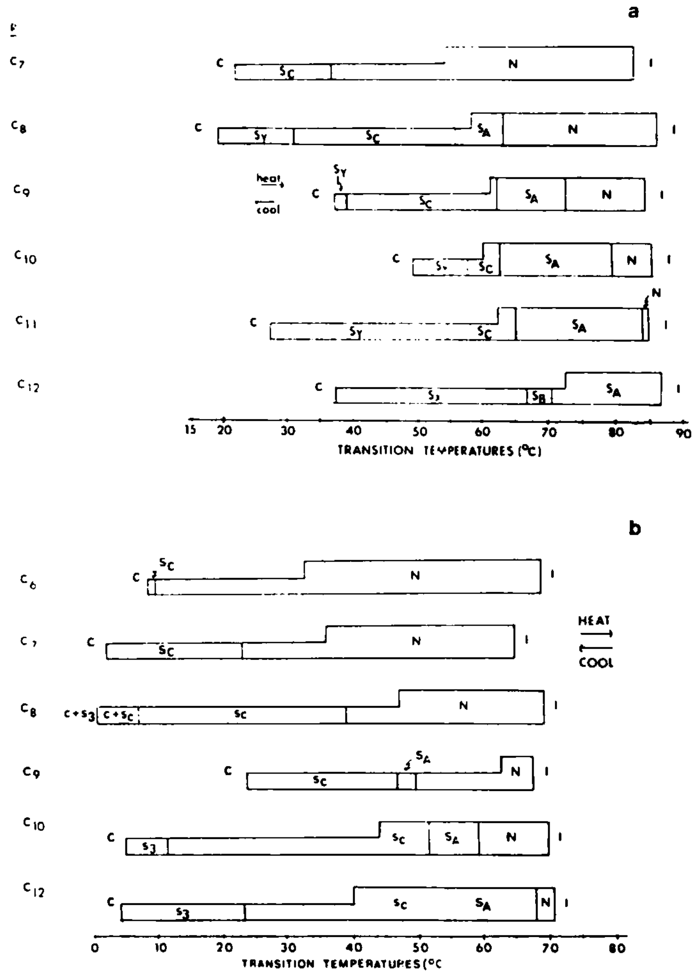
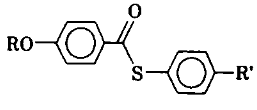
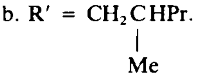


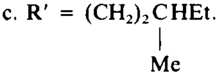
FIGURE 27 Transition temperatures (°C) and mesophases for



a. R′ = C_5H_{11}.



b. R′ = $CH_2\underset{\displaystyle Me}{CH}Pr$.



c. R′ = $(CH_2)_2\underset{\displaystyle Me}{CH}Et$.

d. R′ = $(CH_2)_3CHMe_2$.

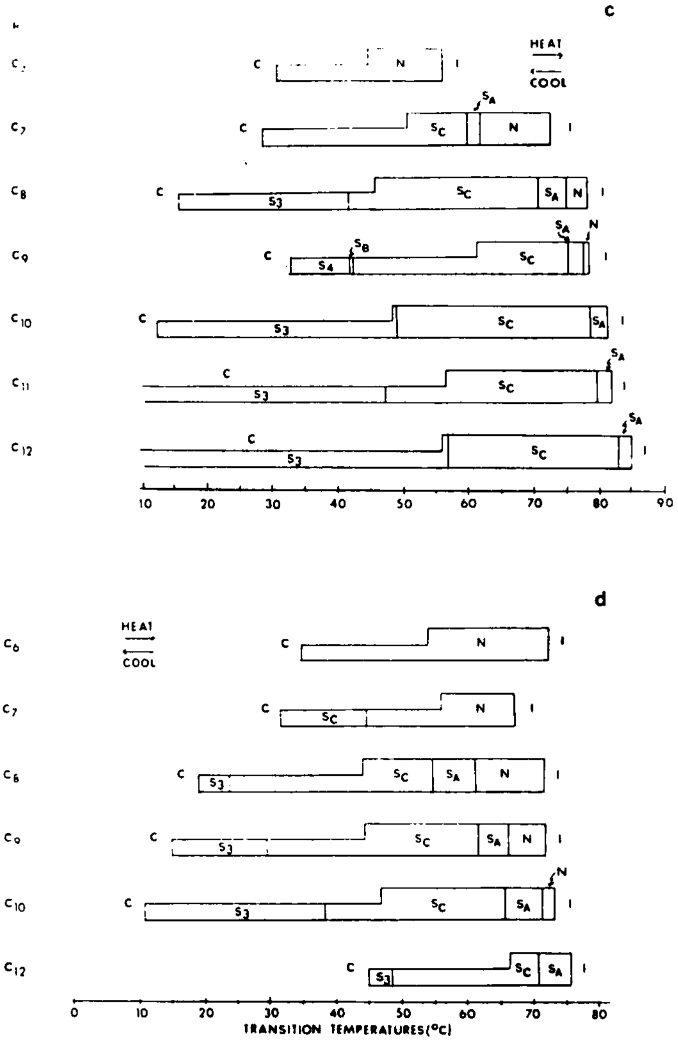


FIGURE 27 (*continued*)

In the 4,5 series where the methyl group is farthest from the ring and therefore should create the least steric hindrance in packing, the combination of mesophases observed are the same for each homolog (except when R = C_{12}) as occurs in the SC series. Thus, this series most resembles the SC one as would be expected. However, there are differences as mentioned earlier: the S_C phase is more favored, the N and S_A phases less so, and the transition temperatures are lowered. Essentially what we have is a mild modification of what we started with. Thus, branching offers the possibility of fine tuning the mesomorphic properties of a liquid crystalline material. That the S_C phase range is the widest in the 3,5 series should be of interest in structural studies of the S_C phase.

Replacing the alkoxy group with a C_9CO_2 group (series 5) caused the disappearance of the S_A phase which also occurs in the analogous SC thioesters (Figure 28). Clearing temperatures were always lower and again the effect on melting temperatures varied. All the compounds studied showed a $N-S_C$ combination and at least one more highly ordered S phase below the S_C phase. Again branching favored the S_C phase while the N phase was less favored in all but the 2,5 series. However, nothing is gained by this modification, as far as a possible ferroelectric material is concerned, since the range of the S_C phase and it's temperature is not as good as that in the 3,5 series with X = $C_{10}O$ (Figure 29) and no S_A phase is present to achieve alignment. Interestingly, the widest range of mesomorphic properties occurs in the 2,5 series as was true in the X = R series but unlike the X = RO series where the 3,5 series has the widest mesophase range. Both melting and clearing temperatures increase as the distance between the methyl group and the benzene ring increases except for the clearing temperature for the 3,5 series (Figure 28).

Our studies with the BC esters and thioesters clearly illustrate the problems of trying to develop structural-properties relationships on the basis of studies done using a small number of compounds and modifications. Simply adding an extra

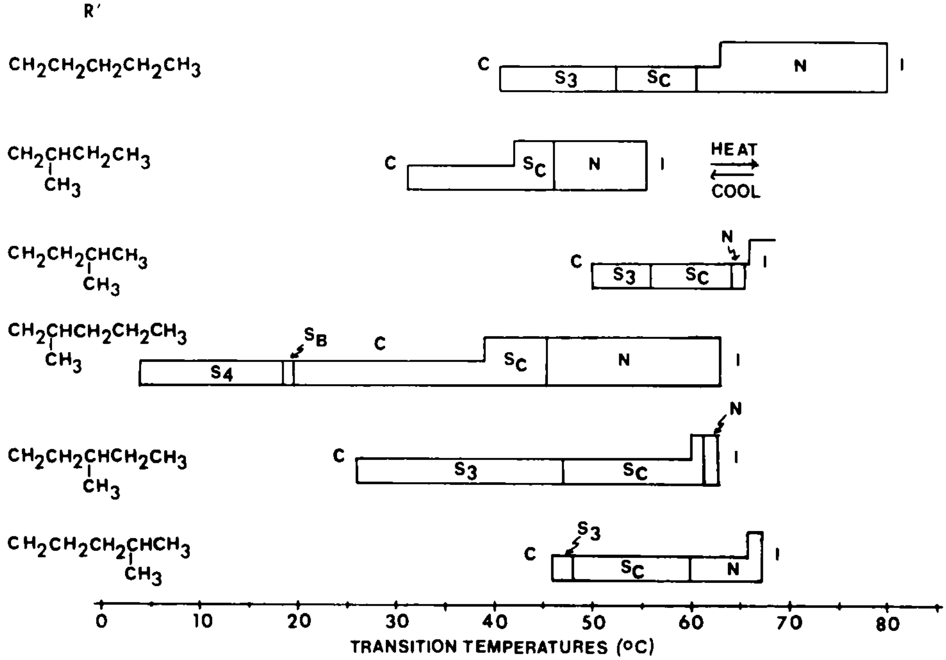
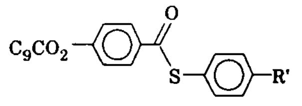


FIGURE 28 Transition temperatures (°C) and mesophases for



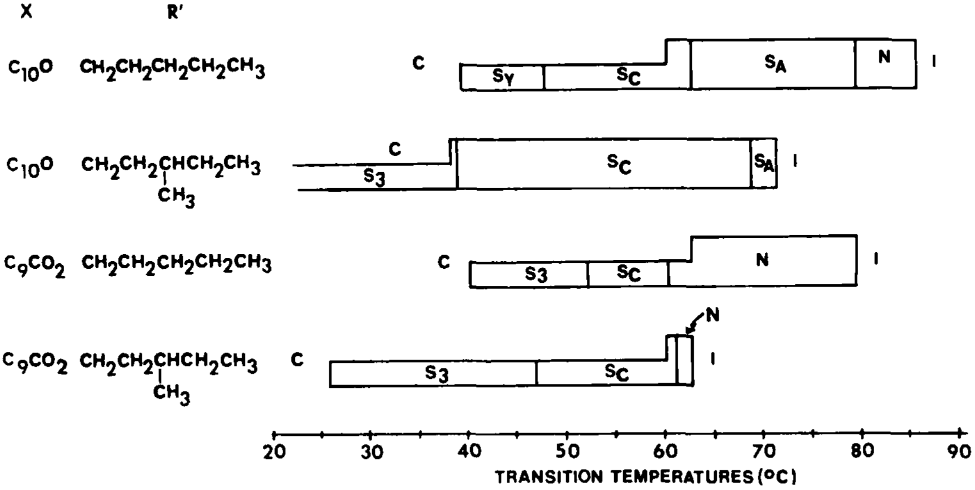
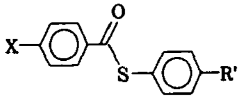


FIGURE 29 Transition temperatures (°C) and mesophases for



methylene group to the BC gave different trends than observed in the C_4 chain esters. As more compounds are prepared and studied, it becomes more difficult to define trends as more exceptions are found. Still, we have learned a great deal. Although we cannot always count on a defined trend to give the expected result, it may occur often enough to be worth a try. The lowering of melting temperatures by alkyl chain branching is one of these trends. Thus far, the lowering of the clearing temperature seems to be an even more definite trend and therefore more useful. The amount of lowering is less well defined and we are still unable to predict the phase ranges of the mesophases. The types of mesophases observed seems to be established by the basic structure of the molecule. For example, although S_E phases are commonly observed in biphenyl esters, we have not observed any in either the phenylbenzoates or thiophenylbenzoates. The phenylbenzoates show no smectic phases more highly ordered than the S_B phase, whereas the thioesters do. Thus far, small structural modifications have not favored the formation of new mesophases in these series. These modifications do, however, greatly affect which of the phases are seen and in what combination, but we are still unable to predict these factors with much certainty.

EXPERIMENTAL

The acids 4-alkyl[18] and 4-acyloxybenzoic[19] were prepared using previously reported methods, whereas 4-alkoxybenzoic acid was obtained from Frinton Laboratories. The synthesis of sodium 4-(+)-(3-methylpentyl)benzenesulfonate is described in Reference 1.

All compounds were analyzed by TLC, IR, and NMR. NMR spectra for the SC sulfonyl chlorides and thiols can be found in Reference 9 and a comparison of NMR spectra for the SC thioesters is given in Figure 2. NMR spectra for the analogous BC compounds were the same except for the aliphatic proton regions. Spectra for this region in the 4BC thiols are given in Figure 1 and for the 5BC phenols in Reference 1. The aromatic protons in the BC thioester series *5* had the following chemical shifts: δ8.01 (d,J = 9.0 Hz, H *ortho* to COS), 7.35 and 7.16 (set of overlapping doublets, J = 9.0 Hz (remaining ArH). All NMR data were determined in CCl_4 on a Varian EM360 instrument using TMS as an internal standard. GLC data were collected on a Varian 3700 instrument using a 3% SP-200 on 80/100 supelcopart (6′ × 1/8″) S.S. column. 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 (including monotropic phases) as described in Reference 20. All samples were cooled at 2°/min until they crystallized (unless otherwise noted) to insure that all monotropic phases occurring before this temperature were observed. Phase abbreviations are as follows: C = crystal, S = unspecified smectic, S_J = smectic J, S_I = smectic I, S_G = smectic G, S_B = smectic B, S_C = smectic C, S* indicates a chiral smectic phase, S_A = smectic A, N = nematic, and I = isotropic liquid. Parentheses indicate monotropic phases. Optical rotations were determined in $CHCl_3$ using a Polyscience SR6 instrument.

Transition temperatures for $\bar{9}$S6 (*4*, R = C_9H_{19}, R′ = C_6H_{13}) are as follows: 66.2–66.9 (C → S_A), 75.3–75.4 (S_A → N), 82.1–82.2 (N → I), 67.2–67.3 (S_C → S_A), 42.3–42.4 (S_y → S_C), and 39.5 (S_y → C).

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