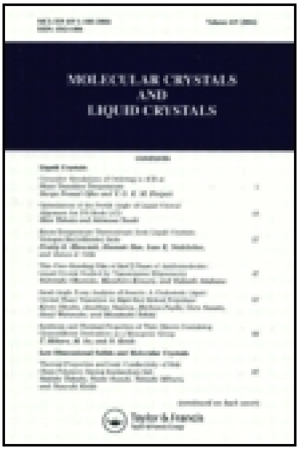

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

The Effect of Two Terminal Alkoxy Groups on the Mesomorphic Properties of 4, 4′-Disubstituted Phenylthiobenzoates

Mary E. Neubert [a], Barbara Ziemnicka-merchant [a b], Michael R. Jirousek [a c], Stanley J. Laskos Jr. [a d], Darrin Leonhardt [a] & Ram B. Sharma [a]

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The Effect of Two Terminal Alkoxy Groups on the Mesomorphic Properties of 4,4′-Disubstituted Phenylthiobenzoates

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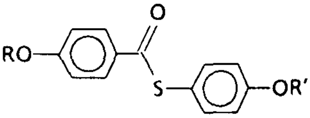
A select variety of homologs of the dialkoxyphenylthiobenzoates



were prepared. Their mesomorphic properties were determined by hot-stage polarizing microscopy and compared with those for the analogous RO—R′ and R—OR′ thioesters and esters. Unlike the esters, the addition of a second alkoxy group did not give more mesophases than were observed with only one alkoxy group. Only nematic and smectic C phases were observed with both these phases being enhanced. Several cyclohexane dithioesters of the type

were also prepared. These showed much poorer mesomorphic properties (only short-range monotropic nematic phases) suggesting that the increased number of phases in

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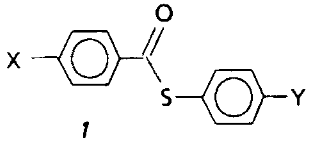
the RO—R′ thiophenylbenzoates, as compared to the esters, is probably an anomaly rather than a trend.

Most of the 4-alkoxybenzene thiols were prepared by a Newman-Karnes rearrangement of the corresponding phenols, but investigation of the sulfonation of alkoxybenzenes and the alkylation of sodium 4-hydroxybenzene sulfonate indicates that these methods can provide better routes to these thiols.

INTRODUCTION

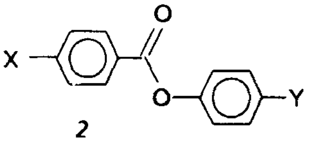
The discovery that the 4-alkylphenylthio-4′-alkoxyphenylbenzoates, *1b*



1

	X	Y
a	R	R′
b	RO	R′
c	R	OR′
d	RO	OR′

had more smectic phases, and often with wider temperature ranges, than the corresponding phenylbenzoates, *2a*,



2

	X	Y
a	RO	R′
b	R	OR′
c	RO	OR′

but still with transition temperatures <100° (see Figures 1a and c)[1–3] has generated considerable interest in these compounds for possible use in display devices[6] and phase transition[7–18] and dielectric studies.[19–20] Since the dialkoxy esters, *2c*, have more mesophases than the alkoxy-alkyl ones, *2a* (Figures 1a and b), it seemed reasonable that the dialkoxy thioesters, *1d*, would have more mesophases than the alkoxy-alkyl ones, *1b*. Thus, we prepared some select homologs in this series and determined their mesomorphic properties. These were compared with the mesomorphic properties of the thioesters, *1a–c*, and the esters, *2*. As a check on the consistency of the trends observed in these comparisons with those observed in other structures, we also prepared several homologs of the cyclohexane dithioesters, *3*,

3

a Y = R′
b Y = OR′

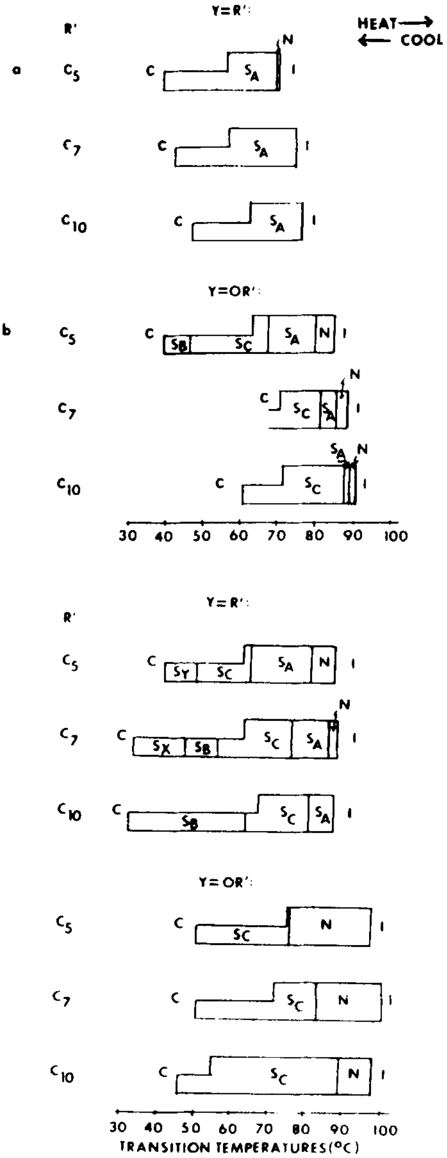
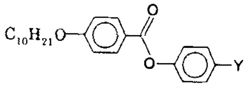


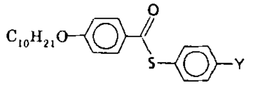
FIGURE 1 Transition temperatures (°C) *vs.* alkyl chain length for

a. and b.



(data from References 4 and 5)

c. and d.



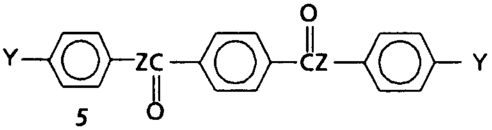
(data for Y = R′ from Reference 3)

and compared their mesomorphic properties with those for the diesters, *4*,

4

a Y = R′
b Y = OR′

Comparisons were also made with the terphthalic acid diesters, *5a* and *b*, and dithioesters, *5c* and *d*,



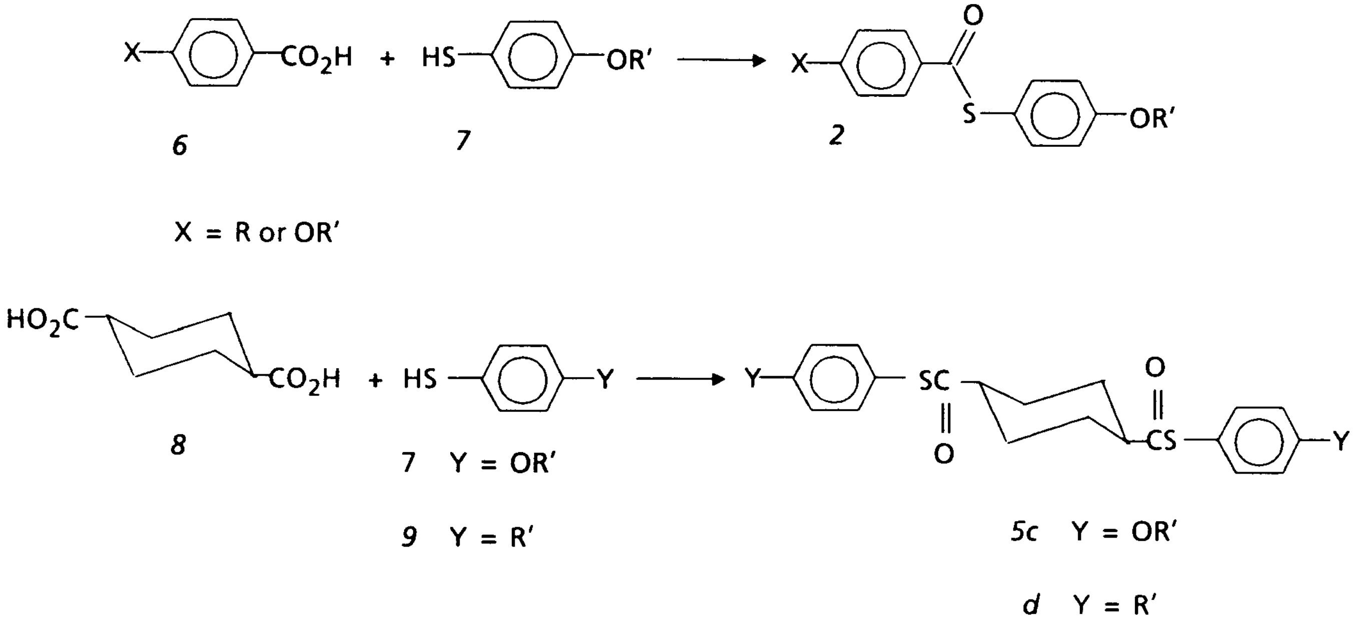
5

	Z	Y
a	O	R′
b	O	OR′
c	S	R′
d	S	OR′

SYNTHESIS

These thioesters were prepared by esterification of the thiols, *7* and *9*, with the appropriate acids, *6* and *8* (Scheme 1), using the acid chloride method as described in Reference 21 or the carbodiimide procedure as described in Reference 3. Details are provided in the Experimental Section.

A variety of methods exist in the literature by which the 4-alkoxythiols, *7*, could be prepared (Scheme 2). The Newman-Karnes' method of converting the phenol, *11*, to the thiol, *7*, via the thiocarbamates, *12* and *13*,[22,23] offers an improvement over the conversion of the aniline, *10*, to the thiol.[24] Most of the 4-alkoxybenzene thiols used in our work were prepared using this method. The O-thiocarbamates, *12*, were easily prepared in high yields (74.1–83.5%). These could be purified by recrystallization; melting temperatures are given in Table I. Use of an excess of the thiocarbamoyl chloride did not improve the yield. Although the O-thiocarbamate can be prepared from cyanophenol using the $Et_3N—CH_2Cl_2$ esterification method, no reaction occurred using these conditions with the alkoxyphenols. This supports the proposed mechanism for this reaction which predicts that this esterification is favored by electron withdrawing groups.[25,26] Rearrangement of the O-thiocarbamates, *12*, to the S-thiocarbamates, *13*, was achieved only if the melt temperature was at least 310°. The S-thiocarbamates were liquid but could not be isolated by distillation from the reaction mixture. They could be purified by



6

7

2

X = R or OR′

8

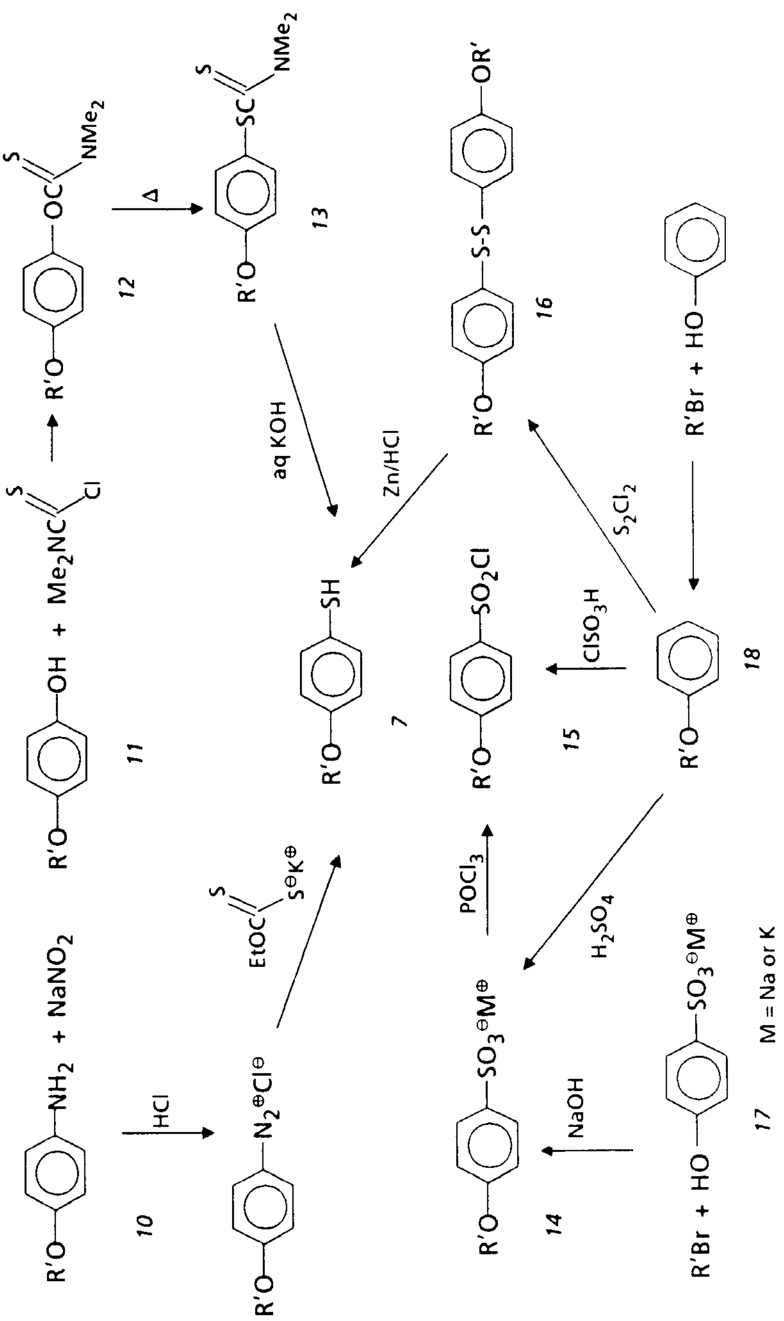
7 Y = OR′

9 Y = R′

5c Y = OR′

d Y = R′

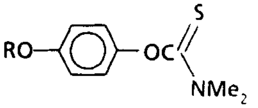
Scheme 1


10
HCl
NaNO2
11
12
13
Δ
aq KOH
Zn/HCl
7
EtOC(S)S⊖K⊕
14
15
16
17
18
POCl3
ClSO3H
S2Cl2
H2SO4
NaOH
R′Br + HO
M = Na or K

Scheme 2

TABLE I

Melting Temperatures for



R	mp (°C)
C_5	53-55
C_7	54-55
C_8	59.0-59.5
C_{10}	61.0-61.5

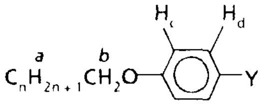
column chromatography on silica gel, but usually crude material was hydrolyzed to obtain the thiols, *7*. These had to be chromatographed to remove trace amounts of the phenol, *11*, and other impurities. All attempts to modify the reaction conditions to avoid contamination of the thiol with the phenol were unsuccessful. Ease of separation at either the S-thiocarbamate or the thiol stage varied with the alkyl chain length. Purified yields from the O-thiocarbamates ranged from 38.1–79.4% with yields being higher for the shorter homologs.

The presence of the phenol in the thiol provided an incentive to find a synthesis which avoided this problem. A few alkoxybenzenes had reportedly been sulfonated in sulfuric acid at 70°;[27,28] the same method we used earlier to prepare 4-alkylbenzenesulfonates.[29] The alkoxysulfonates, *14*, could be converted to the thiols, *7*, via the sulfonyl chlorides, *15*. Sulfonation of anisole with chlorosulfonic acid to give the sulfonyl chloride, *15*, has also been reported.[30,31] However, several attempts to sulfonate octyloxybenzene, *18*, (R' = C_8H_{17}) in concentrated sulfuric acid at 70° failed to give either the sulfonic acid or the salt and octyloxybenzene was not recovered. The salt was isolated in a purified yield of 89%, however, when the reaction was moderated by dropwise addition of the ether to sulfuric acid at 50°. Since this salt was too insoluble to obtain a good NMR spectrum, it was converted after one recrystallization to the sulfonyl chloride and a NMR spectrum obtained. This showed the presence of only the *para* isomer (Table II). Reduction of this material gave the desired thiol, *7*.

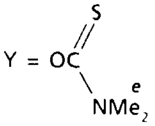
Alkylation of sodium-4-hydroxysulfonate, *17* (M = Na), which is commercially available, with bromodecane using a method similar to

TABLE II

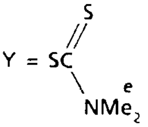
NMR Data for



(CT, EM)



δ	number of protons	multiplicity	J(Hz)	ID
6.77	4	s	- -	c,d
3.84	2	t	6.0	b
3.33	3	s	- -	e
3.24	3	s	- -	e
2.10-0.60	2n + 1	m	- -	a



(CT, EM)

7.25	2	d	9.0	d
6.78	2	d	9.0	c
3.89	2	t	6.0	b
2.98	6	t	- -	e
1.90-0.60	2n + 1	m	- -	a

$Y = \overset{e}{S}H$: (CT, EM)

7.18	2	d	9.0	d
6.68	2	d	9.0	c
3.86	2	t	6.0	b
3.12	1	s	- -	e
2.20-0.60	2n + 1	m	- -	a

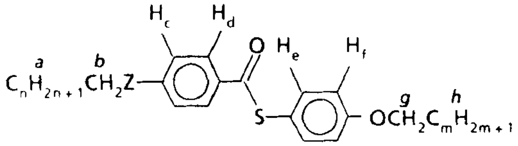
TABLE II (*continued*)

$Y = H$ (CD, FT)

7.31-7.12	2	m	- -	d
6.93-6.78	3	m	- -	c + y
3.86	2	t	6.1	b
2.02-0.80	2n + 1	m	- -	a

$Y = SO_2Cl$ (CT, EM)

7.95	2	d	9.0	d
7.05	2	d	9.0	c
4.05	2	t	6.0	b
2.40-0.70	2n + 1	m	- -	a



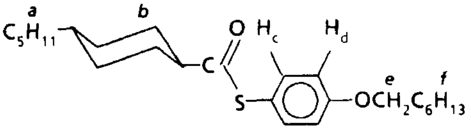
Z = nothing (CD, EM)

7.91	2	d	9.0	d
7.45	2	d	9.0	c
7.22	2	d	9.0	e
6.90	2	d	9.0	f
3.95	2	t	6.0	g
2.64	2	t	7.0	b
2.10-0.60	2n + 1,2m + 1	m	- -	a

$Z = O$ (CT, EM)

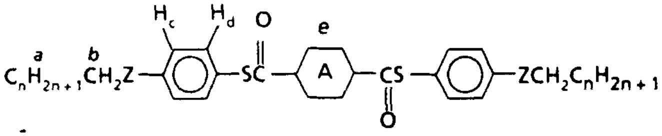
7.90	2	d	9.0	d
7.29	2	d	9.0	e
6.81	2	d	9.0	c,f
3.89	4	t	6.0	b,g
2.25-0.60	2n + 1,2m + 1	m	- -	a,h

TABLE II (*continued*)



(CT, EM)

7.24	2	d	9.0	c
6.81	2	d	9.0	d
3.89	2	t	6.0	e
3.0-0.67	34	m	--	a,b,f



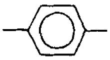
A = , Z = nothing (CT, EM)

8.05	4	s	--	e
7.32	4	d	9.0	d
7.15	4	d	9.0	c
2.60	4	t	7.0	b
2.32-0.5	2(2n + 1)	m	--	a

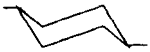
A = , Z = nothing (CD, EM)

7.26	8	s	--	c,d
2.61	4	t	7.0	b
2.40-0.5	2(2n + 1) + 10	m	--	a,e

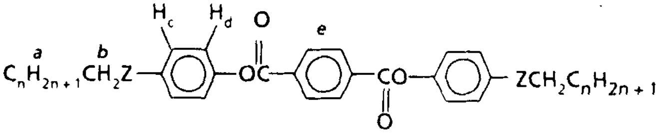
TABLE II (*continued*)

A =  , Z = O (CD, EM)

8.10	4	s	--	e
7.41	4	d	9.0	d
6.96	4	d	9.0	c
3.98	4	t	6.0	b
2.73-0.50	2(2n + 1)	m	--	a

A =  , Z = O (CT, EM)

7.28	4	d	9.0	d
6.88	4	d	9.0	c
3.94	4	t	6.0	b
2.92-0.52	2(2n + 1) + 10	m	--	a,e



Z = nothing (CT, EM)

8.47	4	s	--	e
7.24	8	s	--	c,d
2.68	4	t	7.0	b
2.0-0.65	18	m	--	a

Z = O (CD, FT)

8.30	4	s	--	e
7.15	4	d	9.2	d
6.92	4	d	9.2	c
3.97	4	t	6.1	b
1.79-0.94	2(2n + 1)	m	--	a

that of Carr and Brown,[32] and Gray's method for alkylating 4-hydrobenzoic acid[33] was also successful. This method has the advantage over sulfonation in that the isomeric content is already established in the starting material but has the disadvantage of the low solubility of the salt in reaction solvents. However, we were unable to isolate the thiol, *7*, when octyloxybenzene was treated with S_2Cl_2 followed by reduction of the assumed disulfide, *16*, using the method of Roberts, Wiles, and Kent.[34] Later workers found that a mixture of the sulfide with the di- and tri-sulfides is formed in the first reaction[35] which could explain our results. We were able to isolate a liquid with a boiling point of 90–100° (1.2 mm) which gave an NMR spectrum similar to that observed for the thiols, *7*, but with 2 overlapping aromatic doublets at 7.2 and 6.8δ and no SH peak ($ArCH_2$ triplet at 3.84δ).

Structural identification of the intermediates and thioesters was obtained from IR and NMR spectra. The IR spectra differed in the 1700–1000 cm^{-1} region for the two thiocarbamates and these from the phenol (Figure 2). Little information is available in the literature on IR data for thiocarbamates.[36] Thioamides show absorptions at 1570–1395, 1420–1260, and 1140–940 cm^{-1}. The 1530 cm^{-1} absorption in the spectrum for the O-thiocarbamate, *12*, (Figure 2b) is probably the $C = S$ peak while the peaks at 1600 and 1500 cm^{-1} are probably due to the remainder of the molecule and specifically the benzene ring, since these occur in the IR spectrum of the phenol (Figure 2a). This group also makes a large contribution to the 1290 cm^{-1} peak. Thioesters are known to absorb at 1670 cm^{-1}[1,3] and an amide absorption would be expected to occur at a lower frequency. Figure 2c shows an intense peak at 1650 cm^{-1} for the S-thiocarbamate, *13*, which is therefore assigned to the amide group. The absorption at 1590 cm^{-1} is probably an aromatic one.

Typical NMR data for all new intermediates, thioesters, and esters prepared in this work are presented in Table II. Contamination of the thiols, *7*, with the phenols or of the thioesters with the esters could be detected in the aromatic region.†

MESOMORPHIC PROPERTIES

Transition temperatures (°C) obtained by microscopy for the phenylthiobenzoates, *1c* and *d*, prepared are given in Table III. A N–S_C combination predominates in most homologs of both series with the

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†NMR data for the 4,4′-disubstituted phenylbenzoates can be found in Ref. 4.

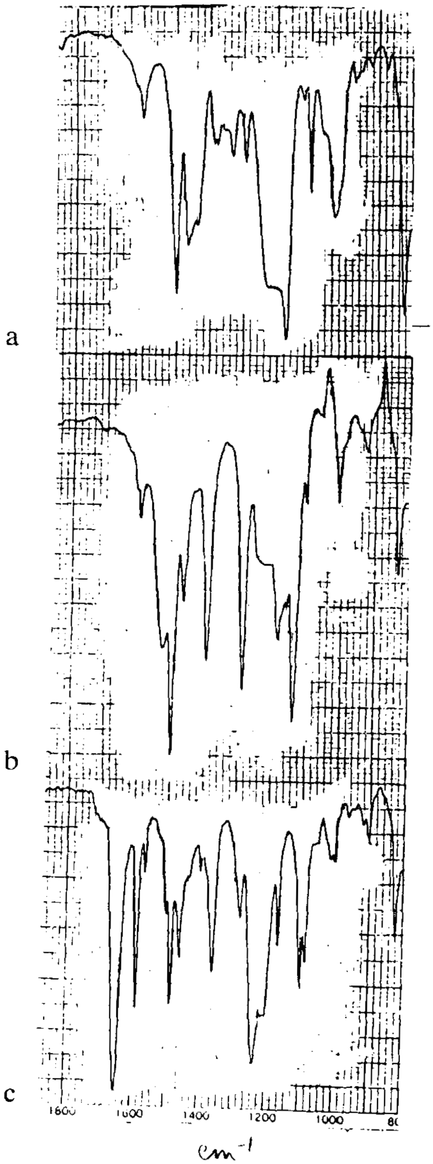
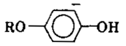
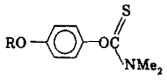


FIGURE 2 Infrared Spectra (CHCl$_3$) for

a.



b.



c.

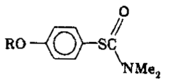
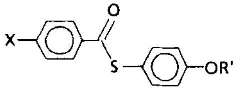


TABLE III

Transition Temperatures (°C) for



X	R'	C	S_B	S_C	N	I
C_{10}	C_7	48.1	---	---	60.2-61.5	69.5-69.9
C_{10}	C_{10}	30.4	(33.0-33.3)	44.1-46.8	59.8-59.9	73.8-74.0
C_{12}	C_{10}	38.7	(54.3-54.5)	61.5-61.7	69.8-70.0	74.2-74.4
C_8O	C_5	44.9		(55.8-56.0)	73.8-74.1	100.3-100.5
$C_{10}O$		49.5		74.3-74.5	75.2-75.3	96.3-96.4
$C_{12}O$		49.8		74.1-74.6	84.5-84.7	93.4-94.0
C_4O	C_7	35.8			62.4-63.4	102.9-103.4
C_6O		53.3			66.5-70.3	102.2-102.4
C_8O		42.3		(61.7-62.5)	63.1-64.4	98.6-99.1
$C_{10}O$		50.0		69.7-71.4	82.3-83.1	98.6-98.8
$C_{12}O$		55.8		75.0-75.2	84.5-84.7	94.3-94.5
$C_{14}O$		48.6	(62.5-62.7)	75.9-76.3	94.8-95.1	95.8-96.0
$C_{16}O$		47.4	(70.1-70.2)	74.8-75.2	---	94.3-95.2
$C_{10}O$	C_8	44.7		65.4-65.8	85.4-85.7	100.0-100.1
$C_{12}O$		53.9		68.7-69.1	92.9-93.5	97.9-98.2
$C_{14}O$		47.5	(65.0-65.3)	77.2-77.5	96.6-97.8	97.8-97.9
C_8O	C_{10}	36.1		63.5-64.1	73.1-74.2	98.7-99.6
$C_{10}O$		45.6		54.6-54.7	88.4-88.8	98.0-98.3
$C_{16}O$		53.2[a]	(52.0-53.2	89.2-92.3	94.6-95.7	96.6-98.1

[a] The S_B phase was observed after slow crystallization began.

addition of a monotropic S_B phase at long chain lengths. No other smectic phases were observed. Mesophases occurred between 54 and 104°. A plot of transition temperatures (Figure 3) *vs.* the alkyl chain length on the acid end for the dialkoxy series, *1d*, with the thiolic alkoxy chain (R') being kept constant at C_7 shows only a slightly rising melting curve and a slightly falling clearing curve, i.e. there is little variation in these temperatures throughout the homologous series when R > C_4. The nematic phase is no longer present at R = C_{16}. The S_C phase enters at R = C_8 and it appears that it will persist to very long chain lengths unless a sharp increase in the melting curve would occur which is not unusual. Interestingly, the S_B phase does not enter until R = C_{14}, occurring only as a monotropic phase. At C_{16}, it occurs at a higher temperature suggesting that it will not continue to exist at much longer chain lengths. A similar plot in which

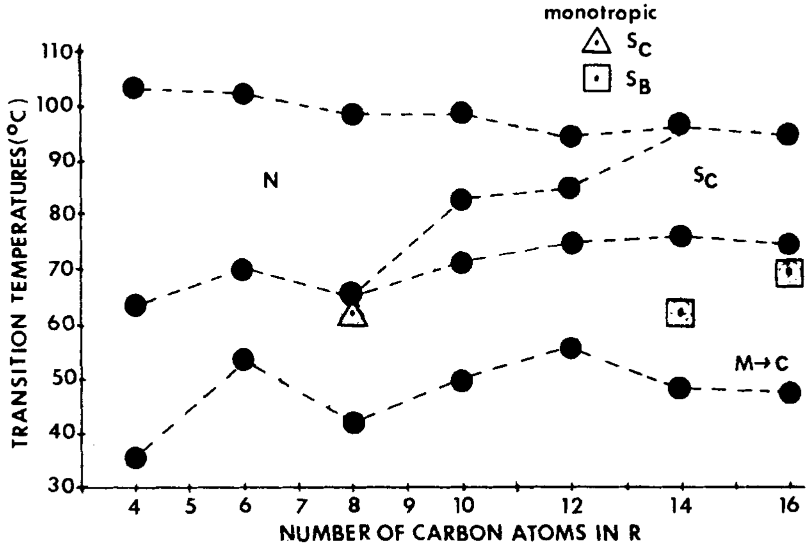
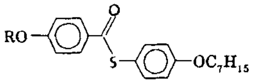


FIGURE 3 Transition Temperatures (°C) *vs.* the Number of Carbon Atoms in R for



the acid alkoxy chain (R) is kept constant at C_{10} while the thiolic chain (R') is varied (Figure 4) shows a nearly flat clearing curve as in Figure 4, but a rapidly falling melting curve. Thus, there seems to be a larger effect on the melting temperature by varying the thiolic alkoxy chain than the acid one.

Only three cyclohexane dithioesters were prepared (Table IV) as this seemed enough to establish mesophase trends. Only short range N phases with transition temperatures between 154 and 172° were observed. Complex crystal changes were also seen, but these were not studied thoroughly enough to obtain accurate data. Very little supercooling was observed, but the crystallization temperature showed more variance than is usually observed with mesophase transitions suggesting these phases are crystalline rather than mesomorphic.

DISCUSSION

Various comparisons of the mesomorphic properties observed for the dialkoxy (RO–OR') phenylthiobenzoates, *1d*, with those for the anal-

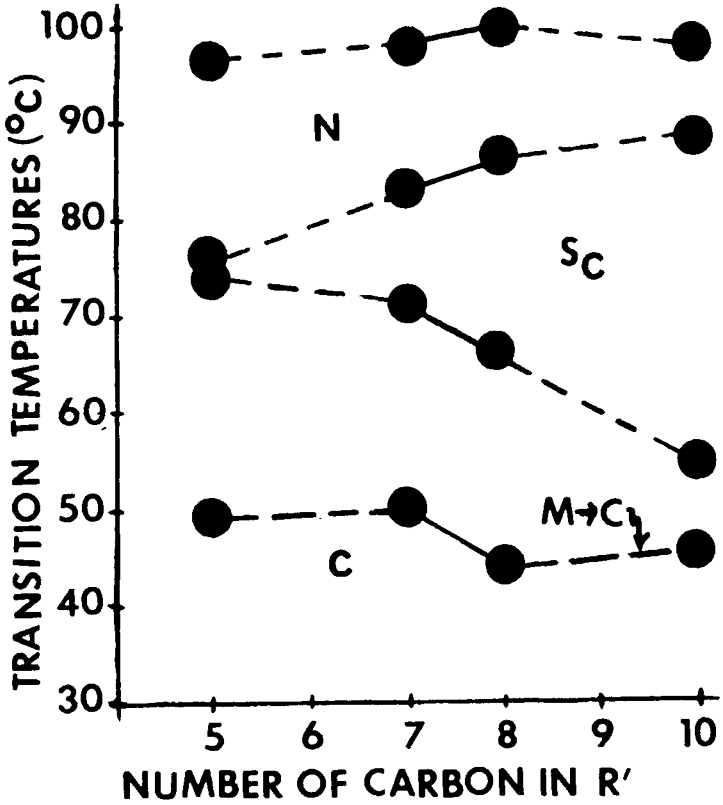
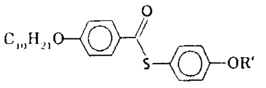


FIGURE 4 Transition Temperatures (°C) *vs.* the Number of Carbon Atoms in R' for



ogous alkoxy-alkyl (RO–R') series 3 (Figures 1c and d, Tables V and VI) show the following trends for the RO–OR' series:

1. higher melting and clearing temperatures with the differences decreasing with increasing chain length,
2. fewer mesophases,
3. narrower temperature ranges for occurrence of the mesophases until R becomes very long, and
4. N and S_C phases are more favored, the S_B phase less so and the S_A and S_X† phases disappear entirely.

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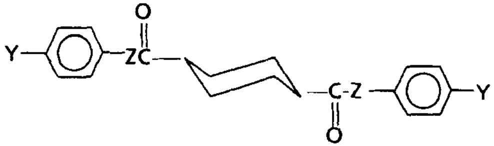
†This is now believed to be a S_G phase. See references 39 and 40.

TABLE IV

Mesomorphic Properties for



Transition Temperatures (°C)

Z	Y	C	$S_?$	S_B	S_C	S_A	N	I
O	C_5[a]	70.0	--	(90.8-92.1)	--	94.9-95.3	128.7-128.8	153.3-153.6
O	C_8[a]	51.5	--	70.3-70.8	--	114.3-114.8	---	139.2-139.6
S	C_5[b]	167.3	--	---	--	---	169.0-169.4	170.0-170.6
S	C_8	156.8	--	---	--	---	---	158.3-158.6
O	OC_7[c]	88	95	96	107	111	---	180
O	OC_8[c]	86	91	93	111	119	---	178
O	OC_{10}[c]	86	(83.8)	87	111	146	---	170
S	OC_7	161.5					161.8-163.6[d]	171.6-172.0
S	OC_8	159.1					158.3-161.0[d]	166.1-167.2
S	OC_{10}	153.8					(~154.5)[e]	154.4-156.4

[a] Data from reference 37.

[b] Although the crystallization temperature shows little supercooling, a DSC scan showed no additional changes below this temperature.

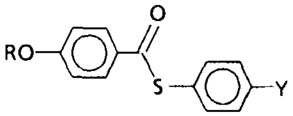
[c] Data from Reference 38.

[d] Changes were observed within the crystal structure both on heating and cooling.

[e] Crystallization occurred before the N → I transition was complete.

TABLE V

Comparison of Melting and Clearing Temperatures (°C) for



with Y = R′ = C_7H_{15} and OR′ = OC_7H_{15}

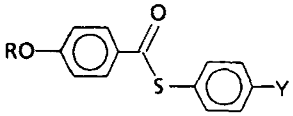
R	Δ melting (°C) $T_{OR'}$-$T_{R'}$ [a]	Δ clearing (°C) $T_{OR'}$-$T_{R'}$
C_8	16.2	15.7
C_{10}	9.8	12.1
C_{12}	6.3	5.9
C_{14}	7.1	6.3

[a] Data from reference 3.

Thus, it is obvious that the trend of more mesophases occurring in the RO–OR′ series than in the RO–R′ series, as was observed in the analogous esters, does not occur in the phenyl thiobenzoates.

TABLE VI

Comparison of Temperature Ranges for Occurrence of Mesophases for



R	Temperature Range (°C) for [a]	
	Y = R′ = C_7H_{15} [b]	Y = OR′ = C_7H_{15}
C_8	55.8	36.1
C_{10}	40.9	27.4
C_{12}	25.5	19.3
C_{14}	21.3	33.5

[a] Includes monotropic phases, i.e. $T_{M\to I}$ is the lowest temperature a phase was observed.

[b] Data from reference 3.

A comparison of the mesomorphic properties of the dialkoxy thioesters with the analogous esters (Figures 1b and d, Figure 5, and Tables VII and VIII) show the following trends for the thioesters:

1. clearing temperatures are always higher, whereas there is some variation in the melting temperatures.
2. the S_A phase is lost,
3. the total range of enantiotropic mesophases is less at shorter chain lengths but quickly increases with increasing chain length.
4. Both the N and S_C phases are more favored. At mid chain length, the N phase length increase is larger than the S_C phase, but at longer chain length the reverse is seen as the S_C phase replaces the N phase (Table VIII). Thus, the replacement of an alkyl with an alkoxy group on the non-acid end favors the N and S_C phases in both the esters and thioesters.

Only a slight enhancement of the N phase in the dialkoxycyclohexanedithioesters, *3b*, was observed as compared to the dialkyl compounds, *3a*, and S_C phases were not observed in either of these series (Table IV). Surprisingly, the mesomorphic properties of these cyclohexane dithioesters were quite poor. Both the alkyl and alkoxy series showed only one mesophase, the N phase, which in all homologs has a very short range, especially for cyclohexane diesters. Both melting and clearing temperatures were higher in the alkyl dithioesters as compared to the esters with the melting temperature increases being much larger than those for the clearing temperatures. Melting temperatures were also higher for the alkoxy thioesters than the corresponding esters, but interestingly not higher than the alkyl thioesters. Clearing temperatures were slightly lower for the alkoxy thioesters than for the esters and only slightly higher than those for the alkyl thioesters. Thus, it is obvious that trends observed in the phenylbenzoate type structure do not necessarily apply to the cyclohexane diester series.

With the data for the dialkoxy thioesters now available, we can compare the types of smectic phases observed in all four series (Figure 6). It is difficult to choose a chain length in all series which is representative of the smectic phases in each series since the maximum number of these phases does not occur at the same chain length. We chose C_{10} which comes close with only two series lacking one smectic phase;† in the esters with $X = Y = C_{10}O$, a S_B phase also occurs in

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†For simplification, we considered only the S_A, S_C, and S_B phases.

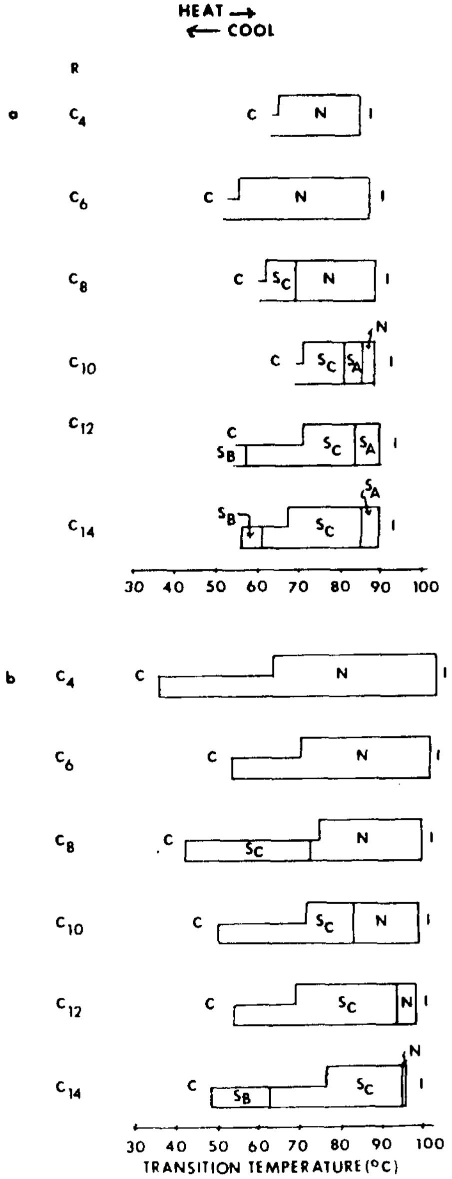
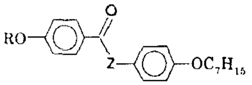


FIGURE 5 Comparison of Mesomorphic Properties for

a.



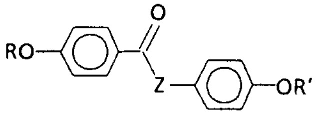
(data from References 4 and 5)

where Z = 0 (a, data from References 4 and 5) and S (b).

TABLE VII

Comparison of Melting and Clearing Temperatures for

for Z = 0 and S

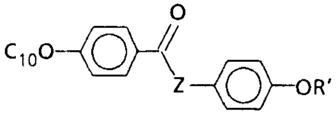


R	R′	Δ melting temperature (°C) T_S-T_O [a]	Δ clearing temperature (°C) T_S-T_O
C_4	C_7	-1.1	18.9
C_6		15.4	15.2
C_8		2.4	10.6
C_{10}		0.4	10.3
C_{12}		4.2	5.0
C_{14}		15.3	6.8
C_{10}	C_5	11.9	11.6
	C_7	0.9	10.8
	C_8	-5.2	9.1
	C_{10}	-16.8	7.8

[a] Data for esters from references 4, 5, and 41.

TABLE VIII

Comparison of Enantiotropic Mesophase Ranges (°C) for



R′	Differences in Ranges for Z = S-O [a]		
	S_C	N	Total
C_5	-4	16	-0.3
C_7	2	13	12
C_8	6	10	15
C_{10}	28	8	24

[a] Ester data from references 4, 5, and 41.

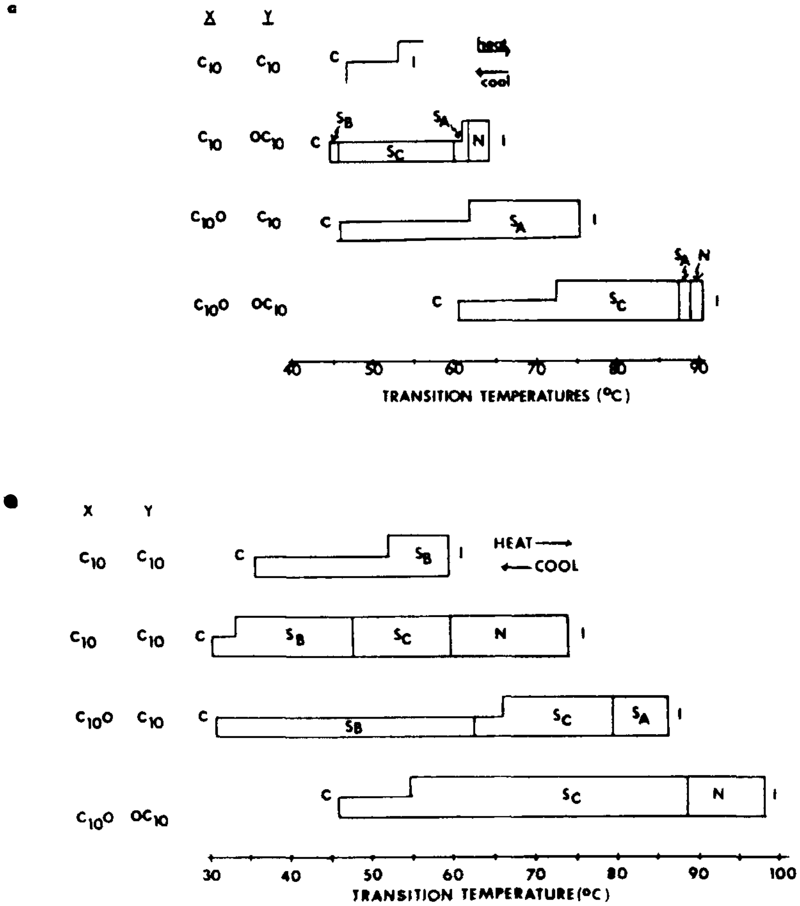
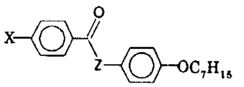


FIGURE 6 Comparison of Mesomorphic Properties for

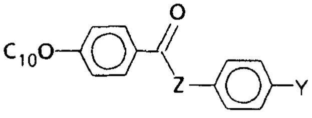


where Z = 0 (a, data from References 4 and 42) and S (b, data for Y = R′ from Reference 3).

other homologs and in the thioester with X = Y = R, a S_A phase is also present (Table IX). If only the C_{10} homologs are compared (Figure 6), there is a replacement of the S_B phase preference observed in the R–R thioester series with a S_C phase preference in the RO–OR′ series with three smectic phases S_B, S_C, and S_A being observed

TABLE IX

Comparison of Mesophases for



Z	X	Y	Mesophases
O	R	R'	N
	R	OR'	S_B,S_C,S_A,N
	RO	R'	S_A,N
	RO	OR'	S_B,S_C,S_A,N
S	R	R'	S_B,S_A,N
	R	OR'	S_B,S_C,N
	RO	R'	S,S_B,S_C,N
	RO	OR'	S_C,N

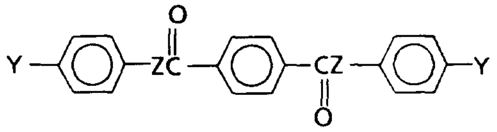
in the mixed R, R'O series. This trend seems to exist in the esters as well but is less obvious. A similar trend occurs in the cyclohexane diesters with S_B–S_A phases in the dialkyl series and the addition of a S_C phase in the dialkoxy series with a decrease in the S_B phase range. The S_A phase, however, has a wider range.

The only other obvious trend in this comparison is the increasing clearing temperatures observed as alkoxy groups are added. In both the esters and thioesters, replacement of one alkyl with an alkoxy group gives higher clearing temperatures when this group is on the acid rather than the phenolic/thiolic end as one would expect. Melting temperatures vary more. With each additional alkoxy group, this temperature increases in the esters, but this is not true in the thioesters; again confirming the unpredictable nature of this temperature.

Another interesting result is the observation that the terphthalic acid dithioesters, *5c* and *d* (Table X), show better mesomorphic properties than the corresponding cyclohexane thioesters, *3a* and *b* (Table IV). This is opposite the trend observed for the corresponding esters. In the terphthalic acid series, the thioesters have higher clearing and lower melting temperatures than the esters. The N, S_C, and S_B phases are more favored and the S_A phase is lost. Replacement of an alkyl with an alkoxy group in the esters gives higher transition temperatures

TABLE X

Mesomorphic Properties for

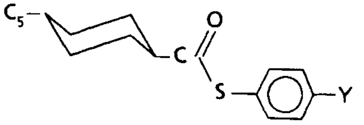


Z	Y	C	Transition Temperatures (°C)				
			S_B	S_C	S_A	N	I
O	C_5[a]	152.2				152.8-154.8	180.8-181.0
	C_{12}	128.7		130.1-131.5	139.8-139.9	- - -	143.0-143.7
	OC_5[a]	163.3		165.4-167.6	169.7-170.4	175.0-175.5	213.9-214.1
	OC_6[a]	155.3		159.8-161.8	177.1-177.5	182.0-182.1	208.1-208.3
	OC_8	147.9		151.6-152.5	179.5-181.2	183.7-184.1	193.1-193.4
	OC_{10}[b]	141.9		145.8-147.0	- - -	174.2-175.2	178.3
S	C_5	94.7		(95.9-96.0)	- - -	109.0-110.8	231.8-232.1
	C_8	97.3	99.0-100.1	113.3-114.1	- - -	166.5-167.0	195.5-195.7
	OC_5	114.8		126.0-128.2	- - -	158.1-159.8	253.3-253.6
	OC_8						

[a] Data from Reference 37.
[b] Data from Reference 21.

and wider range N phases along with S_C phases which are more favored at longer chain lengths; the same trend observed in the phenylbenzoates. Similar trends occur in the thioesters, except the N phase is less favored in the alkoxy series with a strong predominance of the S_C phase occurring.

Fewer mesophases were also observed in the cyclohexane thioesters, *19*



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than in the corresponding esters (Table XI). Interestingly, the clearing temperature is lower in the alkoxy thioester than in the corresponding ester, although the trend towards higher melting temperatures occurs. This again supports the idea that the trend observed in the RO–R′ thioesters of increased mesomorphism, as compared to the esters, is an anomoly rather than a trend.

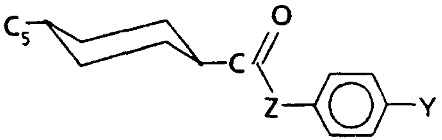
The difference in the mesomorphic properties for the esters (Figure 6) and the thioesters is quite large if one considers that only a small structural change has been made; the replacement of the ester oxygen atom with a sulfur one. This indicates a large sensitivity of mesomorphic properties to molecular structure. The well known effect of chain length on mesomorphic properties shows the same sensitivity and we will provide evidence in later papers on our work on other small chain variations, that these also indicate sensitivity to small structural changes. Thus, it is difficult to imagine how attempts to predict mesomorphic properties on the basis of simplified models can be very accurate. Seemingly, the three dimensional structural shape of the molecule and how it will pack within the smectic layers will determine which phases will be observed.

EXPERIMENTAL

The 4-alkoxyphenols were prepared using the method described in Reference 44. Our experience with using commercially available phenols (usually prepared by alkylation of hydroquinone) is that some of these are contaminated with hydroquinone which is difficult to remove completely by recrystallization. Esters prepared from these phenols could not always be obtained pure by recrystallization. The 4-alkoxybenzoic acids were obtained from Frinton Laboratories or prepared

TABLE XI

Comparison of Mesomorphic Properties for



Z	Y	C	S_G	S_B	S_A	N	I	N range (°C)
O	C_7	0.1			(40.3-41.7)	45.7-46.2	50.4-50.6	4.9
	OC_7		(26)	28	40	57.5	75 [a]	17.5
S	C_7	62.1					72.5-73.1	0
	OC_7	36.1				50.1-50.6	57.7-57.9	7.3

for Y = OC_7 $\Delta T_{mp} = +22.6°$
$\Delta T_{clp} = -17.1°$

[a] Data from reference 43.

by the method described in Reference 44, and 4-alkylbenzoyl chlorides and acids were prepared by the method described in Reference 45. Anhyd. Na_2SO_4 was used to dry organic extracts.

TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with $CHCl_3$ as the solvent, unless otherwise noted, and UV light as the detector. Melting points (°C) were determined using a Thomas-Hoover melting point apparatus and are corrected. IR spectra were obtained using a Pye Unicam 3-200 instrument. NMR spectra were run on either a Varian FT-80 or EM-360 instrument with TMS as the internal standard unless otherwise indicated. Typical examples of NMR data are presented in Table II. Abbreviations used are CT (CCl_4), CD ($CDCl_3$), EM (EM-360), and FT (FT-80).

Transition temperatures (°C) were determined using a Leitz Ortholux or Laborlux 12 Pol polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of 2°/min as described in Reference 46, unless otherwise noted. Mesophases were identified by their textures which were typical of those previously observed for these phases. Abbreviations used for phases are C = crystal, M = mesophase, S = smectic, S_B = smectic B, S_C = smectic C, S_A = smectic A, N = nematic, and I = isotropic liquid. Monotropic phases are indicated in tables by parentheses. Samples were cooled at 2°/min until they crystallized, so no monotropic phases occurring before this temperature were missed.

O-(4-Decyloxyphenyl)-N,N-dimethylthiocarbamate, *12* (R = $C_{10}H_{21}$)

To a stirred soln of 37.6 g (0.15 mole) of 4-*n*-decyloxyphenol in 150 ml dry (over #4A Linde molecular sieves for 17 hr) DMF was added in small portions, 5.0 g (0.16 mole) of 80% NaH dispersion in oil. After hydrogen evolution had ceased, the rxn mixture was cooled in an ice bath and a soln of N,N-dimethylthiocarbamoyl chloride in 50 ml DMF added dropwise within 15 min. The ice bath was removed, the temperature allowed to rise to RT by stirring for 1 hr, and then the mixture heated for 1 hr at 70°. The ice cooled rxn mixture was poured into 300 ml of 2.5% aq KOH and extracted with 3 × 150 ml Et_2O. The organic layer was washed with 150 ml 2.5% aq KOH and H_2O, dried and then filtered. The solvent was removed from the filtrate *in vacuo* to give 53.0 g (quantitative) of the crude product. TLC showed a major spot with R_f = 0.66 and minor ones with R_f = 0.38 (starting phenol R_f = 0.13). This material was recrystallized twice from 200 ml abs EtOH to give 42.6 g (84.3%) of the purified O-thiocarbamate, *12* (R = $C_{10}H_{21}$): mp 61–61.5° and TLC showed one spot with $R_f = 0.58$ (starting phenol $R_f = 0.10$). Purified yields for the other homologs ranged from 74.1–83.5%. Melting points are given in Table I and IR spectra in Figure 2.

S-(4-Decyloxyphenyl)-N,N-dimethylthiocarbamate, *13* (R = $C_{10}H_{21}$)

The O-thiocarbamate, *11* (R = $C_{10}H_{21}$, 5.74 g, 17.0 mmoles) was heated under N_2 at a melt temperature of 315° for 30 min and then cooled to RT. This crude material was usually hydrolyzed to the thiol without purification. It could, however, be purified by column chromatography on silica gel with elution by CH_2Cl_2. The solid isolated was purified further by recrystallization from MeOH to give the S-thiocarbamate, *12* (R = $C_{10}H_{21}$): mp 42.5–44.5°, TLC (CH_2Cl_2) $R_f = 0.36$ (starting material $R_f = 0.59$) and an IR spectrum is given in Figure 2. Purification of the C_7 homolog in the same manner gave a solid with mp = 43.5–44.5°.

4-*n*-Decyloxythiophenol, 5 (R = $C_{10}H_{21}$)

The crude S-thiocarbamate, *12* (R = $C_{10}H_{21}$) from the above reaction was dissolved in a soln of 860 mg NaOH in 25 ml MeOH containing 8.6 ml H_2O and refluxed for 8 hr. The cooled rxn mixture was poured into H_2O and extracted twice with CH_2Cl_2. The organic layer was washed with 10% HCl and then H_2O, dried, filtered, and the filtrate evaporated to give 3.20 g (70.6%) of the crude thiol, *5* (R = $C_{10}H_{21}$). TLC showed several spots with $R_f = 0.72$, 0.18, 0.12, and 0.06 (R_f for phenol, *10* = 0.18) indicating the presence of the phenol, *10*. This material was chromatographed on 50 g of 60–100 mesh silica gel eluting with 15% $CHCl_3$ in hexane to give 2.33 g (51.4%) of the purified thiol, *5* (R = $C_{10}H_{21}$): bp. 148° (0.2 mm),† TLC showed one spot with $R_f = 0.70$ (R_f for starting material = 0.16), IR (film) showed absorptions at 2575‡ (wk, SH), 1595, 1570 (str, Ar) and 830, 810 sh (str, 1,4-aromatic disubstitution) and NMR data are given in Table II. The other homologs were prepared in the same manner in crude yields of 70–100% and purified yields of 38–80%.

n-Octyloxybenzene, *18* (R′ = C_8H_{17})

This compound was prepared by alkylating phenol with *n*-bromooctane in abs EtOH using the method described in Reference 44. The

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†This thiol was also prepared from a sample of the S-thiocarbamate that had been purified by chromatography and distilled to obtain this bp. The C_7 homolog had a bp. 112° (0.2 mm).

‡Not observed in a soln spectra.

crude ether was isolated in a yield of 93.2%. Distillation of this material at 117–119° (1.7 mm) (lit.[47] bp. 285.2°) gave a yield of 86.0% of *n*-octyloxybenzene: TLC ($CHCl_3$) $R_f = 0.78$ (R_f amylbenzene = 0.80) and IR 1600 (Ar) and 1220 cm^{-1} (ether).

Sulfonation of *n*-Octyloxybenzene

n-Octyloxybenzene (10.0 g, 48.5 mmol) was added dropwise with stirring to 13.3 ml concd H_2SO_4 at 50° and stirring continued at this temperature for an additional hr. The rxn soln was cooled in an ice bath, poured into 100 ml ice-H_2O and made basic with concd aq KOH. This soln was boiled to reduce the volume from 150 to 100 ml and then cooled to 5°. The precipitate was collected by filtration and washed with cold H_2O to give 20.3 g of the crude sulfonate salt, *14* ($R' = C_8H_{17}$, M = K). Recrystallization of this material from 75 ml H_2O gave 9.0 g (57.3%) of the purified salt: IR (Nujol) 1595 (wk, Ar) and 1220 and 1190 cm^{-1} (str $SO_3^{\ominus}$). A second crop (5.0 g) was isolated from the filtrate to give a total yield of 89.1%.

This salt was too insoluble to obtain a good NMR spectrum, therefore, it was converted to the sulfonyl chloride, *15* ($R' = C_8H_{17}$) using the $POCl_3$ procedure described in Reference 29 in a crude yield of 58.2%: TLC (CCl_4) $R_f = 0.14$ (R_f for starting material = 0, octyloxybenzene = 0.44).

Alkylation of Sodium 4-*n*-Hydroxybenzene Sulfonate, *17* (M = Na)

A soln of 1.72 g (43.0 mmole) of NaOH in 50 ml 80% EtOH was added to a stirred soln of 10.0 g (43.0 mmole) of sodium 4-hydroxybenzenesulfonate in 100 ml 80% EtOH causing some of the salt to precipitate. To this was added 11.4 g (51.6 mmole) of *n*-bromodecane within 2 min. and the mixture refluxed for 17 hr. A 50% aq NaOH soln (4.3 ml) was added to hydrolyze any ester, refluxing continued for another 2 hr and then the mixture filtered while still hot.† The filtrate was cooled to RT and the precipitate collected by filtration to give 13.6 g (78.2%) of the crude salt, *14* ($R' = C_8H_{17}$, M = Na): mp ~ 328° (dec), IR (Nujol) 1600 (Ar) and 1240 and 1180 cm^{-1} ($SO_3^{\ominus}$). This salt gave the sulfonyl chloride, *15* ($R' = C_8H_{17}$) in a purified yield of 72.0%: bp 201° (1 mm), IR 1600 (Ar), 1380 and 1370 (SO_2Cl) and 1280 cm^{-1} (ether).

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†The solid filtered off was found to be primarily the desired product. Thus, it would probably be better to eliminate this filtration.

Thioesters 1c and d and 3a and b

The thioesters, *2c* and *d*, were prepared using either the acid chloride-Et_3N method described in Reference 21 in purified yields of 86–88% or by the carbodiimide procedure as described in Reference 3 in purified yields of 76–82%. Most of these thioesters were recrystallized from abs. EtOH; exceptions were the homologs with $X = C_{10}$, $R' = C_7, C_{10}$ (4:1 EtOH-EtOAc) and $X = C_{16}O$, $R' = C_{10}$ (EtOH-$CHCl_3$). The cyclohexane dithioesters, *3*, were prepared using the DCC method in purified yields of ~67% and were recrystallized from abs EtOH-$CHCl_3$. The cyclohexane thioesters, *19*, were also prepared using this method in purified yields of 50% and were recrystallized from abs EtOH.

Calcd for $C_{30}H_{44}O_3S$ (*1d*, $R = C_{10}H_{21}$, $R' = C_7H_{15}$): C 74.33, H 9.15, S 6.62. Found: C 74.35, H 9.01, and S 6.67.

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